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Surface Modification of Water Purification Membranes: A Review

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Abstract

Polymer membranes are an energy-efficient means of purifying water, but they suffer from fouling during filtration. Membrane surface modification is one route to mitigate membrane fouling as it helps to maintain high levels of water productivity. Here, a series of common membrane surface modification techniques are reviewed, including surface coating, grafting, and various treatment techniques such as chemical treatment, UV irradiation, and plasma treatment, among others. Historical background on membrane development and surface modification is also provided. Finally, polydopamine, an emerging material that can be easily deposited onto a wide variety of substrates, is discussed within the context of membrane modification. Finally, a brief summary of the chemistry of polydopamine, particularly as it may pertain to membrane development, is described.

Keywords: membranes, fouling, surface modification, water purification, polydopamine

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1. Introduction

Water and energy shortages are global concerns of growing severity. Worldwide, over a billion people lack access to clean drinking water, a fundamental human need. Over two billion are without adequate sanitation, which results in nearly two million deaths annually due to waterborne diseases transmitted via impure water sources or sewage.[1] Food shortages are also often attributable to poor water availability, since agriculture accounts for the consumption of 70% of all water used by humans.[2] On a planet covered in water, precious little is fit for human consumption. Only 2.5% of water on Earth is fresh water, and most must be purified to some degree before it is safe for drinking or other beneficial uses.[2]

The infrastructure required to support the rapidly growing world population places enormous demand on available energy supplies. In 2005, the United States withdrew 410 billion gallons (over 1.5 trillion liters) of water per day, with freshwater accounting for 85% of that amount.[3]

This water was used in the residential, commercial, and industrial sectors, as well as for power generation. Of the total water withdrawn, 41% was used to generate electricity in thermoelectric power stations.[4] Clearly, the availability of water is of paramount importance in the generation of energy. However, with increasing demands on fresh water, non-traditional water sources, such as seawater, which must be subjected to energy-intensive desalination, are increasingly being used. This interdependence of water and energy production is called the water-energy nexus.[3,5–10] Given the importance of water and, therefore, energy in producing food, there is a growing realization that the water-energy nexus is really a nexus among water, energy, and food.[4,11] In the United States, for example, the large water requirements for activities such as hydraulic fracturing to produce energy and the use of food crops, such as corn, to make biofuels, are impacting food supplies.[4,11]

1.1 Membrane Types and Materials

Water purification membranes are capable of removing a wide variety of contaminants, ranging from large colloids, algae, and bacteria, which have a characteristic dimension on the order of microns, to individual ions, which have a hydrated radius on the order of angstroms.[2] Figure 1 shows the relative size of various solutes commonly removed by membrane filtration.

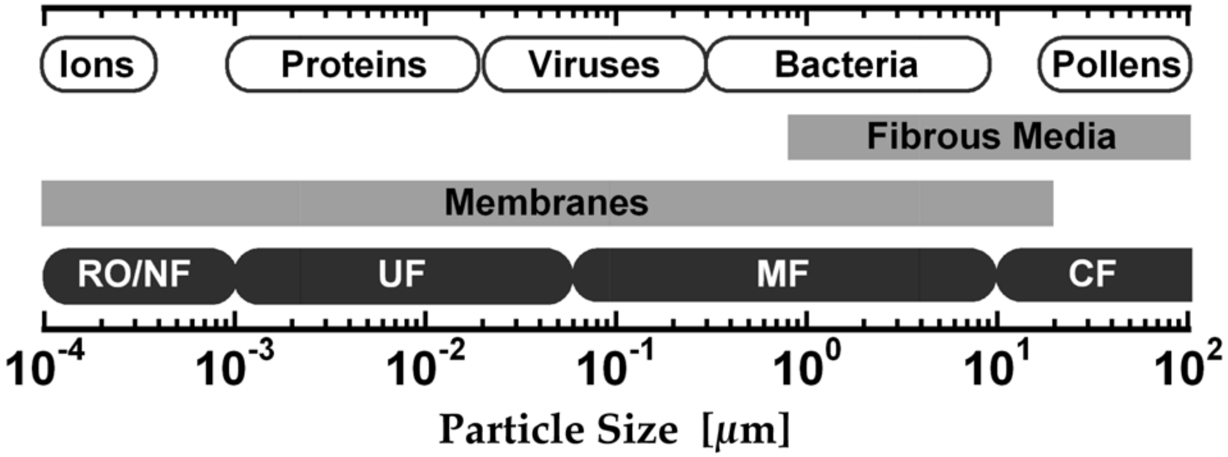


Figure 1. Relative sizes of solutes commonly removed by membrane filtration. Membrane types, including reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) are shown, in addition to conventional filtration (CF). Reproduced with permission, John Wiley & Sons, Inc.[2]

Microfiltration (MF) membranes have pores on the order of 1 μm and are useful for removing large colloids, microbes, cells, and viruses. Ultrafiltration (UF) membranes have smaller pores than MF membranes, and they are used to remove smaller colloids, proteins, and other macromolecules from various media. MF and UF membranes accomplish separation essentially by size exclusion; solutes larger than the membrane pore size are rejected, while solutes smaller than the membrane pore size, including water, flow through the pore structure.[2,12] Reverse osmosis (RO) membranes are dense (non-porous) membranes that can remove salts from water, enabling desalination of brackish water or seawater. Water transport through RO membranes occurs via a solution-diffusion mechanism.[12–14] Nanofiltration (NF) membranes have exceptionally small pores, and the transport of salt and water through their selective layers are described using a combination of diffusive, convective, and electrostatic models.[15] For ionic species, such as salts, NF membranes are typically designed to exhibit high rejection to multivalent ions but not monovalent ions, whereas RO membranes typically exhibit high rejection to both monovalant and multivalent ions.[2,12,16–18] Extensive studies of membrane architecture, transport mechanisms, and applications may be found elsewhere.[2,12,14,19–25]

The mechanical properties, ease of processing, thermal stability, and chemical resistance are important considerations for water purification membrane materials. Many polymers, such as polysulfone (PSf), poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF),[26] cellulose acetate (CA), polypropylene (PP), poly(acrylonitrile) (PAN), and polyamides, have appropriate materials property sets.[12] Additionally, these polymers are available in large quantities at reasonable cost, which contributes to their selection in the manufacture of water purification membranes. Table 1 shows some of the most commonly used polymeric materials for water separation membranes.

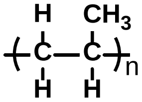
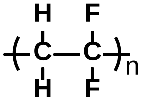
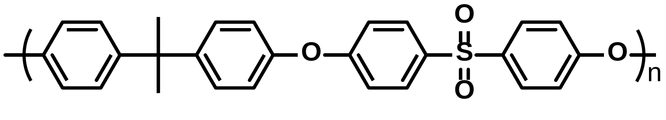
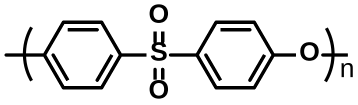
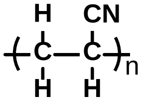
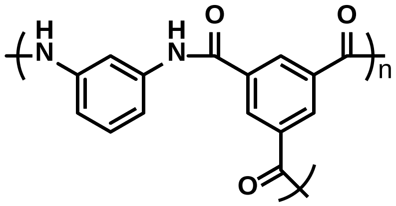
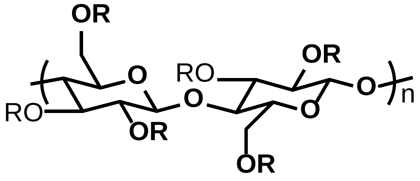
Polymer	*Chemical Structure*	*Membrane Type(s)*
Polypropylene	 $-\!\left(\mathrm{CH_2-CH(CH_3)}\right)_n\!-$	MF
Poly(vinylidene fluoride)	 $-\!\left(\mathrm{CH_2-CF_2}\right)_n\!-$	MF
Polysulfone		UF
Poly(ether sulfone)		UF
Poly(acrylonitrile)	 $-\!\left(\mathrm{CH_2-CH(CN)}\right)_n\!-$	UF
Crosslinked Aromatic Polyamide		NF/RO
Cellulose acetate	 **R = H or CH_3CO**	RO

Table 1. Polymeric materials commonly employed for water purification membranes.

Typically, polymeric membranes are manufactured using processes that require organic solvents. For example, porous MF and UF membranes are often made by a phase inversion process, where the membrane polymer is first dissolved in a polar organic solvent that is miscible with water. The polymer solution is then cast into a thin film, and upon contact with a non-solvent for the polymer (typically water or an aqueous solution), the solvent is rapidly exchanged with the non-solvent, causing the polymer to precipitate, forming a porous, solid membrane.[2,12] This process is called non-solvent induced phase separation (NIPS).[27] Sometimes, additional agents (such as polyvinylpyrrolidone or poly(ethylene glycol)) are incorporated into the polymer solution to aid in pore formation.[12] The phase separation process to produce such porous membranes can also be achieved by contacting the polymer solution with a humid atmosphere (rather than by contact with liquid water), by cooling a hot polymer solution (so-called thermally induced phase separation (TIPS)), or by evaporation of the organic solvent.[2,12] Membranes formed in this manner are typically made from rather hydrophobic (or at least water insoluble) polymers, such as those noted above. The hydrophobicity of the bulk membrane material is useful for maintaining structural integrity when the membrane is used in aqueous environments. However, as described below, if the surface of the membrane is hydrophobic, fouling during operation can be problematic. Figure 2 presents SEM images of typical MF and UF membranes formed by phase inversion.

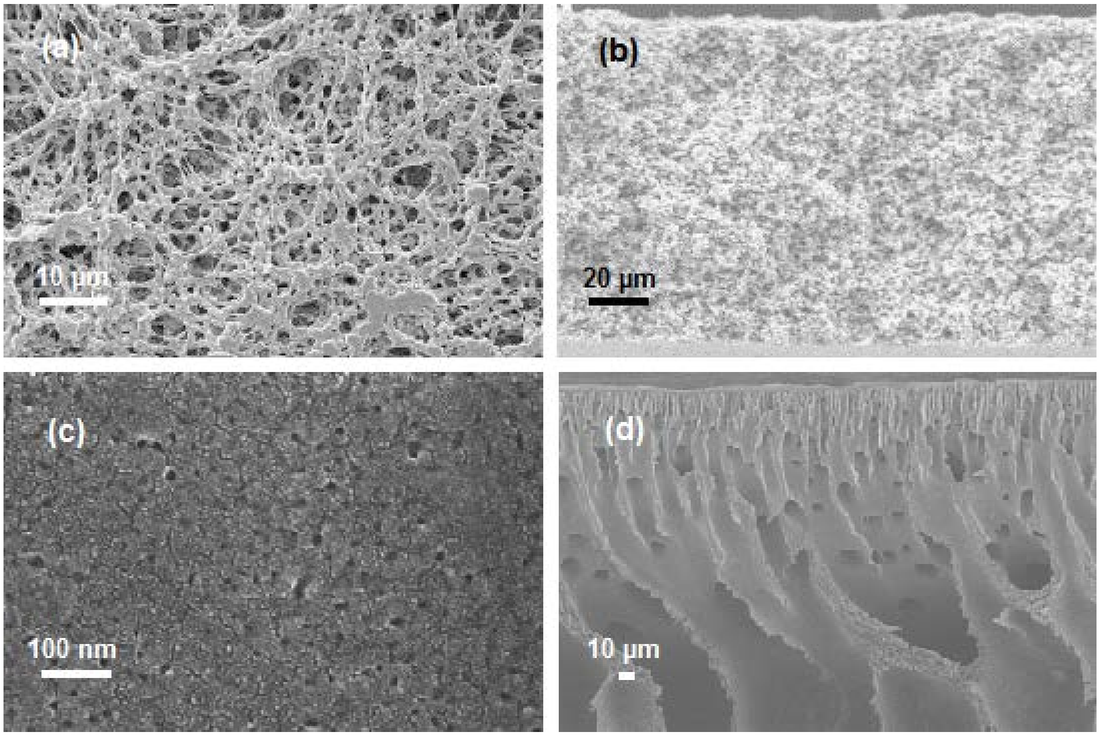


Figure 2. SEM images of typical MF and UF membranes. (a) Top surface and (b) cross-sectional views of an isotropic PVDF MF membrane from Millipore Corporation.[28] (c) Top surface and (d) cross-sectional views of an anisotropic PSf UF membrane cast from solution in NMP using water as non-solvent. PVP was used as a pore-forming agent.[29] Reproduced with permission, Elsevier B.V.

Early RO membranes were produced from CA in a phase inversion process similar to that described above for MF and UF membranes.[30] Currently, most RO and NF membranes are manufactured by interfacial polymerization.[2,12,17,21] In this process, a thin, dense polyamide barrier layer, which is responsible for the salt/water separation, is formed atop a porous support layer, which provides mechanical integrity to the membrane to withstand the pressures required for desalination. Typically, a layer of PSf UF membrane cast onto a polyester fabric backing material is used as the porous support.[17,24] While many different polyamide systems have been tested for use as the barrier layer in desalination membranes,[17] *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC) monomers are the dominant components in most RO and NF membranes.[2] To form the interfacially polymerized barrier layer, the pores of the PSf support membrane are filled with a dilute aqueous solution of MPD. Then, the surface of the PSf membrane is overcoated with a water-immiscible organic solution containing a low level of TMC. The acid chloride units on TMC react readily and rapidly with the primary amines of MPD, forming a crosslinked aromatic polyamide at or near the oil/water interface. The MPD is somewhat soluble in the organic phase, and diffusion of MPD into the organic phase promotes further polymerization with the TMC, building, over the course of seconds, a thin (~100 nm or less) dense polymer layer at the oil/water interface of the PSf UF membrane.[2,17] During this membrane formation process, MPD continues to diffuse through the pores of the support membrane and through the nascent polyamide barrier to react at and in the oil/water interface. This process is self-retarding: as the crosslinked aromatic barrier layer becomes thicker, the diffusion of MPD slows and results in membrane thicknesses of the order of 100 nm. Figure 3 presents SEM images of a thin film composite polyamide RO membrane.

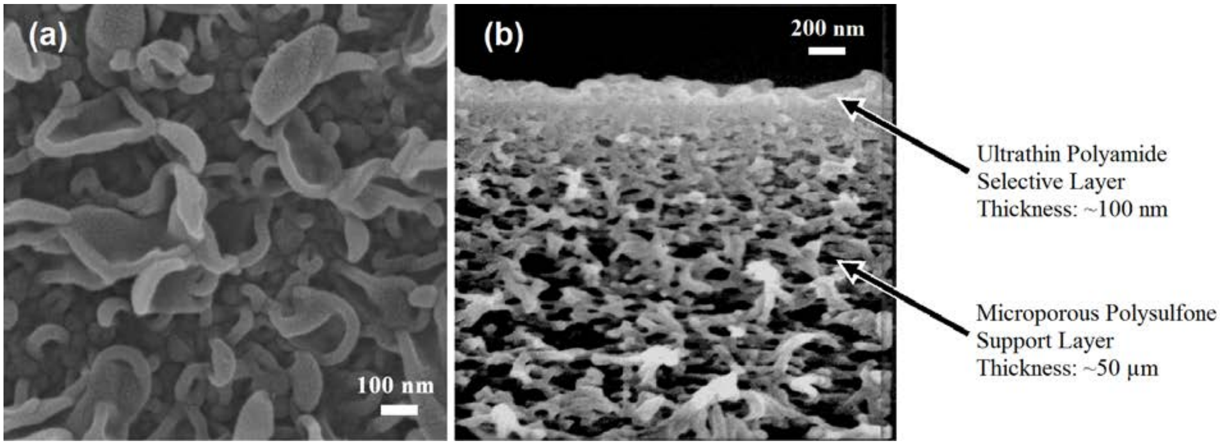


Figure 3. SEM images of a typical polyamide thin-film composite RO membrane. (a) Top surface, showing the complex surface geometry resulting from the diffusion of m-phenylene diamine through the pores of the supporting PSf membrane and into the overcoated trimesoyl chloride solution during polyamide formation. Reproduced with permission, Elsevier B.V.[31] (b) Cross-sectional view, showing the ultrathin (~100 nm) polyamide barrier layer atop the porous PSf supporting layer (~50 µm). Reproduced with permission, John Wiley & Sons, Inc.[2]

1.2 Membrane Fouling

Fouling is the undesirable accumulation of solutes either externally on the membrane surface or, in the case of a porous membrane, internally within the pores, or both.[2,32–34] As foulant builds up on the membrane surface or in the pores, the mass transfer resistance of the membrane to water transport increases, decreasing the membrane productivity.[33–35] Often, fouling is characterized in terms of flux decline at a fixed transmembrane pressure, as shown in Figure 4. In pure water filtration, the only mass transfer resistance to water passage through the membrane is that of the membrane itself.[33] However, if foulant accumulates on the membrane surface, an additional resistance is imposed on water passage, and the flux is lower than during pure water filtration.[19,33] This decrease in flux typically occurs very rapidly when a membrane is first challenged with a fouling feed solution.[33,36] The flux then typically decreases gradually before reaching a steady state value.[33,36] Figure 4 presents a typical flux decline curve.[36]

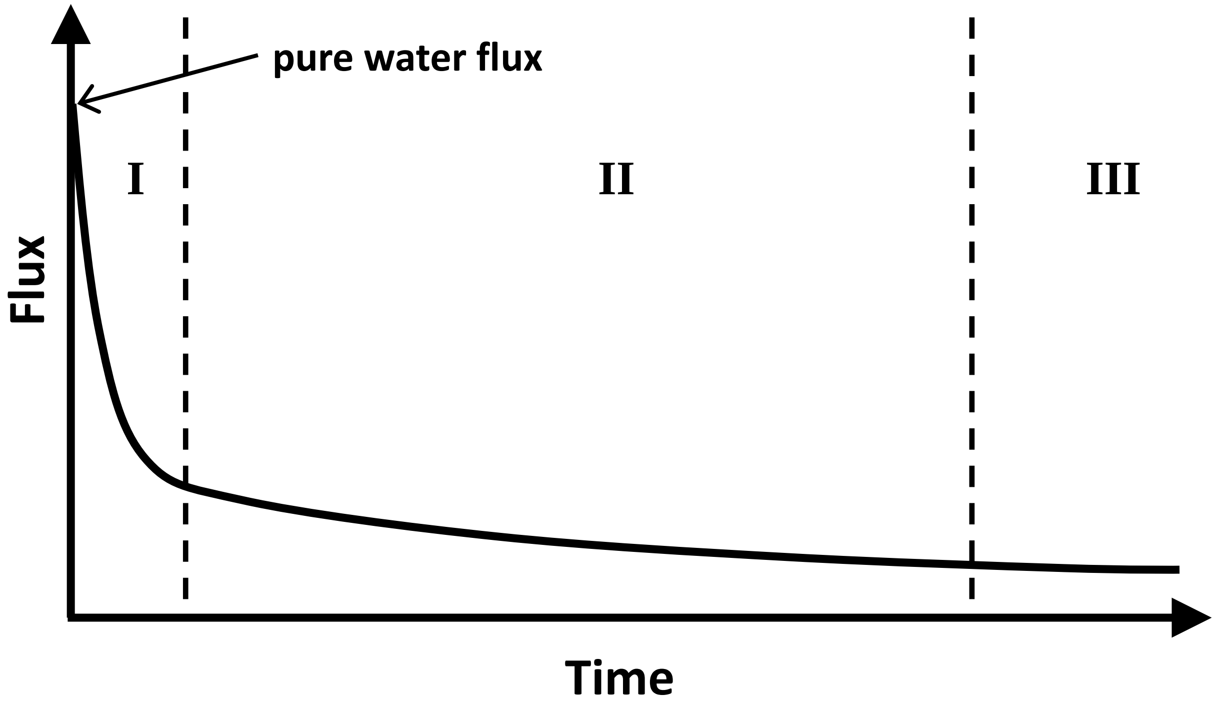


Figure 4. Typical flux decline curve showing (I) rapid decrease in flux when the membrane is challenged with a fouling feed solution, (II) a long-term gradual decrease in flux, and (III) steady-state flux.[36]

An example of membrane fouling is presented in Figure 5, which shows the autopsy of a spiral-wound RO membrane suffering from biological fouling.[37] Heavy accumulation of a brown cake was evident between the membrane leaves. This material appears dense and gel-like, and it could be scraped off the membrane surface using a razor blade. Scanning electron microscopy revealed microbial cells and macromolecular material. Biofouling has historically been a severe problem for municipal and industrial installations of water purification membranes.[37–39]

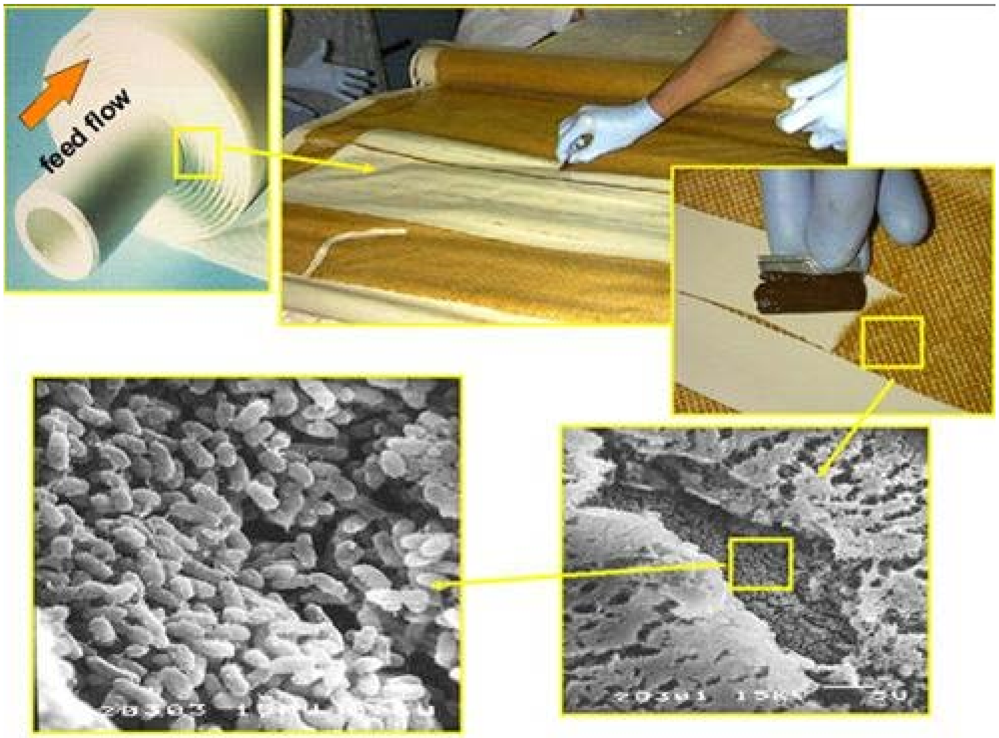


Figure 5. Biological fouling of a spiral-wound RO module from a municipal desalination plant. SEM images revealed the microorganisms comprising a thick brown film that accumulated on the membrane surface. Reproduced with permission, Elsevier B.V.[37]

The many factors contributing to membrane fouling and the mechanisms by which foulant accumulation proceeds are extensively reviewed elsewhere.[33–36,40–43] Fouling is exacerbated by concentration polarization, which is the accumulation of solute near the membrane surface due to the rejection of the solute by the membrane as water permeates through the membrane.[12,33,35,40] A high concentration of solutes near the membrane surface facilitates solute deposition onto the membrane.[12] In UF, concentration polarization can be severe enough to cause precipitation of solutes, forming a gel layer on the membrane surface.[12] In RO and NF, such precipitation results in the formation of mineral scale.[12,16,44] Examples of fouling are shown in Figure 6, which presents SEM images of the top surfaces of PVDF MF and polyamide RO membranes.

Activated sludge fouling has completely obscured the porous matrix of the MF membrane (a)[45] and mineral scale has grown on the surface of the RO membrane (b).[46]

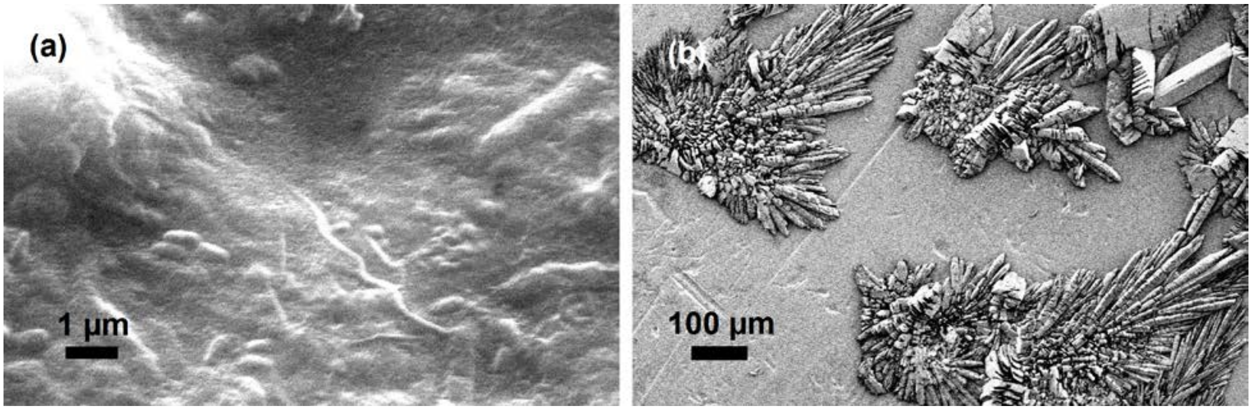


Figure 6. SEM images of the top surfaces of fouled membranes. (a) PVDF MF membrane fouled with activated sludge, showing coverage of the porous structure (cf., Figure 2a).[45] (b) Top surface of a composite polyamide RO membrane, showing formation of mineral scale.[46] Reproduced with permission, Elsevier B.V.

Table 2 summarizes major classes of foulants that cause performance degradation in membrane systems. Many of these foulants are complex in nature, and the susceptibility of a membrane to fouling is the result of various attractive forces between the membrane and the foulant. Proteins,[32,34,40,43,47,48] emulsified oils,[49,50] microorganisms,[49] and the humic substance fraction of natural organic matter[51,52] often have a higher propensity for adhesion to hydrophobic membranes than hydrophilic membranes. For this reason, many surface modifications focus on hydrophilizing a hydrophobic membrane surface. Hydrophilic surfaces are hypothesized to tightly bind a layer of water, which frustrates the deposition of foulants from aqueous media.[21] In this way, hydrophobic-hydrophobic forces between membrane and foulant are mitigated. However, some important foulants, including the hydrophilic fraction of natural organic matter[51,53,54] and biopolymers,[55] are also capable of readily fouling hydrophilic membranes. Hydrophilicity of the membrane surface is widely characterized by contact angle measurements, although the contact angle is known to depend upon other factors, such as surface roughness, pore size, porosity, and time.[56]

Foulant	*Notes*
Proteins/Macromolecules	Typically denature upon contact with a surface, which promotes further protein deposition;[34] protein-surface interaction may be a combination of hydrophobic, electrostatic, and hydrogen bonding forces;[34] protein adhesion appears reduced on hydrophilic surfaces[35]
Emulsified Oil	Common component of industrial waste streams; emulsified oil cannot be removed by gravity separation and readily fouls hydrophobic membranes[57]
Microorganisms/Biofoulants	Microorganisms adhere to surfaces through various interactions including van der Waals, electrostatic, hydrogen bonding, and hydrophobic;[38,39] extracellular polymeric substances secreted by microorganisms contain polysaccharides and proteins and reinforce the biofilm[39,58]
Natural Organic Matter	Contains hydrophilic and hydrophobic components, including a large fraction of humic substances from vegetative matter;[59] hydrophilic and hydrophobic membranes appear susceptible to fouling by natural organic matter[54]
Mineral Scale	Precipitation of minerals from supersaturated solutions near membrane surface;[44] formation appears to be dominated by operational parameters rather than membrane surface characteristics[44]

Table 2. Common foulants of water purification membranes.

Other properties besides hydrophobicity also appear to contribute to membrane fouling. Surface roughness has been implicated as a significant determinant of membrane fouling susceptibility in several studies. For example, thin film composite polyamide RO and NF membranes suffer from fouling despite having a relatively hydrophilic surface. Several studies have suggested that surface roughness, which arises from the interfacial polymerization procedure used to fabricate the membrane, may contribute to membrane fouling susceptibility.[55,60,61] Polyamide membranes formed by interfacial polymerization have relatively hydrophilic, but very rough, surfaces. An atomic force micrograph of a typical commercial polyamide thin film composite RO membrane is shown in Figure 7.[62] The root mean square (RMS) surface roughness of polyamide composite NF and RO membranes can range from 50 nm to over 180 nm.[63] Surface roughness is more difficult to characterize in porous MF and UF membranes, as pore size influences the measurement of apparent roughness. Literature values of RMS surface roughnesses of MF and UF membranes range from less than 1 nm[64,65] to over 300 nm,[66] but typical values are in the range of approximately 40-100 nm for MF membranes[54,65] and approximately 1-20 nm for UF membranes.[54,65,67] Rough membrane surfaces appear to be more susceptible to fouling than smooth surfaces,[55,60,61] especially when the characteristic dimensions of membrane surface features and solutes are similar.[42] Surface roughness has been suggested to be the most important contributor to fouling in RO membranes, particularly since polyamide RO membranes are hydrophilic.[55,60,61] Fouling may increase on rough membranes because foulants can accumulate in valleys, shielding the foulant from crossflow shear forces that otherwise acts to remove the foulants.[55,61]

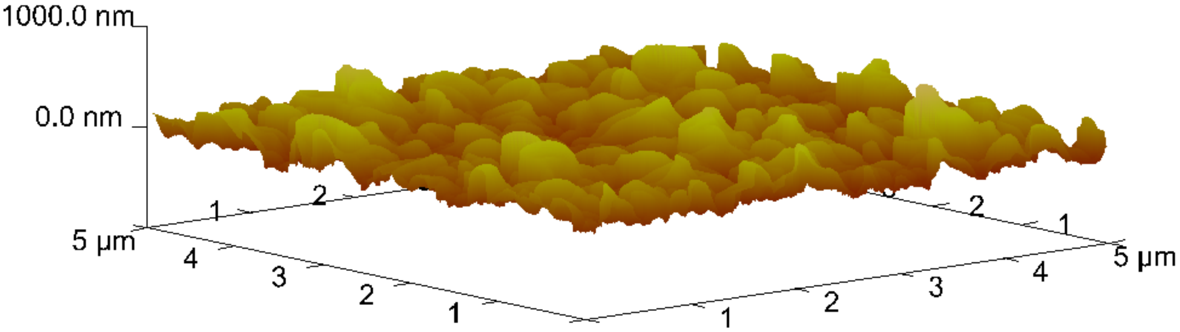


Figure 7. Atomic force micrograph of the surface of a polyamide thin film composite RO membrane. The RMS surface roughness of this membrane was approximately 130 nm. An image of the top surface of a similar membrane is shown in Figure 3a. Reproduced with permission, Elsevier B.V.[62]

Surface charge has also been implicated in membrane fouling. Electrostatic interactions become increasingly important when charged foulants, such as proteins[48] and some components of natural organic matter,[68] are present in the feed. Furthermore, multivalent ions in the feed, especially Ca^{2+}, can electrostatically crosslink charged foulants,[55,69] stabilizing accumulated foulant layers. Thin film composite RO and NF membranes have ionizable groups in the polyamide layer and exhibit a negative surface charge in the pH regime of normal use.[21,68]

A variety of techniques may be used to mitigate fouling during membrane-based water purification. The feed may be pretreated by adjusting its pH,[34,41,48] removal of compounds that are known to worsen fouling[55,70] (with, for example, the aid of coagulants[51]), or by dosing additives such as antiscalants that hinder foulant accumulation on the membrane surface.[16] Operational parameters, such as filtration mode (dead end or crossflow),[35] crossflow velocity[47] and permeate flux,[49] may be adjusted to reduce foulant buildup. Module design characteristics, such as membrane architecture (e.g., hollow fiber or spiral wound),[35] feed spacer thickness,[71] and feed flow hydrodynamics,[35,41] have been shown to affect fouling phenomena. A variety of cleaning procedures, such as permeate backwashing,[47] feed pulsing,[35] gas sparging,[47] or chemical cleaning,[35] are commonly used to remove accumulated foulant and recover membrane flux.

The frequency of these fouling mitigation strategies may be reduced by modifying the membrane to make it less susceptible to fouling. Modification to alter the properties of polymer surfaces has been of interest for many years[72] in a variety of applications, including biomaterials.[73] Whitesides' group at Harvard University published several reports describing interactions of proteins, detergents, and bacteria with polymeric surfaces.[74–78] Surface plasmon resonance was used to measure adsorption of these foulants to self-assembled monolayers of various functional groups on gold substrates. Surface wettability was tailored using various functional groups on the self-assembled monolayers; over 50 different functional groups were screened.[76] Generally, hydrophilic functional groups were most resistant to adhesion of detergents,[75] bacteria,[77] and small proteins.[75,77] Furthermore, hydrophilic functional groups that were hydrogen bond acceptors but not hydrogen bond donors[77,78] and that were electrically neutral[78] were most resistant to protein adhesion. However, large proteins were also able to adsorb, to some extent, even on such hydrophilic surfaces.[75] Self-assembled monolayers containing ethylene glycol were among the most resistant to adhesion of proteins and bacteria. However, protein-resistant surfaces not containing ethylene glycol were also identified. For example, self-assembled monolayers comprised of linear poly(ethyleneimine) and poly(*N*-methylvinylamine) appeared to reduce protein adhesion.[77]

Belfort and colleagues developed a high throughput screening protocol to identify monomers capable of reducing protein adhesion on surfaces. This protocol was used in conjunction with graft polymerization of fouling-resistant polymers to poly(aryl sulfone) UF membranes.[79–83] From a library of over 66 monomers, those that appeared to be most resistant to protein adhesion were hydrophilic, hydrogen bond acceptors (but not hydrogen bond donors), and electrically neutral, in agreement with findings from the Whitesides group.[79] Ethylene glycol derivatives, as well as some amine- or amide-containing monomers, were resistant to both protein and natural organic matter adhesion.[79–83] Interestingly, zwitterionic monomers, which have positive and negative charged moieties but are electrically neutral overall, were effective in reducing adhesion of both proteins and natural organic matter.[80,81] Collectively, the results from such studies corroborated (largely empirical) previous observations regarding membrane fouling and have served to guide selection of fouling-resistant surfaces. Because hydrophobic, rough, highly charged membranes exhibit an increased fouling tendency (as described above), it is hypothesized that hydrophilic, smooth, electrically neutral membrane surfaces may foul less severely. Therefore, modification of surfaces to induce these characteristics has been a significant focus in efforts to prepare fouling-resistant membranes.[2,23,27,32,41,42,47,55,56,84,85]

2. Historical Perspective on Membrane Development and Surface Modification

Among the earliest examples of surface modification of a filtration medium to alter its transport properties may be found in W. Pfeffer's 1877 monograph, *Osmotische Untersuchungen*. Pfeffer described the formation of a copper ferrocyanide layer on porous porcelain. As a professor of botany interested in mimicking the semipermeable nature of plant cell walls, Pfeffer used these membranes to study osmosis following the observations of Nollet, Graham, and others. Pfeffer prepared copper ferrocyanide membranes by saturating porous porcelain with copper sulfate solution, then contacting one face of the porcelain with a solution of potassium ferrocyanide. A solid, thin, brown, copper ferrocyanide skin layer precipitated on the face of the porous porcelain. These semipermeable membranes provided a system by which Pfeffer could measure the osmotic flow of water from a reservoir of pure water on one side of the membrane to a reservoir of saline solution on the other.[86] This method of membrane preparation bears remarkable qualitative similarity to the formation of composite polyamide RO membranes (to be discussed shortly), which was reported over 100 years after Pfeffer's original work.

In 1896, C. J. Martin reported the modification of ceramic Pasteur-Chamerland water filters with gelatin or silicic acid. To modify filters with gelatin, a 10% solution of hot gelatin was fed through a filter under a pressure of 10 atmospheres until it cooled, forming a solid film within the filter pores. Filters were modified with silicic acid by filtering a solution of sodium silicate solution under a pressure of 5 atmospheres until all pores were coated, then immersing the filter in a bath of 3% HCl. After modification of the Pasteur-Chamerland filters, the separation of large proteins, such as albumins, fibrinogen, or hemoglobin, from relatively small molecules, such as water, dextrose, and urea, was possible. Films of these substances were coated within the porous structure of the filter, permitting selective filtration of molecules of relatively large molecular weight from those of relatively small molecular weight.[87]

Preparation of membranes by coating a porous structure continued into the 20th century. As described in a series of papers published in 1907 and 1908, Bechhold (who coined the term "ultrafiltration") fabricated membranes by impregnating filter paper with solutions of collodion, glacial acetic acid-collodion, and gelatin.[88] (Collodion generally refers to nitrocellulose dissolved in a mixture of alcohol and ether. The natural variability of nitrocellulose may have contributed to early difficulties in obtaining reproducible membranes.[89]) The pore size of the membranes could be varied by changing collodion or gelatin solution concentration; using this approach, the size of various solutes could be measured using membranes of differing pore sizes.[88] Later on, the membrane fabrication techniques developed by Bechhold were improved by others, including Elford, Krueger, and Ritter, who produced flat-sheet membranes of uniform thickness in a variety of pore sizes.[90] By 1928, membrane fabrication had advanced sufficiently that it was attractive for industrial use. Duclaux patented a method of producing UF membranes in large quantity by impregnating cloth with solutions of CA.[91] Early reviews of the development of UF membranes were published by Elford[89] and Ferry.[92]

Once membranes could be reproducibly fabricated, attention turned to understanding the effects of membrane surface properties on their transport characteristics. As early as 1920, Jacques Loeb was surface-modifying collodion membranes (prepared as freestanding collodion sacs) with dilute gelatin solutions. He observed changes in the osmotic behavior of membranes following gelatin treatment.[93] This work was extended by Hitchcock, who applied gelatin to flat-sheet collodion membranes. He concluded that the gelatin formed a film inside the pores of the membrane because the decrease in membrane permeability after modification was a linear function of the amount of adsorbed gelatin.[94]

The aggregation of proteins on membrane surfaces and within pores was a focus of early studies of protein filtration. Grollman discussed the effect of protein adsorption on the permeance of collodion membranes, noting that the adsorbed proteins reduced the effective pore size and membrane permeability. Importantly, he also mentioned that hydrophilic adsorbants (such as proteins) would strongly bind water to the membrane.[95] While Grollman stated that this solvent adsorption would further decrease the effective pore size of the membrane, the recognition that water may be strongly bound to membranes via an intermediary, hydrophilic substance forms the basis for much of the fouling mitigation surface modification strategies employed today.

One of the earliest descriptions of fouling mitigation appears in a 1923 publication by Brinkman and Szent-Gyorgyi. When attempting to filter a solution of hemoglobin through a collodion sac membrane, only water was observed to permeate through the membrane. Sodium oleate bound to the hemoglobin, and the membrane did not pass the hemoglobin/oleate complex. However, if a solution of sodium oleate was filtered prior to filtration of a hemoglobin solution, passage of hemoglobin through the membrane was observed. Brinkman and Szent-Gyorgyi concluded that aggregation of hemoglobin on the membrane surface blocked the pores to hemoglobin passage. When sodium oleate was filtered before hemoglobin, oleate adsorbed to the membrane surface, reducing aggregation of hemoglobin on the membrane surface, which helped reduce pore blockage.[96]

Others studied the effect of sodium oleate on filtration of other compounds. Elford, for example, reported the effect of sodium oleate on the passage of dye through collodion ultrafilters in 1933. In his studies, the addition of sodium oleate to a dye solution facilitated passage of the dye through a collodion membrane due to the preferential adsorption of the oleate over dye at the collodion/water interface. This “capillary active substance,” as sodium oleate and other such substances came to be known, was thought to minimize surface forces between the dye and the membrane, eliminating its adsorption to the membrane and encouraging its passage through the pores. Elford described the “protective action of the adsorbed layer of surface active molecules” as a key to the results that were observed.[97]

These substances were the subject of several early studies on filtration of biological solutes such as proteins and viruses using collodion ultrafilters. Publications by Ward and Tang[98] and by Galloway and Elford[99] both described an increase in passage of viruses through membranes when the viruses were suspended in biological broth instead of water. Galloway and Elford attributed this change in virus filterability to “modification of the surface properties of virus and filter owing to adsorption of certain surface active constituents of the broth.” They described the effect as “analogous to lubrication” because frictional forces between the virus and the membrane were reduced.[99]

The increasing availability of synthetic polymers accelerated membrane development throughout the late 1950’s and 1960’s. Practical RO membranes became a reality when Loeb and Sourirajan fabricated asymmetric RO membranes by phase inversion of CA from acetone solution in 1960, later described in a 1963 publication.[30] Glater reviewed much of the early history of RO membrane development.[22] Cationic, anionic, non-ionic, and amphoteric “surface active agents” were also tested when adsorbed to CA Loeb-Sourirajan RO membranes by Vos and Burris in 1969.[100] In this work, the authors were studying the effects of various adsorbents, including nonionic materials (*e.g.* poly(vinyl alcohol), ethylene glycol, glycerol, poly(vinyl methyl ether)), and various commercial anionic and cationic surfactants, on the drying of CA membranes. Membrane drying typically results in an irreversible loss in membrane permeability because, as water evaporates from within the porous substructure, strong capillary forces can bring about pore collapse. The authors found that, once an RO membrane was treated with many of the tested surface active agents, it could be dried and later re-hydrated with no loss of permeability. The authors suggested that surface active agents which acted as humectants—typically hydrophilic substances—were best suited to this application because they strongly attract water molecules to the membrane surface.[100] Presumably, this strongly bound water would not readily evaporate from the porous substructure, preventing pore collapse.

While Loeb and Sourirajan prepared RO membranes by phase inversion of commercial CA from acetone,[30] Hillman attempted direct surface acetylation of regenerated cellulose films.[101,102] This procedure resulted in an asymmetric structure, where the surface was CA and the substructure was cellulose. The most highly-rejecting membrane achieved by this technique had an NaCl rejection of 98%;[101] today, most RO membranes used for drinking water desalination achieve rejections well above 99%.[16]

The modern RO membrane can be traced to the late 1970’s, when Cadotte developed the thin film composite polyamide membrane.[17,103–105] This membrane was the product of work begun in 1967, when porous support membranes were fabricated from PSf by phase inversion. Like the Loeb-Sourirajan membranes, these PSf UF membranes were prepared via phase inversion and had an asymmetric structure. They had small (20 nm) pores on one side and much larger (400 nm) pores on the other. A high flux, high salt rejection, ultrathin barrier layer was formed atop the small pores on one face of the UF support membrane.[104] In this sense, the modern polyamide RO membrane may be considered a surface-modified UF membrane. The UF membrane was saturated with an aqueous solution of m-phenylene diamine, and subsequently contacted with an organic solution of trimesoyl chloride. An interfacial polymerization occurred at the oil/water interface, forming a crosslinked aromatic polyamide atop the PSf support membrane.[105]

By the early 1980's, techniques used to fabricate modern membranes had been developed. Polymers of many types were successfully being used to fabricate MF, UF, and RO membranes. In 1982, Lonsdale published a review describing developments in membrane technology until that point.[25] Since then, a substantial amount of membrane research has focused on improvement of the properties of these basic membrane architectures, and surface modification has played a significant role in that work.

3. Overview of Surface Modification Strategies

This review is organized by modification technique. First, additive blending is covered, where one or more surface-modifying components are incorporated into a polymer used to form the membrane. Although this technique is not a modification of a pre-formed membrane, per se, the surface-modifying reagents typically preferentially partition to the surface of the polymer membrane, forming a membrane that has different surface and bulk properties. Surface-modifying compounds may also be applied to the surface of pre-formed membranes. In the simplest case, these agents, which are often hydrophilic macromolecules, are adsorbed to the surface of the membrane. To improve the durability of these surface modifications, the macromolecules may be coated onto the membrane surface and subsequently cured by crosslinking, forming a hydrogel-like material.

A variety of surface treatment techniques are reviewed, including chemical treatment, plasma treatment, UV irradiation, and other related techniques. These approaches may be used alone or in concert with other methodologies. For example, exposure of a membrane to various plasmas can hydrophilize its surface.[106,107] However, plasma may also be used to activate the surface of a membrane, which then facilitates further modification, such as grafting of hydrophilic macromolecules to the surface.[64,107]

Grafting is a popular technique for modifying the surface of many organic and inorganic substrates. Several reviews have been published describing various applications and techniques for grafting. [108–110] Here, grafting will refer to the attachment of macromolecules to a substrate (e.g., membrane) surface. Grafting has been widely applied in biomaterials, where synthetic polymers, proteins, polysaccharides, and other macromolecules have been applied to surfaces of biomaterials to reduce thrombogenic response upon implantation (reviewed by Amiji and Park[111]). Similarly, grafting of hydrophilic polymers has been used to improve the fouling resistance of membranes. Grafting can be accomplished by either: a) tethering a synthetic or natural polymer chain to the membrane surface ("grafting to") or b) growing a polymer chain from the membrane surface ("grafting from").[27,109] In the case of a "grafting to" reaction, an end-functionalized polymer is covalently bound to a membrane surface containing an appropriate reactive group. These polymers may be synthesized by anionic, cationic, living free radical, group transfer, or ring-opening metathesis polymerizations,[110] which permit fine control over the structure and properties of the polymer prepared.[27] The use of polymer chains with a narrow molecular weight distribution may improve membrane surface uniformity, which has been associated with improved filtration efficiency.[112] However, "grafting to" reactions typically result in relatively low graft densities[27] because the functionalized polymer chains must be able to diffuse freely to the membrane surface; as the layer of grafted polymer builds, this diffusion is hindered.[110] Additionally, special coupling reactions may be required between the membrane surface and the grafted polymers.[27] In contrast, a wide variety of grafting densities may be accessible with polymers that are "grafted from" the surface.[27] However, chain length may be less well-controlled than with polymers "grafted to" the surface, and appropriate initiating species must be present on the membrane surface to begin chain growth.[27] Immobilization of appropriate initiators is generally possible via several techniques, such as plasma, corona discharge, or chemical treatment.[110]

Finally, significant attention is devoted to surface modification via application of polydopamine, which is a recently developed surface modification technique. Polydopamine formation is an aqueous-based process that can be accomplished on nearly any substrate. Surfaces coated with polydopamine become hydrophilic, but the polydopamine coating is thin and conformal so surface geometry is largely unaltered.[113] The chemistry of polydopamine is still not well understood, thus a review of literature describing studies of the chemical structure of polydopamine and related catecholamine compounds is also included, particularly as they may pertain to membrane development and improvement.

4. Additive Blending

Surface modification may be achieved by incorporating a surface modifying additive (e.g., a hydrophilic component) into the membrane casting solution before membrane formation. Many porous water purification membranes (e.g., UF and MF membranes) are formed via phase inversion, in which a solution of the membrane matrix polymer is cast from a solvent to form a film and subsequently immersed in a non-solvent, causing the polymer to solidify.[114] The membrane polymer is often hydrophobic and dissolved in a water-miscible organic solvent; water is commonly used as a non-solvent. A hydrophilic material in the casting solution will tend to migrate to the membrane and pore wall surfaces during phase inversion. In this way, a membrane largely comprised of a hydrophobic polymer, but with a hydrophilic surface, is formed.

Most commonly, so-called "surface modifying macromolecules" are used in this capacity. To enhance the miscibility of the surface modifying macromolecule with the membrane matrix polymer, the surface modifying macromolecule may be a copolymer comprised of the hydrophobic membrane matrix polymer and a hydrophilic polymer. For example, Mayes *et al.* used atom transfer radical polymerization to synthesize amphiphilic comb copolymers of PVDF and poly(oxyethylene methacrylate) (POEM). X-ray photoelectron spectroscopy showed surface segregation of the POEM blocks in PVDF membranes. Membranes prepared by phase inversion from a blend of PVDF and PVDF-*g*-POEM showed higher hydrophilicity and lower protein adhesion than a pure PVDF membrane.[115] Mayes *et al.* also synthesized similar amphiphilic comb copolymers comprised of a PVDF backbone with poly(methacrylic acid) side chains,[115] a poly(methacrylate) backbone with poly(ethylene oxide) side chains,[116] and a PSf backbone with poly(ethylene glycol) (PEG) side chains.[117]

In related studies, polyurethanes were end-capped with PEG and incorporated into PES solutions, which were then used to cast UF membranes. Membranes containing the hydrophilic surface modifying macromolecules showed higher flux than control PES membranes when filtering river water.[118] Fluorine-containing surface-modifying macromolecules have also been considered. Although these macromolecules are generally hydrophobic (rather than hydrophilic, as is more typical), they were investigated because fluorinated surfaces have very low surface energy. Fluorinated surface modifying macromolecules based on PES[119] and on a methylene bis-phenyl diisocyanate/propylene diol copolymer[120] were incorporated into PES UF membranes. Membranes containing surface modification macromolecules generally showed improved flux when filtering river water[119] or oil/water emulsions[120] relative to control membranes that did not contain such surface modification macromolecules. The kinetics of migration of surface modifying macromolecules to the surface of polyethersulfone membranes have also been investigated.[121]

Commercial amphiphilic copolymers have also been studied for this application. For example, Jiang *et al.* incorporated a PPO-PEO-PPO triblock copolymer (from the family of Pluronics polymers) into PES UF membranes. They also blended PEO into the casting solution as a pore-forming agent, which was rinsed away after membrane solidification. Membranes incorporating the triblock copolymer showed reduced fouling relative to PES control membranes during oil/water emulsion fouling experiments.[122,123] Figure 8 shows the improvement in flux realized for a membrane formed with 15% of Pluronic F127 in the casting solution relative to a control PES membrane. Three cycles of oil/water emulsion ultrafiltration followed by washing with sodium dodecyl sulfate surfactant solution were performed. The modified membrane maintained improved flux during emulsion filtration and was able to more completely recover flux during washing.[123]

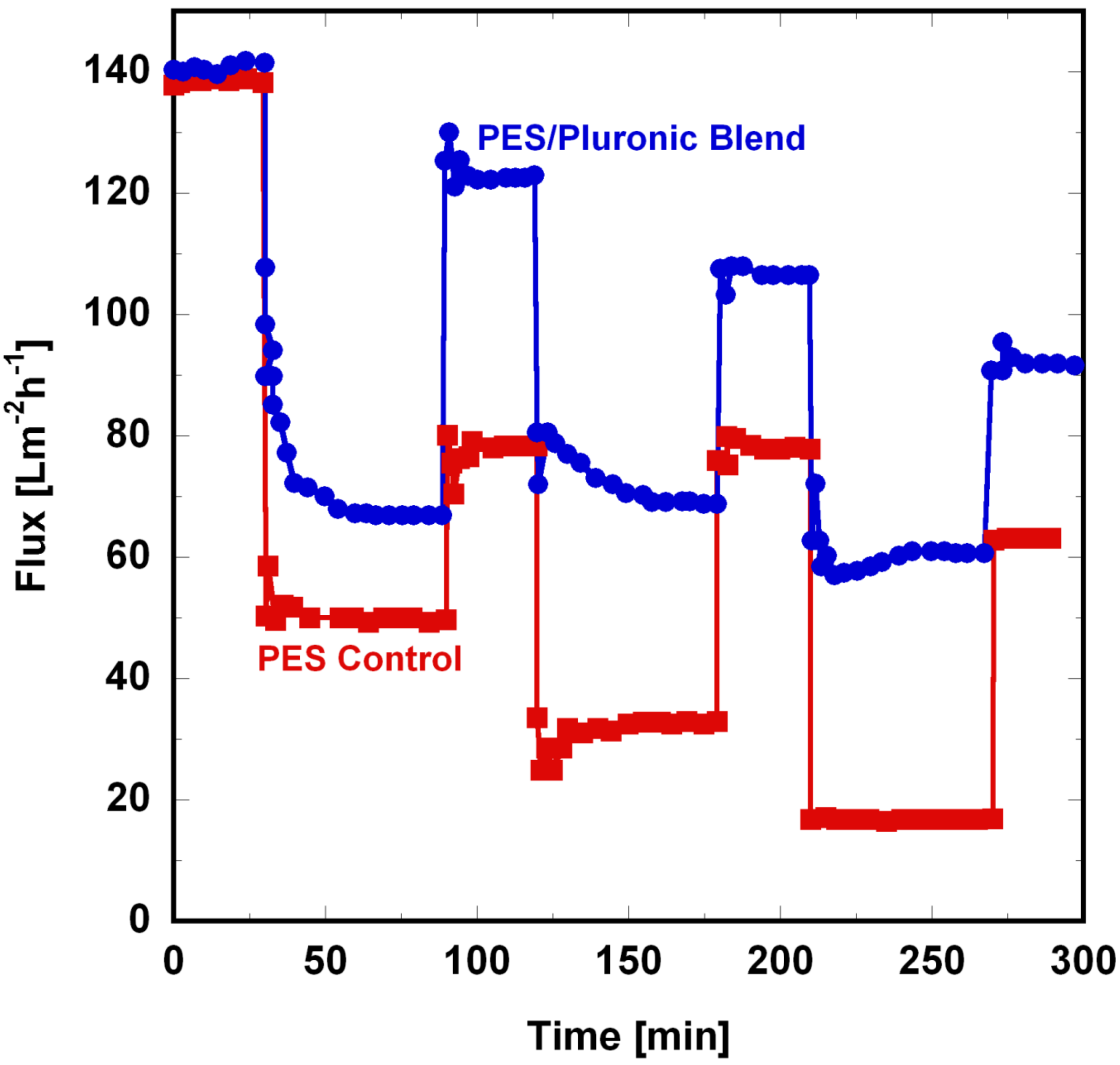


Figure 8. Ultrafiltration performance of PES control membranes and PES/Pluronic blend membranes. Blend membranes contained 15% F127 Pluronic material. The membranes were alternately challenged with a soybean oil emulsion feed and washed with an SDS surfactant solution. The blend membrane exhibited higher flux during oil emulsion filtration and improved flux recovery upon being cleaned.[123]

5. Adsorbed Coatings

Rather than incorporating a material into the casting solution to preferentially migrate to the surface during membrane formation, the membrane may be directly coated, after formation, with another material that imparts desirable characteristics to the surface. In this section, coatings that are non-covalently bound to the membrane surface will be considered. Such coatings may consist of material that is simply adsorbed to the membrane surface via secondary interactions (e.g., van der Waals or electrostatic interactions) or materials that are cured (e.g., crosslinked) *in situ* on the membrane surface to afford enhanced stability. The strength of these secondary interactions depends upon the nature of the polymer surface and of the surface modifier, but generally electrostatically-adsorbed modifiers, such as those applied by layer-by-layer (LBL) deposition, exhibit robust adhesion. Covalent coupling to membrane surfaces will be considered in later sections.

5.1 Uncured Coatings

Membrane surface properties may be modified by adsorbing "surface active agents" to the membrane. The surface active agent is held to the membrane surface by strong secondary interactions; no chemical coupling is required. This approach allows modification of membranes after preparation, thus separating the membrane formation and membrane modification steps. This method is reminiscent of the studies of Brinkman and Szent-Gyorgyi, who adsorbed sodium oleate to collodion filters.[96] Early work from Fane *et al.* focused on adsorbing various polymers and surfactants to PSf UF membranes. Nonionic surfactants,[124] anionic surfactants,[125] and uncharged polymers[126] were employed. Adsorption of these substances to the membrane surface generally caused a decrease in membrane permeability to pure water, but the flux of the modified membrane during filtration of protein solutions was higher than that of an unmodified membrane. The treated membranes showed an advantage when tested over the course of several usage cycles, each of which included surface treatment, filtration, and cleaning.[124,126] Langmuir-Blodgett deposition was also used to coat UF membranes with a variety of oriented, non-ionic surfactant monolayers. Modified membranes showed an improvement in flux during protein filtration relative to untreated membranes.[127] Speaker patented a technique for surface-modifying RO membranes with fluorinated, amphiphilic molecules using the Langmuir-Blodgett technique to produce smooth, fouling-resistant membranes.[128] Self-assembly of trimethylamine oxide, a small amphiphilic molecule, reduced the adhesion of proteins to a hydrophobic alkane-thiol surface by up to 75%.[129]

Reinhard *et al.* coated thin film composite polyamide RO membranes with a layer of polyether-*b*-polyamide copolymer.[62,130] This hydrophilic polymer, known as PEBAX® (Figure 9a), was adsorbed to the membrane surface by dip-coating the membrane in a 1% polymer solution (Figure 9b). The resultant membranes were more hydrophilic and smoother than the native membranes, indicating that the adsorbed polymer was able to fill the deep valleys of the rough polyamide membrane surface. The addition of the copolymer coating to the membrane surface decreased pure water flux due to the additional resistance to water transport imparted by the coating.[62,130] Despite this decrease, the coated membrane exhibited a higher flux during oily water fouling tests than an unmodified membrane.[62]

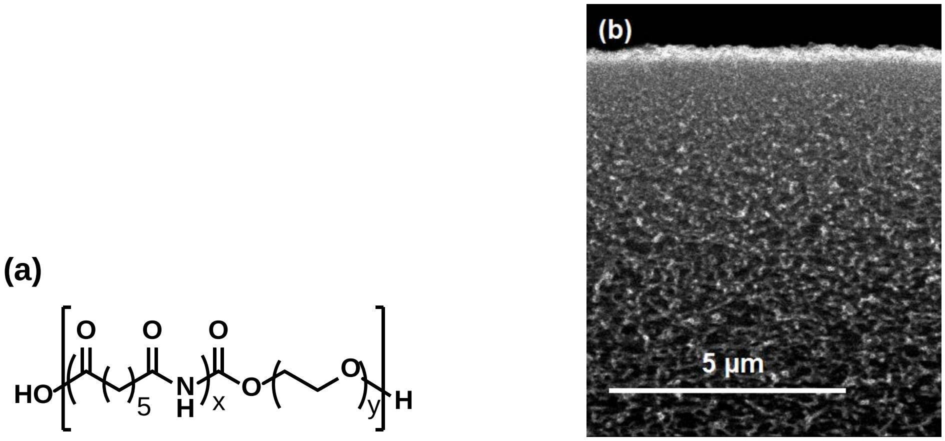


Figure 9. (a) Structure of PEBAX® employed by Reinhardt *et al*. (b) Cross-section of modified composite RO membrane, showing PEBAX® coating atop the selective layer. Reproduced with permission, Elsevier B.V.[62]

Hyun *et al.* synthesized comb copolymers with a poly(methyl methacrylate) backbone and oligoethylene glycol side chains. The copolymers were adsorbed to PSf membranes formed by phase inversion; severe reductions in membrane permeance were avoided by optimizing the coating conditions. Modified and unmodified membranes were challenged with a variety of biological feeds, including bovine serum albumin solution, alginate solution, and a cell suspension. With all feeds, the modified membranes maintained higher flux than the unmodified membranes during filtration over several days. Modified membranes exhibited a much greater response to cleaning cycles than unmodified membranes. These performance improvements were attributed to the increased hydrophilicity of the modified membranes.[131]

Polyelectrolytes have also been widely used in adsorptive conditioning of membranes. Nyström observed that fouling severity was reduced during protein filtration when polyethylenimine was adsorbed to PSf UF membranes. This reduction in fouling was attributed to the shielding effect provided by the charged polyethylenimine against charged proteins. Fouling reduction was further improved when the ionic strength of the feed was increased, which presumably increased the charge density on the modified membrane surface and on the protein. While fouling alleviation might only be expected when the membrane surface bears the same charge as the foulant, Nyström found significant improvement in fouling tendency when a negatively charged membrane was challenged with a feed containing positively charged proteins. The hydrophilicity of the membrane (which is heightened when either positively or negatively charged) may play a greater role in fouling resistance than the sign of its charge.[132]

Reddy *et al.* modified polyethersulfone UF membranes of various molecular weight cutoff (MWCO) values with poly(sodium 4-styrene sulfonate) (PSS). Membranes with a relatively low MWCO were modified primarily on the top surface while membranes with a high MWCO were modified on the surface and within the pores. Surface modification with polyelectrolytes was shown to be an effective way of imparting ion rejection to UF membranes through a charge repulsion mechanism; typically, NF or RO membranes are required for ion separation, which reject ions on a size exclusion basis. Additionally, relative to unmodified membranes, modified membranes showed enhanced ability to be cleaned after fouling with PEG or dextran.[133]

Polyelectrolytes have been employed in many other studies of LBL deposition of surface coatings. A variety of substrates have been modified by the application of alternating layers of oppositely-charged polyelectrolytes. The layers are held together by the electrostatic interactions between the layers, and the rigidity of the assembly increases as more layers are added.[134] LBL surface modifications offer good adhesion due to the large number of charged groups on each molecule and are relatively insensitive to small surface imperfections.[135] For example, LBL deposition was used to coat commercial PP MF membranes. PP MF membranes were first treated with CO_2 plasma to create peroxides on the membrane surface, and then acrylic acid was grafted from the peroxides. This pretreatment process provided a high density of negatively charged sites on the membrane surface on which to build a multilayer structure. Polyelectrolytes were tethered to the membranes by successive dipping in oppositely charged solutions. As a result, LBL modification may be used to test the effect of charge on membrane fouling. Meier-Haack and Müller showed that protein adhesion was reduced with identical charges on the membrane and protein and enhanced with opposing charges.[136]

In addition to fundamental work on the effect of charge on membrane fouling, LBL deposition of polyelectrolytes has also been used to fabricate NF membranes with high selectivities for monovalent ions over multivalent ions. The Bruening group published a number of reports describing LBL deposition techniques for fabrication of NF membranes using alumina supports, as illustrated in Figure 10.[137–139]

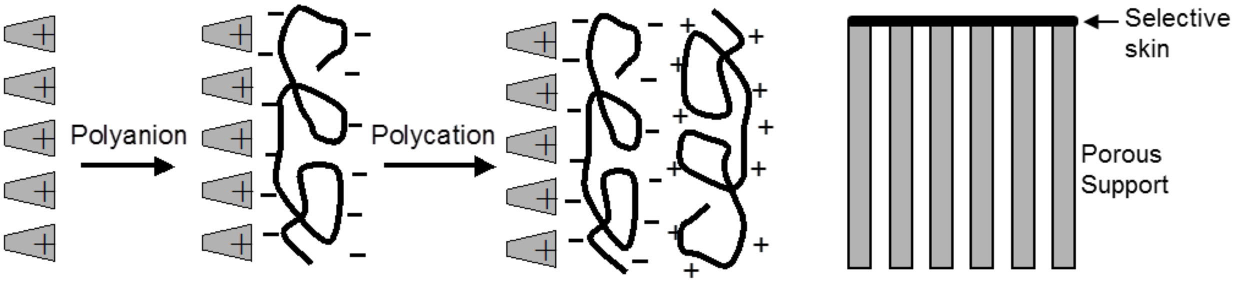


Figure 10. LBL deposition technique employed for fabrication of salt-selective NF membranes atop a porous substrate. Multilayer films were constructed by repetitive, alternating deposition of positively- and negatively-charged electrolytes. Reproduced with permission, John Wiley & Sons, Inc.[139]

Poly(pyromellitic dianhydride-phenylenediamine) (PMDA-PDA) and poly(allylamine hydrochloride) (PAH) bilayers were alternately deposited on a porous alumina substrate. After the deposition was complete, the composite membrane was heat-treated which generated a solid polyimide from imidization of the PMDA-PDA layer. Membrane selectivity for monovalent ions over divalent ions was high, and it could be tuned by heat treatment and number of PMDA-PDA/PAH bilayers.[138,139] For example, Cl^-/SO_4^{2-} selectivities as high as 1100 were realized for membranes with 2.5 bilayers treated at 180 ºC and K^+/Mg^{2+} selectivities as high as 310 were realized for membranes with 3.5 bilayers treated at 150 ºC.[138] Variation in charge density through the use of different polyelectrolytes, which consequently results in tighter or looser packing within the selective polyelectrolyte layers, allowed for fabrication of membranes on porous alumina with a range of MWCO values, permitting size discrimination of neutral compounds.[140] Breuning et al. extended this technique to polymeric substrates by depositing polyelectrolyte bilayers onto PES UF membranes to form high-flux, ion-selective NF membranes.[141] Membranes prepared in this fashion achieved Cl^-/SO_4^{2-} selectivities of up to 28 and pure water permeances of approximately 8.5 L m^{-2} h^{-1} bar^{-1}.[141] Commercial polyamide NF membranes, in comparison, typically exhibit pure water permeances of approximately 9 - 15 L m^{-2} h^{-1} bar^{-1}.[63,142] Similarly, Hollman and Bhattacharyya deposited alternating layers of the charged polypeptides poly(L-lysine) and poly(L-glutamic acid) inside the pores of polycarbonate track-etch MF membranes to yield ion-selective NF membranes. Pure water permeances of 16 L m^{-2} h^{-1} bar^{-1} and Cl^-/SO_4^{2-} selectivities of up to 8.2 were reported.[143]

A number of authors have reported that the adsorption of TiO_2 nanoparticles on membrane surfaces mitigates fouling. TiO_2 nanoparticles are hydrophilic and effectively impart fouling resistance when coordinated with free hydroxyl groups on the surfaces of PES UF[144] and PES/polyimide blend NF[145] membranes. Figure 11 shows two proposed coordination mechanisms for TiO_2 to a PES membrane surface.

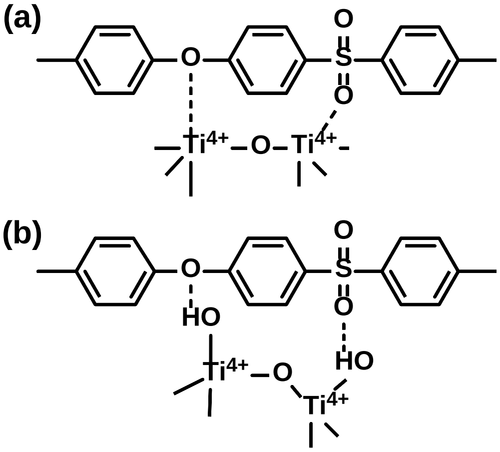


Figure 11. Proposed bonding of TiO_2 to PES. TiO_2 may bond directly to the sulfone groups (a) or by hydrogen bonding through a hydroxyl moiety on the TiO_2 nanoparticle surface (b).[144]

Bae and Tak assessed the effect of TiO_2 nanoparticles on fouling of PSf UF membranes in membrane bioreactors. Immobilization to the membrane surface was accomplished in two ways.

Nanoparticles were embedded within the membrane matrix by incorporation of TiO_2 nanoparticles in the membrane casting solution (which also included the polymer and n-methyl-2-pyrrolidone). Membranes were formed by casting the solution onto a polyester nonwoven fabric followed by solvent-induced phase separation in water. Alternatively, nanoparticles were deposited on the membrane surface by soaking a membrane (prepared without inclusion of nanoparticles in the casting solution) in a TiO_2 nanoparticle suspension. Both types of modified membranes were compared to unmodified membranes (without embedded or deposited nanoparticles). The hydrophilic, modified membranes exhibited higher flux than unmodified membranes when challenged with mixed liquor from a submerged membrane bioreactor plant.[146,147] This fouling mitigation was most pronounced when TiO_2 nanoparticles were adsorbed to the surface; nanoparticles entrapped within the membrane matrix were not as effective in reducing fouling.[147]

In a similar study, Kwak *et al.* aimed to leverage the photobactericidal properties of TiO_2 to address biofouling on composite polyamide RO membranes. When exposed to UV light, TiO_2 generates active oxygen species, such as hydroxyl radicals, which attack cell membranes. Composite polyamide RO membranes, prepared on PSf UF supports, were dipped in colloidal suspensions of TiO_2 nanoparticles, which coordinated with residual carboxylic acid moieties on the membrane surface. Modified membranes showed a bactericidal effect against *E. coli* after UV exposure.[148,149] *E. coli* cells attached to the surfaces of membranes containing TiO_2 were essentially unable to survive after four hours of UV exposure, compared to 40% survival on unmodified membranes with four hours of UV exposure and 60% survival on unmodified membranes without UV exposure.[148] Membranes modified with TiO_2 and exposed to UV light exhibited approximately a 10% decrease in flux due to *E. coli* biofilm growth. For comparison, unmodified membranes exhibited approximately a 20% decrease in flux, and unmodified membranes not exposed to UV light exhibited approximately a 30% decrease in flux. Unmodified composite polyamide RO membranes had a salt rejection of 94.7%, and membranes modified with TiO_2 nanoparticles had a salt rejection of 96.0%; salt rejection during biofilm growth was not reported.

Removable coating layers adsorbed on the membrane surface have been explored for foulant removal. During filtration, if the flux reaches a very low level, a membrane modified with such a coating could be backwashed, causing the coating layer to be removed, thereby lifting accumulated foulant away from the membrane surface. Galjaard *et al.* developed a means of pre-coating MF or UF membranes with a highly permeable, incompressible, removable layer of particles by exposing the membrane to a particle suspension before use. The study largely employed commercially available commodity particulates, including titanium dioxide, zeolite, kaolinite, iron oxide, and others. Some of the particles, such as TiO_2, quartz, and zeolite, appeared to clog the membrane, resulting in decreases in membrane pure water permeance by 13 - 26%. Other types of particles, such as diatomite, kaolinite, and FeO, exhibited no effect on membrane permeance, likely because they settled atop the membrane surface and formed a highly-permeable coating layer. Membrane fouling propensity was evaluated by challenging modified and unmodified membranes with raw lake water. After backwashing, membranes that were pretreated with a layer of diatomite fully recovered their permeance, whereas unmodified membranes suffered a 28% irreversible reduction in permeance.[150]

5.2 Cured Coatings

A significant disadvantage of membrane surface modification by adsorption is that, because the adsorbed material is not covalently bound to the surface, it may leach from the surface over time. Such coating deterioration may be reduced by a curing step after application, such as crosslinking, which provides mechanical integrity to the coating layer and may offer some physical coupling to the membrane due to the inherent roughness of the membrane surface.

For example, crosslinked PEG-based hydrogel coatings have been explored to improve the fouling resistance of UF and RO membranes to oil/water emulsions. A family of fouling-resistant coating materials were prepared from poly(ethylene glycol) diacrylate (PEGDA, a crosslinker) alone[151,152] or in combination with various other hydrophilic co-monomers, including acrylic acid, 2-hydroxyethyl acrylate, and poly(ethylene glycol) acrylate.[153–156] Crosslinking was accomplished by UV-induced free radical polymerization in the presence of a photoinitiator, 1-hydroxycyclohexyl phenyl ketone. In the most fundamental studies, the transport properties of the hydrogels were studied as a function of prepolymerization solution water content and PEGDA crosslinker chain length. Figure 12 shows cryoSEM images of crosslinked PEGDA hydrogels containing (a) 0 wt% water in the prepolymerization solution, (b) 80 wt% water in the prepolymerization solution, and (c) cross-sectional SEM of a crosslinked PEGDA hydrogel applied to a PSf UF membrane.

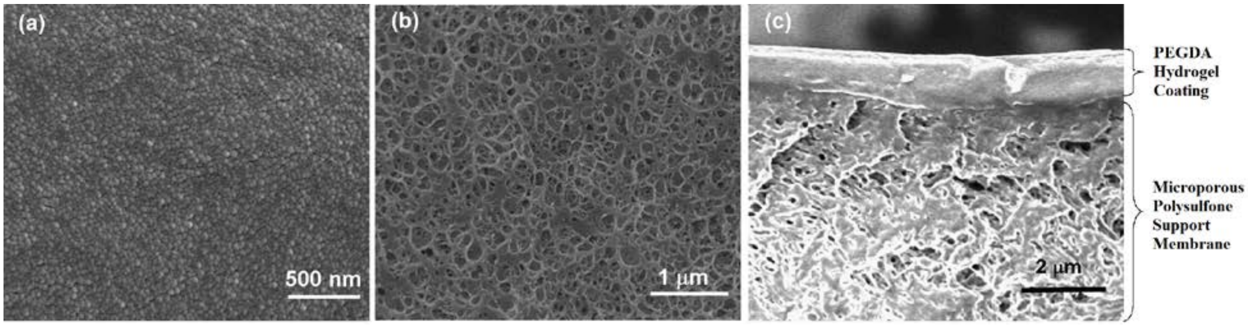


Figure 12. (a) CryoSEM image of crosslinked PEGDA hydrogel with 0 wt% water in the prepolymerization solution. (b) CryoSEM image of crosslinked PEGDA hydrogel with 80 wt% water in the prepolymerization solution. (c) SEM image of crosslinked PEGDA coating (0 wt% water in the prepolymerization solution) on a porous PSf support membrane. Reproduced with permission, Elsevier B.V.[151]

A tradeoff between water permeability and organic solute rejection was identified, where increasing the prepolymerization solution water content and PEGDA chain length led to higher water permeability and decreased organic rejection.[152] Similarly, hydrogels with high water permeability also exhibited high salt permeability.[153,154,156] Salt permeability was strongly correlated with free volume element size, which was characterized by positron annihilation lifetime spectroscopy analysis of both dry and hydrated samples. Free volume element size appeared to be a function of the prepolymerization solution water content, comonomer concentration, and PEGDA chain length; increasing any of these variables resulted in decreases in crosslink density and, therefore, increases free volume element size.[153] Studies of BSA adhesion revealed that the hydrogels may be useful materials to reduce membrane fouling propensity.[152,156] Similar results were obtained with hydrogels comprised of *N*-vinyl-2-pyrrolidone monomer and *N*,*N'*-methylenebisacrylamide crosslinker.[157]

PEG-based hydrogels have been applied to commercial PSf UF[151] and thin film composite polyamide RO[155] membranes. A polymerization-induced phase separation occurred in hydrogel films containing greater than 60 wt% prepolymerization solution water content (visualized by cryoSEM, cf., Figure 12b).[152,156] These porous hydrogels were especially suitable for coating onto porous PSf UF membranes because they had high water permeabilities. The application of PEGDA hydrogels containing 80 wt% water in the prepolymerization solution to PSf UF membranes reduced the water permeance from 141 L m^{-2} h^{-1} bar^{-1} to 36 L m^{-2} h^{-1} bar^{-1}. However, following 20 hours of crossflow filtration of a 1500 ppm emulsified oil emulsion feed, a coated membrane exhibited a flux of approximately 60 L m^{-2} h^{-1}, and the uncoated membrane had a flux of approximately 20 L m^{-2} h^{-1}, as shown in Figure 13a. Additionally, the organic rejection following the same filtration was 98.0% for the uncoated membrane and 98.5% for the coated membrane (Figure 13b).[151]

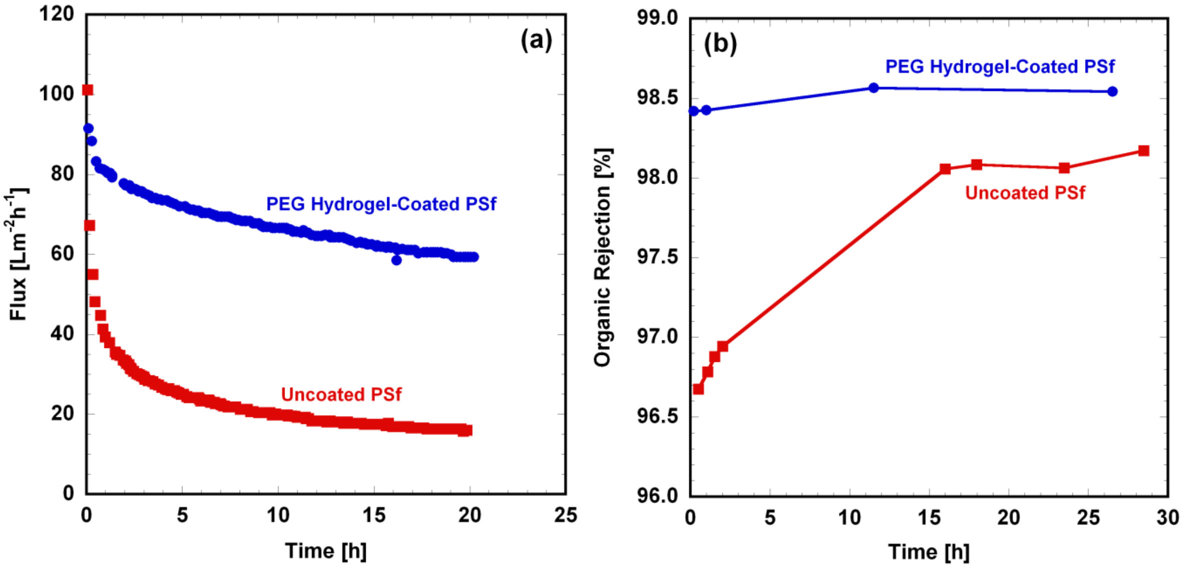


Figure 13. Flux (a) and organic rejection (b) of an uncoated PSf membrane and a PSf membrane coated with a crosslinked PEG hydrogel. Membranes were challenged with a 1500 ppm soybean oil emulsion in crossflow filtration. The coated membrane exhibited improved flux and organic rejection relative to the unmodified membrane.[151]

Polyamide RO membranes were coated with hydrogels containing 60 wt% water in the prepolymerization solution, which provided improved mechanical properties but lower water permeability relative to the 80 wt% water hydrogels used for UF membranes. For example, after 24 hours of crossflow filtration with an oil emulsion feed containing n-decane and DTAB surfactant, an unmodified RO membrane exhibited a water flux that was 26% of its initial value, whereas a coated RO membrane was able to maintain a water flux that was 76% of its initial value.[155]

Other similar fouling resistant membrane coatings have been reported. For example, La *et al.* incorporated aluminum-containing monomers into the prepolymerization solutions for PEG-based hydrogels to impart antimicrobial properties on the membrane coating. These hydrogels were crosslinked by UV irradiation. Modified membranes exhibited both resistance to oil emulsion fouling and antimicrobial activity.[158] Similarly, Emrick *et al.* coated PVDF UF membranes with coatings comprised of amphiphilic polyolefin-PEG graft copolymers. Graft copolymers were synthesized by ring opening metathesis polymerization of cyclooctene-*g*-PEG monomers that had been functionalized with phenyl azide moieties. Chains were crosslinked by decomposition of the phenyl azides upon UV irradiation. Modified membranes initially exhibited lower permeance during oily water emulsion crossflow fouling studies, but after eight days of fouling, the modified membrane exhibited higher permeance than unmodified membranes. Modified membranes also had higher organic rejection during fouling than unmodified membranes.[159] Finally, PSf UF membranes have also been coated with uncrosslinked PEG-chitosan hybrid films. Solutions containing poly(ethylene glycol) diglycidyl ether and chitosan were coated onto UF membrane surfaces and evaluated by pure water permeation, organic rejection, and crossflow fouling tests. Modified membranes exhibited reduced pure water permeability but enhanced flux during oil/water emulsion filtration relative to unmodified membranes. For example, a membrane modified with a thin (0.2-0.45 μm) coating of 1:1 composite of PEG:chitosan had an initial permeance of 35.4 L m^{-2} h^{-1} bar^{-1} and a permeance of 24.8 L m^{-2} h^{-1} bar^{-1} after 24 hours of crossflow filtration with an oil/water emulsion, a decrease of about 30%. In comparison, an unmodified membrane had an initial permeance of 362 L m^{-2} h^{-1} bar^{-1}, but its permeance decreased to 10.6 L m^{-2} h^{-1} bar^{-1} after oil emulsion filtration, a decrease of 97%.[160]

Fabrication of composite membranes, based on coating scaffolds or other porous supports, has been a field of interest to several groups; hydrogels have been widely used in this application. Crosslinked poly(vinyl alcohol) has been a popular choice and has been coated on various substrates, including PSf UF membranes,[161–163] regenerated cellulose membranes,[164] and nanofibrous PVA scaffolds.[165] Composite RO and NF membranes were fabricated from PSf UF membranes. A PVA solution was cast onto UF membranes, dried, and then contacted with a solution of malic acid, a crosslinking agent, and acetic acid, a catalyst. By coating with PVA hydrogels, UF membranes were capable of removing approximately 90% of NaCl from a 2000 mg L^{-1} NaCl feed.[162] While these composite membranes did not exhibit salt rejections competitive with current commercial NF or RO thin film composite RO membranes ($\geq$98.0%[166]), they appeared to resist degradation by hypochlorite.[161] Li and Barbari spin-coated PVA hydrogels onto regenerated cellulose membranes, which improved the membranes' resistance to irreversible fouling.[164] Following protein ultrafiltration, unmodified membranes recovered 88-90% of their initial flux, while PVA-coated membranes recovered 94-100% of their flux, with thicker hydrogel coatings providing more irreversible fouling resistance.[164]

A variety of other materials have been used in composite membrane fabrication. Mayes *et al.* coated commercial PVDF UF membranes with a film of PVDF-*g*-poly(oxyethylene methacrylate) (POEM), an amphiphilic copolymer. The PVDF backbones created a continuous, semicrystalline phase while the POEM side chains created size-selective transport channels in the nanofiltration regime. The PVDF-*g*-PEOM-coated membrane exhibited a pure water flux 10 times higher than a comparable polyamide composite NF membrane. Furthermore, during filtration of oil/water emulsions, the PVDF-*g*-PEOM-coated membrane had a flux 16 times higher than the polyamide composite membrane.[167] Similarly, Hsaio, Chu, and co-workers fabricated a high flux UF/NF membrane by depositing a chitosan coating atop a two-layer support structure consisting of an electrospun PAN scaffold and non-woven PET fabric. Membrane performance was evaluated by filtration of oil/water emulsions. After 24 hours of crossflow filtration, the chitosan-coated membranes had fluxes that were approximately 15 - 20 times higher than a conventional thin-film composite polyamide NF membrane. The organic rejection of the chitosan-coated membrane was greater than 99.95%, while that of the conventional polyamide membrane was 99.4%. [168]

5.3 Surface Coatings on Commercial Membranes

Surface modification is an important aspect of commercial membrane production. Fouling has long plagued many industrial membrane installations.[169] By 1996, nearly 50% of all MF membranes on the market were surface-modified.[20] Several reviews of RO membrane technology describe industrial modification techniques for improved fouling performance.[24,170] Surface coating is currently a preferred method for mitigating fouling of RO and NF membranes,[170] and the coatings are robust enough to be considered “permanent.”[171] Authors from both Hydranautics[171,172] and Dow[173,174] have contributed reports of field experience with modified RO and NF membranes. Although the exact nature of the surface modification is typically not described in detail, these studies demonstrate that surface modification is a viable means of improving performance of commercial membrane products. Hydranautics had identified surface charge and hydrophilicity as being primary contributors to membrane fouling propensity, and they aimed to develop membranes with neutral, hydrophilic surfaces for highly-fouling feedwaters.[171] The LFC1 was the first such membrane developed by Hydranautics and was brought to market in 1996;[24] an updated version, the LFC3-LD, was introduced in 2005.[24,175] The LFC membranes are targeted at wastewater reclamation applications. In field tests, LFC membranes exhibited low fouling rates and improved performance relative to conventional membranes. For example, an LCF1 module and an uncoated polyamide composite RO module were used to remove salts from ultrafiltrate at a municipal water treatment facility. The modules were operated at a constant flux of 17 L m^{-2} h^{-1}; the LFC1 module initially required a higher transmembrane pressure than the uncoated module to achieve this flux. However, after 2000 hours of filtration, the LFC1 module required a transmembrane pressure of 7 bar to maintain the desired flux, whereas the uncoated polyamide module required 11 bar.[171]

The Millipore Corporation has a long history of research in surface coatings for fouling mitigation. In 1986, Steuk was granted a patent for water purification membrane surface treatment.[176] This patent describes the preparation of a composite membrane, which consists of a microporous membrane coated with a crosslinked layer of hydrophilic polymer. The coating, which is applied to both the top surface of the membrane and inside the pore walls, relies on no intermediate binding agent and makes the membrane surface hydrophilic. To form the coating, a monomer solution, containing a crosslinkable monomer and a free radical initiator, is applied to the membrane surface and subsequently crosslinked by exposure to an energy source, such as UV irradiation. Many different membrane and coating combinations are claimed, but a preferred combination is a PVDF microporous membrane coated with crosslinked hydroxyalkyl methacrylate. Membranes modified in this way exhibited low protein adsorption.[176] Millipore continued to develop this surface coating technology; a number of their patents describe various polymeric coatings, including crosslinked hydrophilic coatings,[177] crosslinked hydrophobic coatings,[178] crosslinked charged coatings,[179] multilayered coatings,[180] and perfluorocarbon copolymer coatings,[181] for several different applications.

Dow has also reported the mitigation of membrane biofouling via surface modification. In a report summarizing four years of field experience with low-fouling RO modules, Coker and Sehn concluded that surface modification effectively reduced microbial attachment, which delayed biofilm formation and reduced cleaning requirements. Other changes to the module architecture or operation, such as shortening the membrane leaves in spiral wound membrane elements and optimizing flow distribution, also facilitated reducing biofouling.[174] Khan and co-workers described laboratory techniques for evaluating membrane biofouling and correlating it with membrane productivity. They also reported that the addition of aromatic groups to membrane surfaces was more effective in reducing biofouling than the addition of aliphatic groups.[182]

Tang and co-workers published a series of reports describing surface characteristics of 17 commercial RO and NF membranes by four different manufacturers, including Dow Filmtec, Hydranautics, GE Osmonics, and Saehan Industries.[63,183,184] Some of the membranes had fully aromatic polyamide barrier layers (based on trimesoyl chloride and 1,3-benzenediamine (i.e., m-phenylene diamine)), while others had semi-aromatic polyamide barrier layers (based on trimesoyl chloride and piperazine). The surface layers (if any) were probed by atomic force microscopy, contact angle, streaming potential measurement, transmission electron microscopy, attenuated total reflection Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The presence of a surface coating was deduced from results of several of these techniques. FTIR and XPS revealed chemical differences between coated and uncoated membranes. Coated membranes generally had more hydrophilic, more neutral, and smoother surfaces than uncoated membranes. Uncoated membranes included the Hydranautics SWC4 and ESPA3, Dow Filmtec XLE, LE, NF90, and NF270, Saehan NE90, and GE Osmonics HL. Coated membranes included the Hydranautics LFC1, LFC3, and NTR729HF, Dow Filmtec SW30HR and BW30, and Saehan NE70.[63,183,184] The coatings on these membranes were rich in oxygen, and the oxygen appeared to be mainly associated with hydroxyl groups. These findings led the authors to conclude that the surface coatings are likely comprised of poly(vinyl alcohol).[183] The GE Osmonics DK, DL, SG appeared to have an aliphatic surface modification (such as a polyester), but the exact chemical composition of the surface modification was not determined.[63,184]

6. Chemical Treatment

To improve coating durability, surface modifying agents may be covalently coupled to the membrane polymer. These agents may be either small molecules or, more commonly, polymers. There are many pathways through which covalent coupling to the membrane surface may be achieved. This section will cover traditional chemical techniques, while plasma- and radiation-based techniques will follow.

6.1 Small Molecule Coupling

Various reagents may be used to introduce desired chemical moieties on a membrane surface. Sulfonation is a popular way of introducing hydrophilic groups on hydrophobic polymers such as poly(aryl sulfone)s (e.g., PSf[185] and PES[186]), which are often used in water purification membranes. A common method to introduce aryl sulfonic acid groups to poly(aryl sulfone)s is via contact with chlorosulfonic acid which, after neutralization, yields highly hydrophilic sulfonate groups directly connected to the aromatic rings of the polymer backbone.[186,187] A downside of this approach, however, is possible chain cleavage and subsequent branching or crosslinking.[187] Noshay and Robeson developed an alternative sulfonation route where PSf was contacted with a solution containing a 2:1 sulfur trioxide:triethyl phosphate complex. Sulfonation resulted in substantial increases in hydrophilicity and T_g relative to the unsulfonated polymer. Depending upon the degree of sulfonation, the hydrophilicity, water uptake, and mechanical properties could be varied over a wide range.[185] These techniques rely on sulfonating polymers after the polymerization is complete and can be difficult to control to achieve precise and reproducible levels of sulfonation.

More recently, McGrath and colleagues developed strategies to prepare sulfonated monomers that can then be incorporated into standard condensation polymerization routes to prepare sulfonated polysulfones. This approach allows more precise control of the content and location of sulfonated groups, while avoiding polymer degradation issues associated with post-polymerization sulfonation strategies.[188] While surface-sulfonated poly(aryl sulfone)s could potentially be used in MF or UF applications, homogeneously sulfonated poly(aryl sulfone)s are currently under investigation as desalination materials.[2,187,189] The aromatic polyamide thin films comprising the selective layer of most RO membranes are sensitive to chlorine-containing oxidants, such as sodium hypochlorite, which are frequently used in disinfection and cleaning steps in water treatment facilities. Sulfonated poly(aryl sulfone)s are far less sensitive than aromatic polyamides to chlorine exposure.[2,189] Figure 14 shows: (a) salt rejection and (b) water permeability of a traditional thin film composite polyamide RO membrane (SW30HR from FilmTec) and a sulfonated PSf membrane (BPS-40H) as a function of chlorine exposure. The thin film composite polyamide membrane exhibits catastrophic decreases in salt rejection and an increase in water permeability, which suggest that the chlorine is degrading the membrane.[189] Sulfonated poly(aryl sulfone)s have also been described in a publication on the preparation of RO membranes from partially sulfonated copolymers of biphenol and aryl sulfone by researchers at Dow.[190]

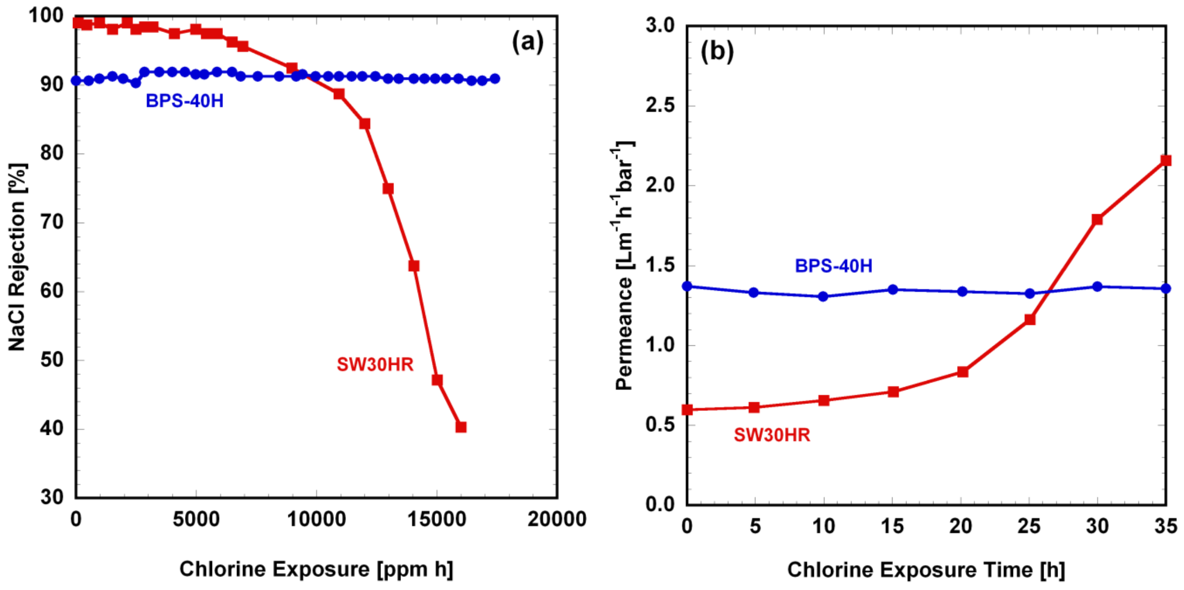


Figure 14. (a) Salt rejection and (b) permeate water flux of traditional thin film composite polyamide RO membranes (SW30HR) and sulfonated PSf RO membranes (BPS-40H TFC) as a function of chlorine exposure. Decreases in salt rejection and increases in water permeability indicate chlorine degradation of the thin film composite polyamide membrane. In contrast, the sulfonated PSf membrane exhibits stable salt rejection and permeate water flux as a function of chlorine exposure.[189]

Other routes to introduce sulfonate groups into polymer membranes have also been explored. Higuchi and co-workers, for example, described the surface sulfonation of PSf hollow fibers by propane sultone with Friedel-Crafts catalysts.[191,192] This reaction resulted in a short propyl chain between the sulfonate group and the aromatic rings of the PSf backbone as shown in Figure 15.

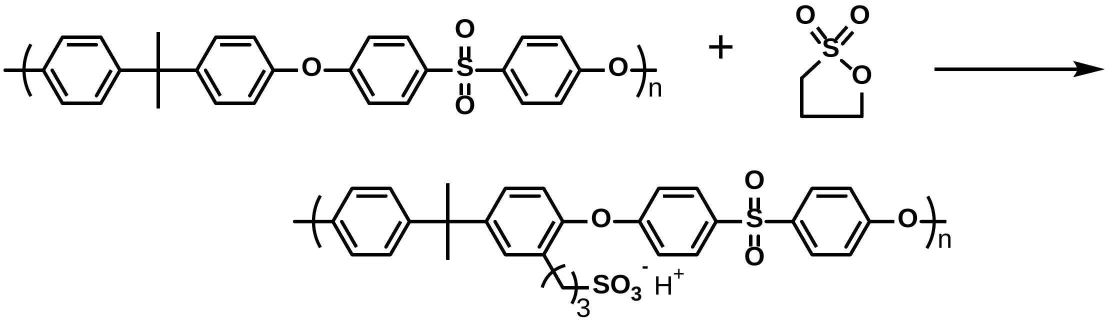


Figure 15. Sulfonation of PSf by addition of propane sultone.[191]

The addition of this short chain to the membrane surface was thought to be responsible for the increase in PEG (M_w approx. 2000, 3350, 8400, and 15000 Da) rejection and decrease in water flux observed upon sulfonation of PSf UF hollow fibers. For example, unsulfonated membranes exhibited nearly zero rejection of 8400 Da PEG, whereas modified fibers exhibited rejections of 22 - 78%, depending upon the reaction conditions used to modify the fibers.[191] Sulfonation could be accomplished on either the exterior surface or both surfaces of the hollow fiber membrane.[191] Fibers modified with propane sultone exhibited fluxes up to three times greater than unmodified fibers during BSA filtration.[192] The flexibility of the propane chains on the surface of the propane sultone-modified membrane was thought to more effectively hinder adsorption of foulants to the membrane surface than the fixed sulfonate groups on the polymer backbone.[193] Higuchi *et al*. have also reported the use of Friedel-Crafts catalysts to couple propylene oxide chains to PSf UF hollow fibers, as shown in Figure 16. Membranes modified with propylene oxide had fluxes up to three times higher than unmodified fibers.[193]

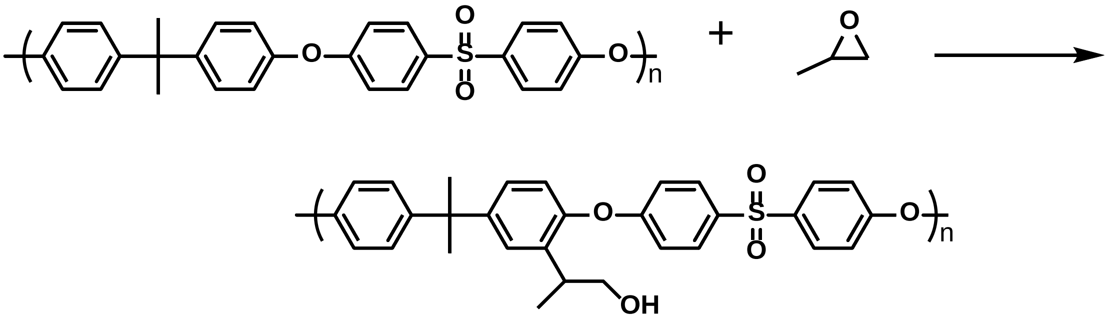


Figure 16. Coupling of propylene oxide to of PSf.[193]

Chemical modification of membrane surfaces can also create useful intermediates for subsequent reactions. Chloromethylation of PSf hollow fibers was accomplished with Friedel-Crafts catalysts.[194] Triethylaminated and ethylenediaminated membranes were prepared by dipping chloromethylated membranes into triethylamine or ethylenediamine, respectively. Acetylated PSf fibers were produced by refluxing chloromethylated fibers in a solution containing potassium acetate; subsequent saponification led to a hydroxymethylated fiber.[194] Guiver *et al*. described heterogeneous (surface only) lithiation of PSf UF membranes using *n*-butyllithium.[195] Lithiated membranes were quenched using CO_2, forming lithium carboxylate moieties, which were then converted to carboxylic acids by reaction with strong acid. After drying, membranes were reacted with sulfur tetrafluoride to generate acyl fluorides, which were analyzed to determine degree of substitution on the polymer surface. The reaction scheme is shown in Figure 17.

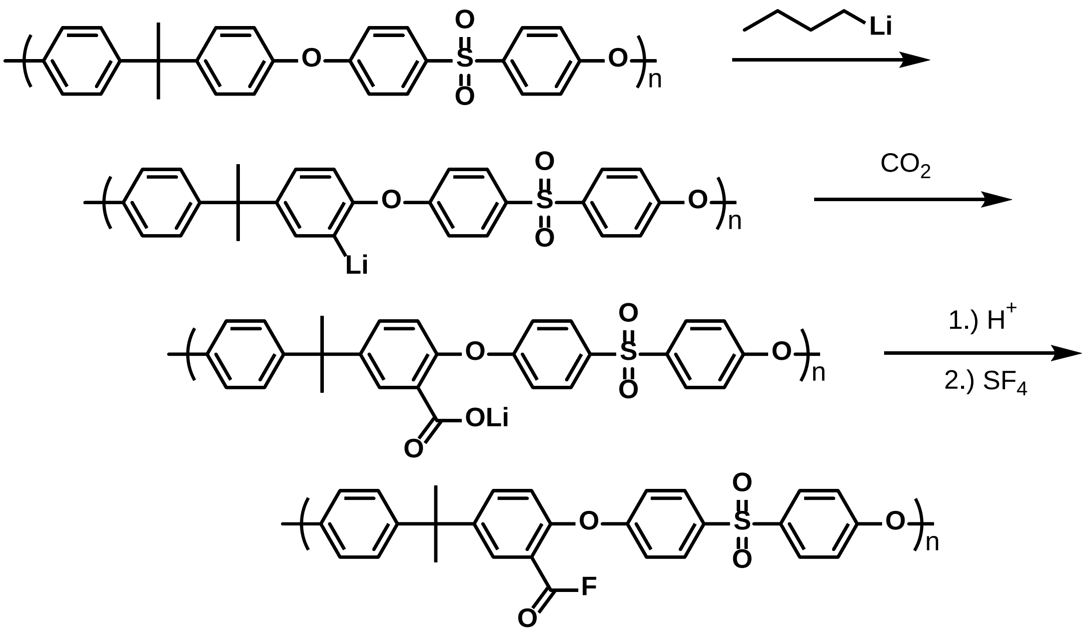


Figure 17. Lithiation and subsequent acyl fluorination of PSf.[195]

While poly(arylene sulfone)s have received substantial attention in the literature, the chemical modification of other membrane materials has been reported. The hydrophilization of commercial thin film composite polyamide RO membranes was described by Gill *et al.*[196] Membranes contacted with binary and ternary solutions of water, alcohol, and various acids, including hydrofluoric, fluorosilic, hydrochloric, phosphoric, nitric, and sulfuric, exhibited increased water flux. In some cases, a decrease in salt rejection accompanied the increase in water flux, but no loss in rejection was observed for treatments with hydrofluoric, fluorosilic, and hydrochloric acids.[196,197] The surfaces of ceramic membranes have also been chemically modified. Zirconia and titania UF membranes were treated by immersion in solutions of phosphoric or alkyl phosphoric acid. Modified membranes were used to evaluate effects of charge and hydrophobicity on protein adsorption, protein rejection, and water flux.[198]

Enzymes are proteins capable of catalyzing very specific biochemical reactions. Payne and co-workers published several reports describing the use of tyrosinase to graft various phenols to surfaces of natural and synthetic polymers.[199–202] Tyrosinase catalyzes the conversion of phenols to *o*-quinones, which are more reactive than phenols, permitting subsequent coupling to a polymer. Therefore, rather than forming reactive sites on the polymer surface, which has been the methodology employed in most of the surface modification studies reviewed here, a freely diffusible reactive agent can be formed *in situ* with the polymer. Chitosan was surface-modified by enzymatic action when contacted with buffered solutions of tyrosinase and various phenols, including phenol,[199] catechol,[199] 4-hydroxyphenoxyacetate,[199] butylcatechol,[199] and hexyloxyphenol.[201] Coupling was between the *o*-quinone and amino groups on the chitosan. Using a similar methodology, chlorogenic acid was coupled to chitosan films; chlorogenic acid-modified chitosan was water soluble over a much larger pH range than unmodified chitosan.[200] Finally, Payne et al. demonstrated that tyrosinase was capable of oxidizing phenols present in the synthetic polymer poly(hydroxystyrene) to *o*-quinones, although only a few phenolic moieties per chain were converted. Subsequent reaction between the *o*-quinones and nucleophilic reagents, such as aniline, was demonstrated.[202]

6.2 Chemically Induced Grafting

In the simplest scenario, the membrane surface natively contains functional groups that may be utilized for grafting. Polyamide RO and NF membranes typically have residual free carboxylic acids and primary amines left over following the interfacial polymerization used to prepare the polyamide membrane. Freeman *et al.* grafted poly(ethylene glycol) diglycidyl ethers to these free moieties to create fouling-resistant RO and NF membranes.[142] The resultant grafted PEG chains generally decreased the membrane pure water permeance by about 30-50%, depending upon the membrane type (RO or NF) and the molecular weight of PEG diglycidyl ether (200 or 1000 Da) used. Furthermore, coating RO membranes increased their salt rejection from 99.1% to 99.3-99.5%, and coating NF membranes increased their salt rejection from 97.8% to 98.7%. The increase in salt rejection was attributed to PEG chains filling minute defects in the thin polyamide layer that otherwise permit salt passage. Relative to unmodified membranes, modified membranes generally exhibited improved fluxes during fouling with charged surfactants or *n*-decane emulsions. Based on contact angle measurements, the grafting of PEG chains to the membrane surface did little to increase membrane hydrophilicity since the polyamide was already rather hydrophilic. However, the bulky PEG chains may sterically hinder the approach of foulants to the membrane surface, reducing their adsorption.

Mickols *et al*. at Dow obtained several patents based on surface modification of RO and NF membranes. These patents utilize the free amine and carboxylic acid functionalities that remain on the surface of a thin film composite polyamide RO or NF membrane following formation of the separation layer by interfacial polymerization. Covalent coupling of poly(alkylene oxides),[203–209] polyacrylamide,[204] oxazolines,[206,210] thiazolines,[206,210] triazines,[207] imidazoles,[208] acetophenone,[209] and various small molecules[211] to polyamide surfaces was described. Such modifications were generally shown to improve solute rejection. For example, grafting poly(ethylene oxide) diglycidyl ether (MW = 3400 Da) to the surface of an RO membrane from 4 wt% aqueous solution at 60ºC resulted in an improvement in salt rejection from 99.04% to 99.58%.[203] Such coatings also reduced surfactant fouling. An RO membrane grafted with poly(ethylene oxide) diglycidyl ether (MW = 200 Da) from 0.3 wt% aqueous solution at 60ºC exhibited a flux loss of 31% when challenged with a feed solution containing 1500 ppm NaCl and 100 ppm sodium dodecyl sulfate, compared to a flux loss of only 20% for an unmodified membrane. After 3 hours of such filtration and rinsing the membrane with a solution containing no surfactant, the modified membrane fully recovered its initial flux, whereas the unmodified membrane suffered an irreversible flux loss of 16% of its initial flux.[203]

If suitable functional groups are not natively present on the membrane surface, additional reagents may be used to prepare the surface for grafting. For example, PEG chains were tethered to poly(acrylonitrile-*co*-maleic acid) membranes by Xu *et al.* after refluxing the membrane with acetic anhydride, which converted carboxyl moieties on the membrane surface to anhydrides.[212,213] The activated membrane surfaces were reacted with PEG chains of varying lengths, resulting in PEG brushes covalently bound to the membrane surface. Relative to unmodified membranes, membranes modified in this way showed enhanced resistance to fouling when challenged with a 1 g L^{-1} BSA solution. After 30 minutes of BSA filtration, an unmodified membrane had a flux of 164 L m^{-2} h^{-1}, whereas the modified membrane had a flux of 644 L m^{-2} h^{-1} (both at a feed pressure of 1 bar).[212]

Polymer surfaces may also be activated by oxidation with ozone. Exposure of a polymer surface to ozone can induce the formation of peroxides, whose subsequent decomposition permits radical polymerization from the surface. Ozone treatment successfully induced formation of peroxides on films of PP, PE, polyurethane, PMMA, PET, and a vinyl alcohol-ether copolymer.[214,215] Following surface activation, polyacrylamide and poly(methyl methacrylate) were formed by radical polymerization on polyurethane[214] and PP[215] films, respectively. Peroxides were not detected on films of poly(hexafluoropropylene) and PTFE upon ozone treatment.[214] Following this work on solid films, PP MF membranes were activated by ozone treatment and subsequently grafted with poly(hydroxyethyl methacrylate).[216] These modifications improved membrane resistance to irreversible fouling. Following crossflow filtration of BSA solution and subsequent rinsing with pure water, an unmodified membrane exhibited less than 30% of its initial flux, whereas a modified membrane retained more than 90% of its initial flux.[216] Increases in ozone treatment duration resulted in greater graft density, higher hydrophilicity, but prolonged ozone treatment embrittled the membranes.[216] Chang *et al.* grafted poly(ethylene glycol) methacrylate (PEGMA) to PVDF UF membranes by first treating the membranes with ozone to form peroxides, then thermolytically decomposing the peroxides to form radicals by immersion in a PEGMA monomer solution at 80 °C. Modified membranes exhibited reduced irreversible fouling of proteins[112] and platelets[217] relative to unmodified membranes.

Belfer and co-workers used redox initiators to induce oxygen-centered radicals on several different commercial membranes, including composite polyamide RO, [218–223] composite polyamide NF,[222,224] PAN UF,[221] and PES UF[225] membranes. Once activated by a redox initiator, such as potassium persulfate/sodium metabisulfite, vinyl monomers undergo polymerization from the membrane surface. The monomers employed in these radical polymerizations included sulfopropyl methacrylate,[220–225] PEGMA,[218–220,222–225] methacrylic acid,[218,221,222,224,225] acrylic acid,[222,224] 2-(dimethylamino)ethyl methacrylate ,[224] hydroxyethyl methacrylic acid,[224] and 2-acrylamido-2-methylpropane sulfonic acid.[223] Grafting was verified by ATR-FTIR spectroscopy,[218–225] X-ray photoelectron spectroscopy,[218] and energy dispersive X-ray spectroscopy.[224] Interestingly, ATR-FTIR spectroscopy was also used to quantify the adsorption of foulant to the surfaces of modified and unmodified membranes.[221] Generally, modification of the RO membranes decreased membrane pure water permeability by up to 25% (depending upon the modification and the underlying membrane) and increased salt rejection by about 1%.[218,223] Relative to unmodified membranes, modified RO or NF membranes exhibited decreased adsorption of foulants from natural surface water.[223] To demonstrate that the grafting procedure could be applied to entire membrane modules, an RO module was modified with PEGMA and used in a pilot test for seawater filtration.[220] The flux of a modified module decreased by 23% over the course of 40 days, and the flux of an unmodified module decreased by 31%.[220] While this grafting process improved performance of membrane test coupons relative to unmodified membranes, the modified module still suffered from fouling of the stainless steel housing.[220] That is, the membrane fouling performance was improved, but, as expected, fouling of other wetted components of the system, such as the module housings, was not improved.

Uncontrolled radical polymerizations suffer from chain termination events such as radical recombination and disproportionation.[226] Living radical polymerizations, in contrast, offer robust, well-controlled chain growth and have found favor in polymer synthesis applications requiring precise molecular weights and architectures.[226] Non-uniform chain growth on a membrane surface may increase roughness,[112] which has been linked to exacerbated fouling.[55,60,61] Metal-catalyzed living radical polymerizations, such as atom transfer radical polymerization (ATRP), are commonly employed and are reviewed elsewhere.[226] ATRP relies on an initiator to begin chain growth, and if this initiator is immobilized on a surface, well-controlled brushes may be grown from the surface. Fukuda et al. have reviewed surface-initiated “living” radical graft polymerization reactions.[227]

Husson *et al*. used ATRP to graft several polymers to the surfaces of MF and UF membranes. Because ATRP permits controlled chain growth, the pore size in regenerated cellulose[228,229] and PVDF[230] membranes could be tuned, with modified membranes exhibiting decreasing pure water flux and molecular weight cutoff values with increasing polymerization time. For example, an unmodified 100 kDa MWCO CA membrane had a pure water flux of approximately 1000 L m^{-2} h^{-1} at a transmembrane pressure of 2 bar. The membrane flux decreased to approximately 100 L m^{-2} h^{-1} after grafting poly(ethylene glycol) methacrylate by ATRP for 10 min; the flux decreased further to approximately 50 L m^{-2} h^{-1} after grafting for 60 min.[228] An unmodified 300 kDa MWCO CA membrane rejected approximately 90% of 300 kDa dextran; upon grafting of PEGMA to the membrane surface via ATRP for 10 min, 60 min, and 120 min, 90% rejection was achieved with 200 kDa, 100 kDa, and 70 kDa dextran, respectively.[228]

The same group used ATRP to prepare high-capacity membrane absorbers. Poly(acrylic acid)[229] and poly(vinyl pyridine),[230] polymers capable of ion exchange, were grafted to regenerated cellulose and PVDF membranes, respectively. The chain length of the grafted ion exchange layers could be controlled by polymerization time, so the ion exchange capacity increased with increasing polymerization time.[229,230] For example, increasing the ATRP grafting time of poly(vinyl pyridine) to a PVDF membrane from 1 to 8 hours increased the membrane ion exchange capacity from 0.0225 meq g^{-1} to 0.0732 meq g^{-1}.[230]

Surface modification need not be limited to flat-sheet polymeric membranes. For example, Xu *et al*. grafted poly(acrylic acid) to microporous hollow fiber PP membranes by using a benzoyl peroxide initiator in the presence of acrylic acid monomer. Acrylic acid was grafted to the outside of the fibers from a toluene solution. The poly(acrylic acid) formed a thin, dense layer atop the PP membrane.[231] Higuchi *et al*. reported grafting poly(N-vinyl pyrrolidone), a highly hydrophilic polymer, to PSf hollow fibers to improve their hemocompatability.[232] Fibers were first chloromethylated using a Friedel-Crafts process, then reacted with ethylenediamine followed by *N*-succinimidylacrylate to introduce vinyl functionality to the PSf. Redox initiated polymerization of vinyl pyrrolidone from the membrane surface was then performed. This reaction scheme is shown in Figure 18. This modification reduced the adhesion of blood plasma proteins from approximately 6 μg cm^{-2} to approximately 2 μg cm^{-2} and the adhesion of blood platelets from approximately 1 x 10^6 cells cm^{-2} to approximately 2 x 10^5 cells cm^{-2}.[232]

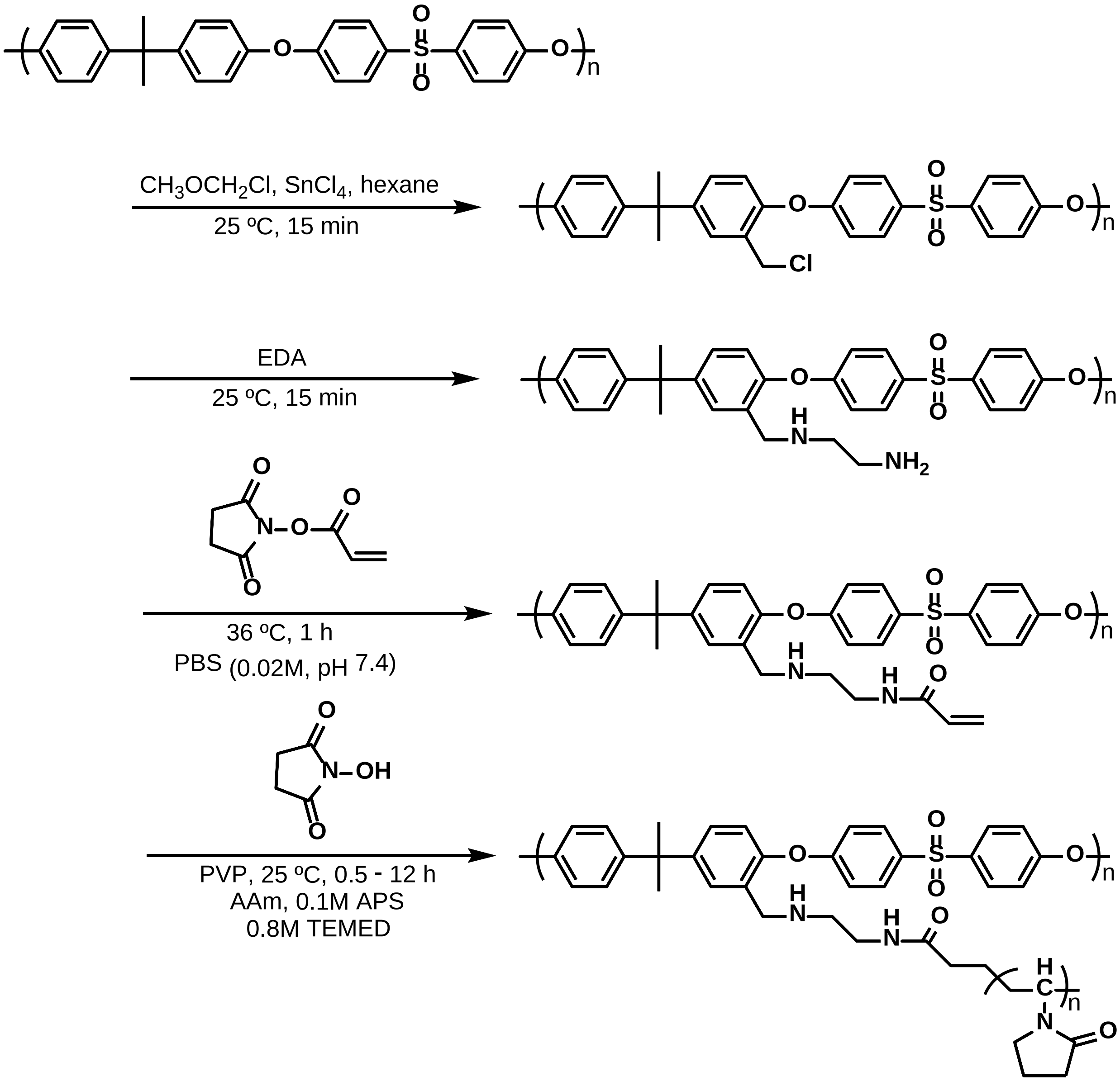


Figure 18. Modification of PSf membranes by grafting of polyvinylpyrrolidone (PVP). PSf is first chloromethylated using an $SnCl_4$ Friedel-Crafts catalyst. Membranes were then reacted with ethylenediamine (EDA). Vinyl groups were introduced on the surface of ethylenediaminated membranes by immersion in phosphate buffered saline solution (PBS) containing *N*-succinimidylacrylate (NSA). Finally, polyvinylpyrrolidone was grafted to the membrane surface by immersion in vinylpyrrolidone monomer solution containing ammonium persulphate (APS) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TEMED) as redox initiators.[232]

Surface grafting can also be used to modify inorganic membrane surfaces. For example, Cohen, Castro, and Monbouquette successfully grafted PVP to the surface of porous silica membranes.[233] Cohen and Faibish also grafted PVP to zirconia membranes.[234,235] PVP brushes with a molecular weight of 10.3 kDa had an average height of 7.3 nm and a graft density of 1.09 mg m^{-2}, and brushes with a molecular weight of 4.9 kDa displayed an average height of 4.4 nm and a graft density of 0.807 mg m^{-2}.[234] The addition of the PVP brushes to these membranes decreased the hydraulic permeability of the membranes from 4.7×10^{-16} m^2 to 2.67×10^{-16} m^2 (10.3 kDa brushes) and 2.89×10^{-16} m^2 (4.9 kDa brushes). However, when challenged with oil/water emulsions, native membranes were irreversibly fouled, with their hydraulic permeability decreasing from 4.7×10^{-16} m^2 to 3.47×10^{-16} m^2, even after caustic cleaning. PVP-modified membranes did not suffer irreversible fouling and fully recovered their initial hydraulic permeability following cleaning. Modified membranes also exhibited improved oil rejection, which was attributed to narrowing of defects in the membrane.[234,235]

7. Plasma Treatment

Plasma treatment has found extensive use in polymer surface modification. Several reviews describing plasma treatment of polymer surfaces have been reported.[236,237] Plasma is an ionized gas, typically produced by a strong electrical discharge in a low-pressure environment. Interactions of the plasma species with the polymer surface can induce electronically excited states in the polymer atoms, resulting in homolytic bond cleavage and leading to formation of free radicals and unsaturated bonds. In this way, crosslinking within the polymer substrate or reactions with other molecules brought into close proximity to the polymer surface are facilitated.[237] For example, post-plasma exposure to oxygen or water can induce incorporation of oxygen-containing functionalities into the polymer,[238] potentially increasing surface hydrophilicity. Therefore, the aim of plasma treatment is typically to improve membrane fouling resistance, although other effects, such as increased resistance to chlorine-containing compounds in thin-film composite polyamide RO membranes,[239] have been reported. Like UV irradiation, plasma treatment has been used as an activation technique for grafting from the backbone, which will be discussed later.

7.1 Plasma Treatment without Polymer Coupling

Several studies on the plasma treatment of PAN,[106,107] PSf,[107] and PES[64] UF membranes have been reported. Exposure of such membranes to air or water vapor following treatment with a helium or helium/water plasma resulted in a significant increase in their hydrophilicity due to formation of peroxides and, subsequently, oxidation products on the membrane surface. To evaluate the hydrophilicity, membranes were immersed in water, and the contact angle of an air bubble on the membrane surface was measured. With as little as 10 seconds of plasma treatment, the static contact angle on a PES membrane decreased from 67° to 24°, indicating an increase in surface hydrophilicity.[64] Water permeabilities were measured as a function of plasma treatment power and time. The permeability of PAN and PES membranes changed little after plasma treatment, but PSf membranes exhibited increases in water permeability, suggesting degradation of the membrane. For example, the pure water flux of a PSf membrane at a transmembrane pressure of 1 bar doubled from approximately 95 L m^{-2} h^{-1} to approximately 185 L m^{-2} h^{-1} following a 30 s, 25 W plasma treatment. To minimize damage of the membrane polymer (surface etching) while still producing the desired increase in hydrophilicity, the authors recommended the use of low power and short plasma treatment times. This work compliments the studies of graft polymerization from plasma-activated membranes.[64,106,107]

Because many different functionalizable surface moieties may be encountered in polymers used for water purification membranes, the mechanisms governing plasma surface modification are not fully understood.[240] Many reports of membrane surface modification focus on correlations between membrane performance and plasma treatment conditions, but Fisher *et al.* investigated the penetration of the plasma modification into the membrane, permanence of the modification, and the chemical processes occurring at the plasma/membrane interface.[240–242] PSf, PES, and PE membranes were modified with a water plasma to produce a permanent hydrophilic surface.[241,242] A laser-induced fluorescence (LIF) technique was used to image the interaction of radicals generated by H_2O plasma with the surfaces of PSf, PES, PE, and PTFE membranes. Efficacy of plasma modification was found to inversely correlate with the energy required for cleavage of bonds in the substrate polymers, allowing incorporation of hydrophilic –OH, C-O, and $C\text{-}O_x$ groups.[240–242] Consequently, PSf and PES membranes, which contain relatively labile C-S and C-O bonds, were readily modified by plasma, whereas the C-C bonds in PE membranes were more difficult to modify, and the C-F bonds in PTFE membranes were most difficult to modify. Results were corroborated by XPS analysis.[240,242] The surface modification was complete (*i.e.*, on all exposed surfaces) in PSf[241,242] and PES[242] MF and UF membranes, even in the case of highly asymmetric membrane architectures. The permanence of the hydrophilic modification was directly correlated with the rigidity of the polymer backbone. PSf and PES membranes, which have relatively stiff backbones, remained completely wettable for over a year following treatment and storage in ambient air. PE membranes, in contrast, exhibited a loss of hydrophilicity within six weeks of treatment, likely due to surface rearrangement facilitated by mobile polymer chains. XPS revealed 95% carbon content on the surface of PE membranes six weeks after water plasma treatment, nearly the same as untreated PE.[242] The remarkable stability of Fisher's plasma-modified PSf and PES membranes stands in contrast to results from other studies, where plasma-modified membranes exhibited partial reversion of the surface hydrophobicity within hours or days of plasma treatment under similar storage conditions.[241] The superior durability of the modifications performed by Fisher *et al.* were thought to result from the mild, optimized plasma treatment conditions employed in their study.[241]

Many membrane/plasma combinations have been studied. For example, Park *et al.* used oxygen plasma to hyrophilize PSf UF membranes.[243] Nitrogen-containing plasma systems are widely used; Fisher *et al*. treated microporous PES membranes with N_2, NH_3, Ar/NH_3, and O_2/NH_3 plasmas.[244] Xu *et al*. hydrophilized PP MF membranes for use in membrane bioreactors by NH_3,[245] CO_2,[246] and N_2[247] plasma treatment. Bryjak, Gancarz, and co-workers studied hydrophilization of various polymer membranes and polymer films with plasma. Early studies investigated the effects of air plasma on surface properties of polyethylene (PE)[248] and PAN[249] membranes, but work was later extended to PSf membranes treated with CO_2,[250,251] Ar,[252] N_2,[250,253] *n*-butylamine,[250,254] allylamine,[254] NH_3,[255] and NH_3/Ar[255] plasmas. The expected increase in hydrophilicity was observed for plasma-modified membranes, and the acidity/basicity of the PSf surface could be tuned by changing the composition of the plasma. CO_2 and NH_3/Ar plasma treatment produced acidic surfaces, *n*-butylamine or NH_3 plasma treatment produced basic surfaces, and N_2 plasma treatment resulted in amphoteric surfaces (as measured by surface titration).[250,255] The amphoteric surfaces created by N_2 plasma were thought to be the result of oxygen impurities present in the N_2 feed to the plasma reactor.[250] Membranes treated in this way suffered etching damage during plasma treatment. For example, PSf membranes exhibited an overall increase in pore sizes and a widening of the pore size distribution after a two minute CO_2 or N_2 plasma treatment, as shown in Figure 19.[251,253]

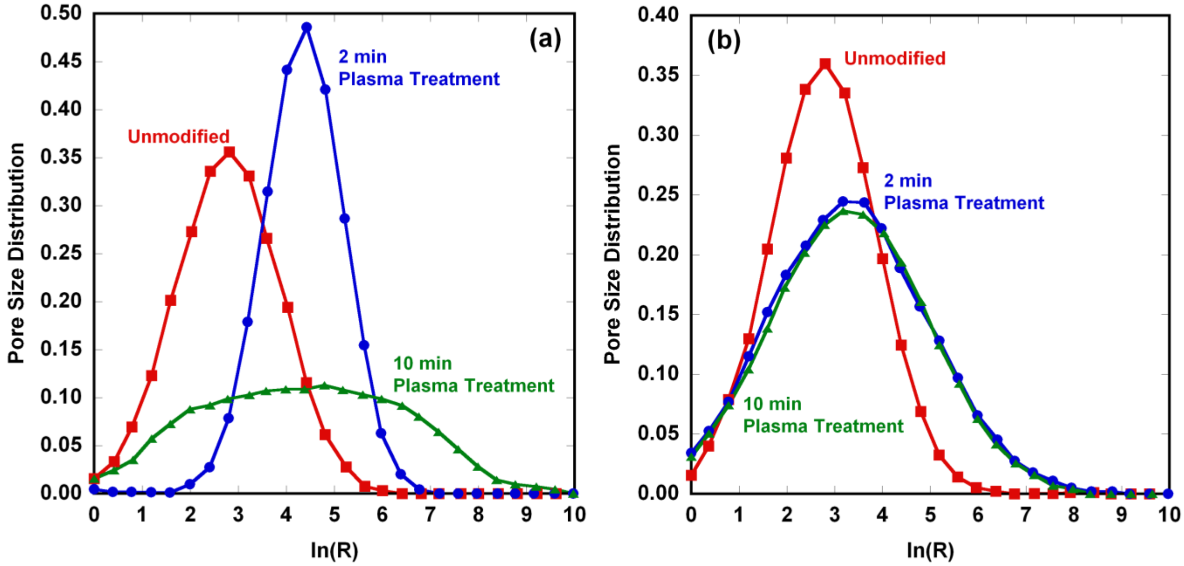


Figure 19. Effect of CO_2[251] (a) and N_2[253] (b) plasma treatment on the pore size distribution of PSf UF membranes. Pore radius (R) is measured in nm. CO_2 plasma aggressively etched the membrane, causing an increase in pore size and widening of the pore size distribution. In contrast, exposure to N_2 plasma resulted in relatively little change in the pore size distribution, likely due to re-deposition after ablation.

NH_3/Ar plasma aggressively etched PSf UF membranes, which caused substantial changes in the porous structure with as little as one minute of treatment. Interestingly, prolonged exposure to CO_2 plasma resulted in further membrane degradation,[251] but prolonged exposure to N_2, NH_3, or NH_3/Ar plasmas resulted in little change in the pore size distribution, suggesting a balance of ablation and re-deposition phenomena.[253,255] The increased surface hydrophilicity of plasma-treated membranes resulted in improved regeneration of protein-fouled membranes during cleaning.[248,251,253,254]

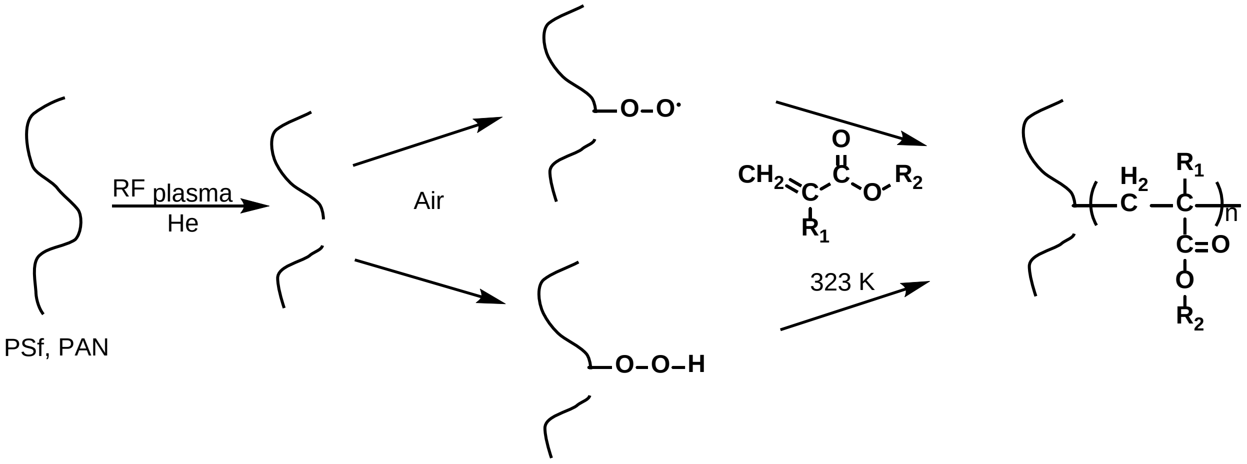
Plasma treatment is employed in the commercial manufacture of polymer membranes. The Pall Corporation has used plasma treatment to hydrophilize membranes for processing biological fluids.[256] The use of various plasmas, including oxygen, ammonia, organic, and inorganic plasmas are disclosed in various Pall patents. Porous media treated with plasma gas exhibited improved passage of platelets and increased retention of leukocytes, increasing efficiency in the separation of leukocytes from blood products. For example, a web of melt-blown poly(butylene terephthalate) microfibers was treated with oxygen plasma and subsequently used to filter platelet concentrate. Using the modified filter, 99.9% of the leukocytes were removed from the platelet concentrate with only 15% platelet loss; for comparison, platelet losses were 50 - 80% using an unmodified filter.[256]

7.2 Plasma Coatings

Plasma treatment may also be used to coat a membrane surface with a crosslinked polymer. When plasma is used for surface treatment or surface activation, the interaction of ionized gas molecules with the membrane introduces hydrophilic or reactive moieties to the surface. However, if the plasma is comprised of monomers or low molecular weight polymer chains, those molecules may recombine on the membrane surface, forming a robust coating of highly-crosslinked polymer.[257] Zou *et al.* deposited a PEG-like polymer atop thin film composite RO membranes by plasma polymerization of triethylene glycol dimethyl ether monomer for 10-120 seconds. Unmodified membranes had a pure water permeance of approximately 1.1 L m^{-2} h^{-1} bar^{-1}. With increasing plasma treatment time, pure water permeance decreased to approximately 0.9 L m^{-2} h^{-1} bar^{-1} after 120 s of plasma treatment. Despite its initially higher pure water permeance, the flux of an unmodified membrane was lower than that of all modified membranes after 200 min of filtration of a protein solution at a transmembrane pressure of 55 bar. For example, the unmodified membrane had a flux of approximately 22 L m^{-2} h^{-1}, and a membrane treated with plasma for 10 s had a flux of approximately 31 L m^{-2} h^{-1}.[257]

7.3 Plasma-Induced Grafting

Just as plasma may be used to activate the surface of a membrane to react with small molecules like water or oxygen to form hydrophilic moieties, plasma activation can induce grafting of vinyl monomers to the membrane surface.[107] Plasmas may be used to form peroxides on the membrane surface, which are then undergo thermolysis to form radicals that trigger polymerization reactions.[106,107] For example, PAN and PSf UF membranes have been treated with helium or helium/water plasma to form peroxides on the membrane surfaces, as validated by a peroxide assay. The PSf membrane suffered some degradation due to the plasma treatment, as evidenced by increased water permeance. For example, a 30 s He/H_2O plasma treatment at 25 W resulted in a pure water flux increase from approximately 95 L m^{-2} h^{-1} to 185 L m^{-2} h^{-1} at a transmembrane pressure of 1 bar. Once activated by plasma treatment, the membranes were placed in solutions of 2-hydroxy-ethyl methacrylate, acrylic acid, or methacrylic acid at 50 °C to form polymer brushes on the membrane surfaces. The polymerizations were halted by immersing the samples in water.[107] Figure 20 shows the proposed pathway of plasma-induced chain scission, followed by oxidation in air and subsequent graft polymerization.



Monomer	R_1	R_2
AA	H	H
MAA	CH_3	H
HEMA	CH_3	CH_2CH_2OH

Figure 20. Proposed pathway of graft polymerization to polyacrylonitrile (PAN) or polysulfone (PSf). In the first step, radio frequency (RF) plasma induces polymer chain scission. In the second step, oxidation in air induces the formation of peroxides. In the third step, graft polymerization is carried out with acrylic acid (AA), methacrylic acid (MAA), or 2-hydroxy-ethyl methacrylate (HEMA).[107]

The graft polymerization bestowed the PSf membrane surface with hydrophilic properties as water/octane contact angles decreased from 98° for an unmodified, hydrophobic membrane to 26° for a hydrophilic membrane following a 30 s exposure to He/H_2O plasma at 25 W. The polymer grafting conditions, such as monomer concentration and reaction time, were used to tune the permeability of the grafted membrane. Hydrophilic membranes, particularly those with poly(2-hydroxy-ethyl methacrylate) brushes, exhibited reduced protein adsorption and improved resistance to fouling during ultrafiltration of protein solutions.[107] During filtration of BSA, PSf-*g*-HEMA membranes exhibited 32% higher flux and improved solute retention relative to unmodified membranes. Chen and Belfort grafted N-vinyl-2-pyrrolidone to PES UF membranes using a similar procedure.[64] Degradation upon plasma treatment was also observed for the PES membranes. Membranes with grafted brushes exhibited a reduced fouling tendency during protein ultrafiltration and improved response to cleaning by backflushing with sodium hydroxide solution.[64]

Wavhal and Fisher grafted hydrophilic polymers to PES UF membranes to reduce their susceptibility to protein fouling.[258] Membranes were first only treated with Ar plasma, which increased membrane hydrophilicity. Hydrophilicity was evaluated as the time required for membrane wetting when a water droplet was placed on the membrane surface. The selective face of the unmodified PES US membrane exhibited a time-independent contact angle of approximately 90º. A membrane modified with Ar plasma and aged for one week exhibited an initial contact angle of approximately 55º, and the contact angle decreased to approximately 15º in about 10 s. However, a membrane that was aged for two months following plasma treatment, exhibited an initial contact angle of 65º; the contact angle decreased to approximately 30º in 65 s. Thus, while the aged membrane was more hydrophilic than the unmodified membrane, the hydrophilicity was lower than that of a membrane which was aged for one week.[258] Other reports by Fisher *et al*. have suggested that hydrophilic modification resulting from He/H_2O plasma are long-lasting (>16 months) on polymers with stiff backbones, such as PES, since surface rearrangement of stiff chains is hindered.[241,242] Because a deterioration in hydrophilicity was observed for PES modified with Ar plasma, the permanence of the surface modification may also be a function of the type of plasma used. Therefore, grafting of a hydrophilic polymer to the plasma-treated membrane was viewed as a means to permanently alter the surface characteristics. Acrylamide[259] and acrylic acid[258] were grafted to PES membranes by introducing vaporized monomer into a reaction chamber immediately following plasma treatment. Even after aging for two months, membranes modified with acrylic acid exhibited an initial contact angle of 55º, and the contact angle decreased to approximately 10º within less than four seconds.[258] Membranes grafted with acrylamide exhibited reduced protein fouling and improved flux recovery after cleaning during protein ultrafiltration. For example, an unmodified membrane suffered a flux reduction of about 70% during BSA ultrafiltration, whereas modified membranes suffered flux reductions of 57 - 62%. Furthermore, modified membranes recovered 67 - 78% of their flux after cleaning, whereas an unmodified membrane recovered only 50% of its flux after being cleaned.[259]

Chang *et al*. modified PVDF UF membranes with PEGMA by several grafting techniques.[112] Brush-like PEG was formed by surface-initiated ATRP of PEGMA monomer and by ozone treatment followed by thermal decomposition of the resulting surface peroxides (discussed in Section 6.2) in PEGMA monomer solution at 80 °C.[112] Network-like PEG was grafted to the membrane surface by plasma-induced polymerization of PEGMA monomer.[112] Figure 21 shows a schematic of the three architectures.[112] The well-controlled chain growth inherent to ATRP allowed formation of brushes with uniform chain lengths and without crosslinking. Network structures, which were largely inhomogeneous (resulting in increased membrane surface roughness) were thought to derive from the formation of plasma-induced radicals on PEG chains followed by radical coupling among chains and with unreacted monomer. Formation of the network structures resulted in a high weight of grafted polymer on the membrane surface. This grafted polymer had a much larger hydration capacity than the brush structures. However, the network structures caused a severe reduction in flux, even during protein ultrafiltration, relative to the unmodified or brush-modified membranes.[112] Grafting efficiency, measured as the weight of polymer grafted per unit surface area during a designated grafting time, was higher for membranes modified by ATRP than for membranes modified by thermally-induced polymerization, but lower than that of membranes modified by plasma-induced polymerization. For example, grafting levels of nearly 0.8 mg cm^{-2} were achieved in 12 h on membranes modified by plasma-induced polymerization, whereas grafting levels of approximately 0.2 mg cm^{-2} and 0.05 mg cm^{-2} were obtained on membranes modified by ATRP and thermally-induced polymerization, respectively.[112]

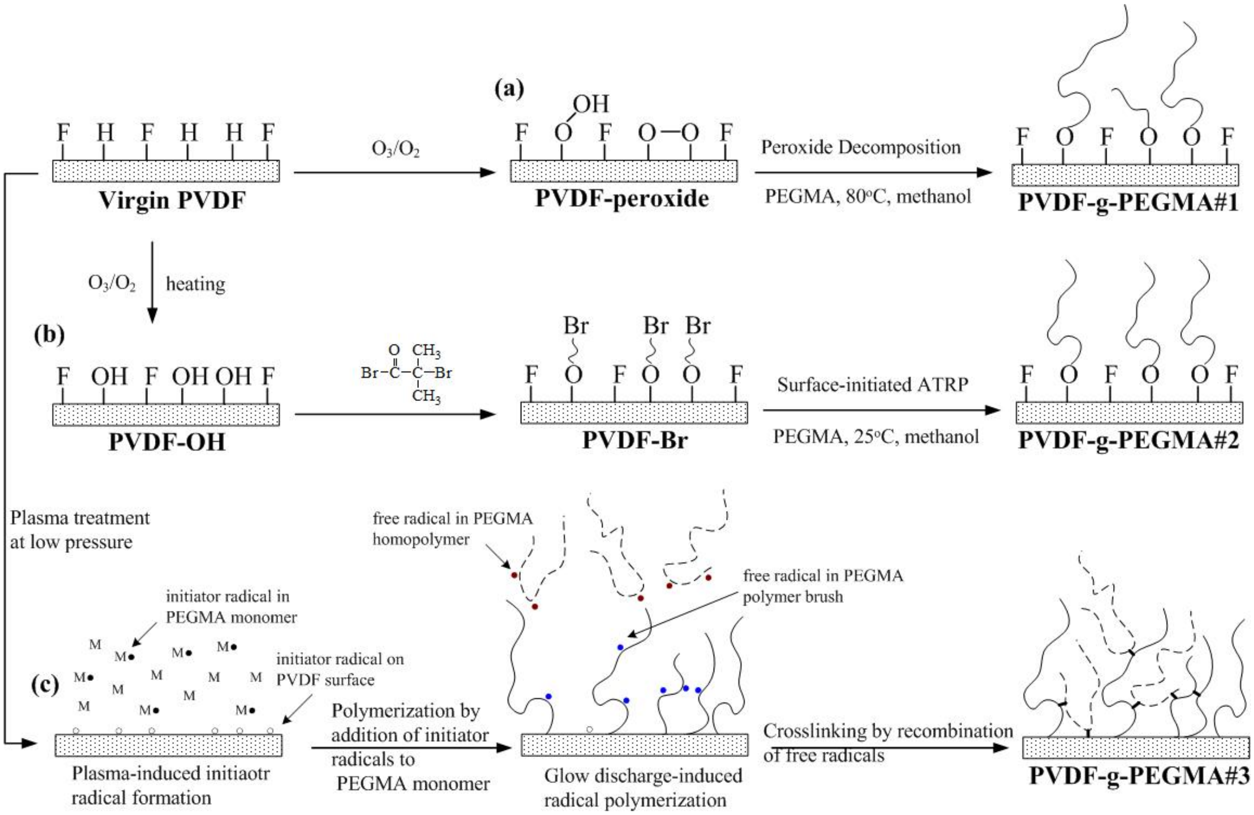


Figure 21. Schematic showing the formation of brush-like PEGMA with chains of varying length (top, PVDF-g-PEGMA #1), brush-like PEGMA with chains of similar length (middle, PVDF-g-PEGMA #2), and network-like PEGMA (bottom, PVDF-g-PEGMA #3). This figure demonstrates the differences in graft architecture possible using various grafting techniques, including uncontrolled free radical polymerization from the membrane surface (top), surface-initiated ATRP from the membrane surface (middle), and grafting to the membrane surface (bottom). Grafting was accomplished on PVDF membranes. Reproduced with permission, Elsevier B.V.[112]

Plasma treatment may be used to modify membranes that are traditionally difficult to surface-modify. PTFE, for example, is a particularly difficult polymer to surface-modify due to the excellent chemical stability of perfluorinated polymers.[260] While this inertness makes PTFE a robust polymeric material suitable for fabrication of durable membranes, the surface of PTFE membranes are very hydrophobic.[261] Plasma treatment has been explored to polymerize several monomers from the surface of PTFE films, including acrylamide, acrylic acid, 4-styrenesulfonic acid, N,N-dimethylacrylamide, and (N,N-dimethy1amino)ethyl methacrylate.[262] Exposure of PTFE films to Ar plasma causes defluorination and oxidation of the surface, resulting in uptake of atmospheric oxygen to form (predominantly) peroxide species, with some hydroxyl, carbonyl, and ester moities as well. Decomposition of these peroxides permits monomer reaction with the PTFE surface. Graft density increased with plasma treatment time (up to 50 s) due to the formation of additional reactive sites. However, plasma exposure for longer than 50 s caused crosslinking on the surface due to formation of radicals on adjacent PTFE chains, which could react with each other, thereby reducing the grafting efficiency.[262]

Plasma treatment may also be used to modify membranes in forms other than flat sheets. For example, α-allyl glucoside was grafted from the surfaces of PP MF hollow fiber membranes. Such carbohydrates are highly hydrophilic and may be useful monomers for membrane modification. Membrane hollow fibers were dipped in monomer solutions and subsequently treated with N_2 plasma, resulting in the development of a robust, hydrophilic surface. For comparison, a membrane only treated with plasma, and not grafted with α-allyl glucoside, recovered its intrinsic hydrophobicity within about two weeks. When challenged with a BSA feed solution, membranes grafted with α-allyl glucoside suffered a flux loss of approximately 60%, while the flux of an unmodified membrane decreased by 72%. Furthermore, modified membranes were able to recover at least 85% of their pure water flux by cleaning following BSA ultrafiltration, whereas an unmodified membrane was able to recover only 62% of its flux by cleaning.[263]

While most membrane surface modification studies focus on improving hydrophilicity, a few reports describe the influence of other characteristics, such as surface geometry, on fouling mitigation. For example, the alteration of surface nanostructure of polyamide RO membranes has been explored to inhibit scale formation. Thin-film composite RO membranes were activated by contact with H_2/He plasma and then exposed to oxygen to stimulate peroxide formation on the membrane surface. Radical polymerization of methacrylic acid[264,265] or acrylamide[265] to form surface brushes was then accomplished from aqueous solution at 60 - 70 °C. Characteristics such as surface polymer layer thickness, feature density, and distribution of feature heights (*i.e.*, Gaussian vs. skewed) were varied by adjusting plasma exposure time, polymerization temperature, and monomer concentration. Mineral scaling was reduced for modified membranes relative to unmodified membranes. For example, membranes exposed to H_2/He plasma for 10 s followed by grafting methacrylic acid using a 10% v/v monomer solution at 60 °C most significantly retarded the onset of gypsum scaling. In crossflow testing, the flux decline due to scaling began after 4.5 hours for an unmodified membrane, whereas the flux of a modified membrane remained stable for 10.2 h.[264]

All of the aforementioned examples of plasma-induced grafting have been “grafted from” the membrane, where polymer chains are grown from an initiating site formed on the membrane surface. Alternatively, an already-formed polymer chain may be “grafted to” the surface by coupling the chain to a receptor site on the membrane.[27] Plasma may be used to induce such coupling if polymer chains are adsorbed to the membrane surface prior to plasma treatment. For example, PVDF MF membranes were pre-coated with PEG solutions and exposed to argon plasma which facilitated the grafting of PEG to the PVDF surface.[28]

7.4 Corona Discharge Treatment

Corona discharge treatment (also called glow discharge treatment) is closely related to plasma treatment, and it has been used as a surface activation technique for subsequent grafting to polymer surfaces. In corona discharge treatment, electrodes induce ionization of oxygen near the membrane, resulting in the formation of hydroxyl and peroxide groups on its surface.[266–268] The corona discharge treatment alone can render a membrane surface hydrophilic, which may improve fouling resistance.[269] However, if the membrane is immediately immersed in a monomer solution following corona discharge treatment, radical polymerization ensues as the peroxides decompose. Ito and co-workers used glow discharge treatment to graft poly(acrylic acid), poly(methacrylic acid), and poly(ethacrylic acid) chains to the surface of track-etched polycarbonate membranes having a nominal pore size of 0.2 µm. The grafted polymers were pH-sensitive, and their swelling was used to control the rate of water permeation through the membranes.[270,271] For example, an unmodified membrane mounted in a dead-end ultrafiltration cell had a pH-independent pure water permeance of approximately 12,500 L m^{-2} h^{-1} bar^{-1}. In contrast, a membrane grafted with poly(methacrylic acid) had a permeance of approximately 5000 L m^{-2} h^{-1} bar^{-1} at pH 2 and a permeate rate of nearly zero at pH 6.[271]

Zhu *et al*. grafted poly(acrylic acid) to PES UF membranes by corona discharge, which caused both the membrane surface and pore walls to become hydrophilic. Like plasma treatment, corona discharge treatment can degrade membranes; the tensile strength of the PES UF membrane decreased as the corona discharge power and treatment duration increased.[272]

For example, the tensile strength of a membrane treated with a 50 W corona discharge treatment for 30 s decreased from approximately 8.5 MPa to 8.0 MPa. The tensile strength of an identical membrane treated with 200 W decreased from 8.5 MPa to less than 1.0 MPa over 30 s.[272] Figure 22 shows the effect of corona discharge treatment intensity and time on tensile strength of a PES UF membrane. Membrane mechanical integrity is crucial to ensure consistent product quality.[273] For example, membranes in water purification plants may be exposed to stress during manufacture, delivery, installation, and operation.[273–275] Cleaning operations such as air scouring and backwashing expose membranes on a frequent basis to stress and vibration. Without adequate mechanical properties, hollow fibers, for example, can break, thereby compromising their separation properties.[273,274]

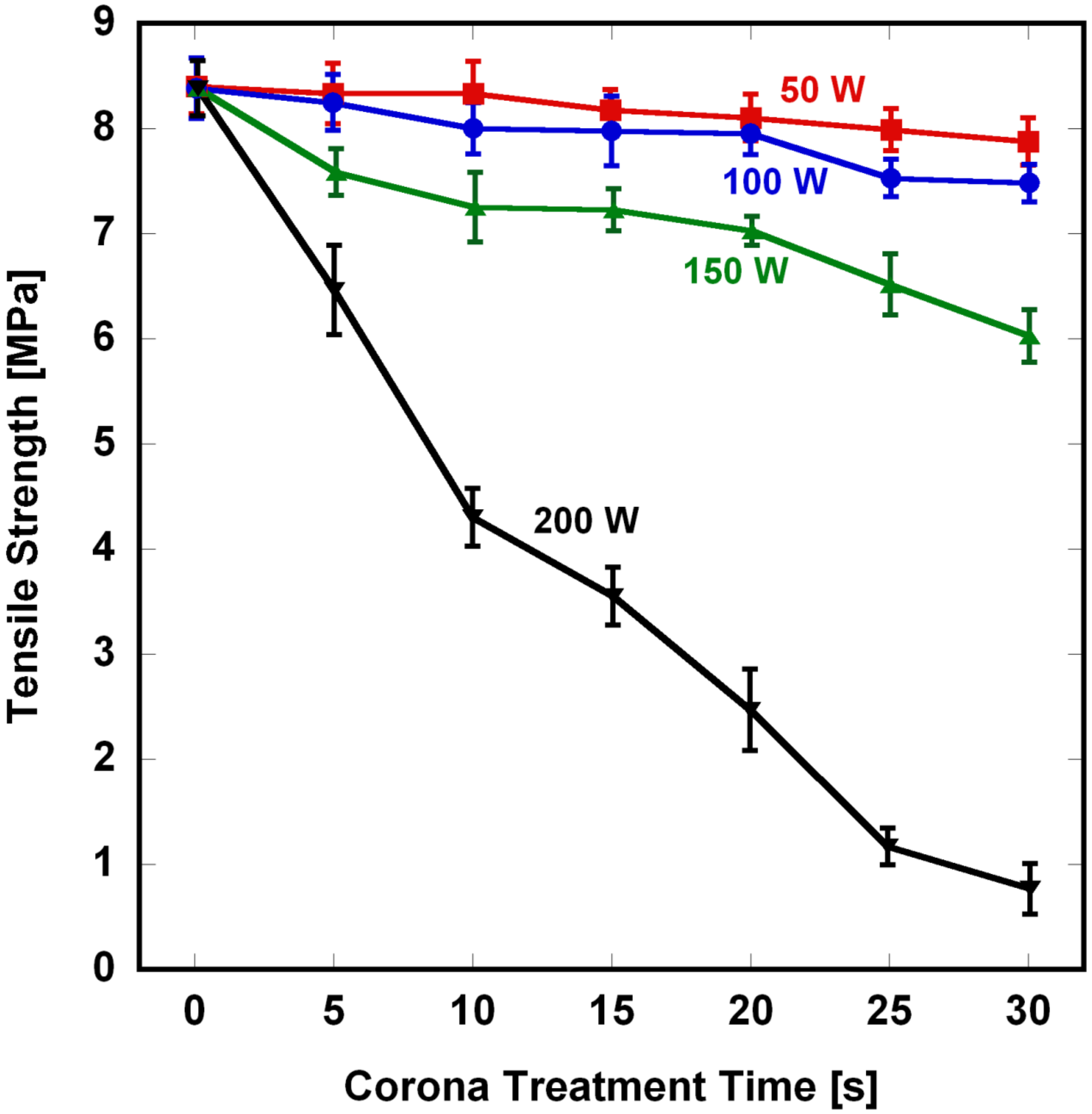


Figure 22. Effect of corona discharge treatment intensity and time on tensile strength of a PES UF membrane. Increases in intensity and time coincided with decreases in membrane tensile strength.[272]

In addition to "grafting from" reactions, where vinyl monomers are reacted with decomposed peroxides on the membrane surface, corona discharge treatment permits "grafting to" reactions in which polymer chains are coupled to a membrane surface. Ulbricht *et al.* grafted poly(N-vinyl-2-pyrrolidone) to PP MF membranes by first adsorbing the polymer to the membrane and subsequently subjecting the membranes to corona discharge treatment.

Membrane surface hydrophilicity was evaluated by measuring the contact angle of a captive air bubble at a water/membrane interface. Unmodified, hydrophobic membranes had a contact angle of approximately 100º. The contact angle decreased, indicating an increase in hydrophilicity, with increasing degree of PVP immobilization, reaching a minimum of approximately 42º with 13 wt% PVP immobilized on the membrane surface. Relative to unmodified membranes, modified membranes also exhibited improved resistance to protein fouling during ultrafiltration.[276] For comparision, unmodified membranes lost about 70% of their flux when challenged with a 1.0 g L^{-1} BSA feed solution. Moreover, flux loss decreased with increasing immobilization of PVP as a membrane modified with 14 wt% PVP exhibited only a 33% loss in flux. PEG was also grafted to PSf UF membranes in a similar fashion.[277]

8. Irradiation

Various forms of radiation, including both ultraviolet (UV) and higher-energy radiation, have been successfully employed in membrane surface modification. Like plasma, radiation may be used alone or to induce grafting of polymers to the membrane surface.

8.1 UV Irradiation

Nyström *et al.* studied modification of PSf UF membranes by UV irradiation.[85,278] An increase in pure water flux was observed after only a few minutes of UV exposure in aqueous media. Pure water flux doubled with a 10 min UV irradiation, and a six-fold increase in pure water flux occurred after 20 min irradiation. This result was explained based on chain scission, which resulted in both a loosening of the polymer matrix and formation of radicals that induced formation of carboxylic and sulfonic acid groups by reaction with dissolved oxygen. UV irradiation also increased membrane surface hydrophilicity. Receding contact angles decreased from approximately 70° to just over 20° with only 10 min of irradiation. The zeta potential became more negative, indicating the formation of acidic moieties.[85,278]

Yamagishi, Crivello, and Belfort corroborated the results of Nyström in studies of UV treatment of poly(aryl sulfone) UF membranes. While photosensitizers or photoinitiators are frequently required to induce radical formation in polymers via UV exposure, they reported that PSf and PES were photoactive on their own. The molecular weight of irradiated PES decreased with time, and the chain scission was most likely to occur at the phenoxyphenyl sulfone groups in the backbone of both PSf and PES. Figure 23 shows the proposed chain scission sites in the PES backbone. Radical formation by UV exposure was used to polymerize vinyl monomers directly from the PSf or PES backbones; UV-induced grafting will be discussed below.[279]

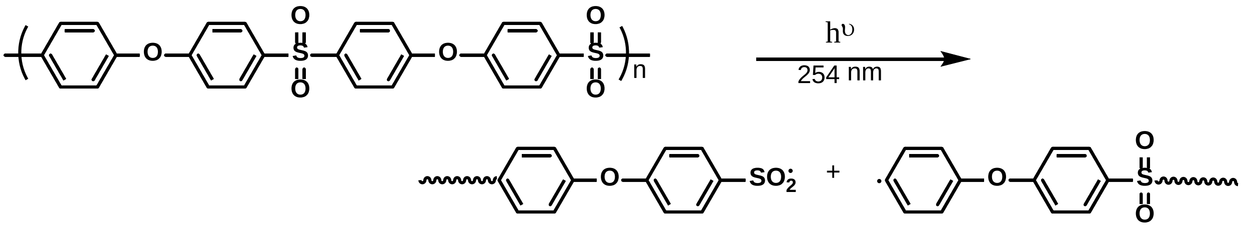


Figure 23. Chain scission in PES by UV irradiation.[279]

8.2 UV-Induced Grafting

Plasma- and corona discharge-induced grafting requires specialized equipment to produce the low-pressure reaction conditions necessary for plasma formation. Membrane surface activation by UV irradiation, which can induce radical formation with or without a photoinitiator, has therefore garnered substantial interest. Compared to plasma treatment, UV irradiation involves relatively mild reaction conditions (including ambient temperature and pressure) and relatively unspecialized equipment (other than a UV light source), meaning that the process is relatively low cost.[280]

Photografting by UV exposure has been performed on a wide variety of membrane substrates, including PAN,[281–283] PP,[284–289] PE,[290] PSf,[291,292] PES,[291,293] PET,[294] PVDF,[295] and nylon.[287] PAN, used in many of the early studies of Ulbricht *et al.*, was chosen because it exhibits good stability to UV irradiation.[281] In contrast, poly(aryl sulfones) such as PSf and PES tend to degrade under UV exposure, leading to chain scission and pore enlargement. Belfort *et al*. later took advantage of the photosensitivity of PSf and PES to induce radical formation on the membrane surface directly,[279,296] which will be discussed below. With the exception of PSf and PES, most of these membranes are not sufficiently photosensitive to use without an initiator, so photoinitiators are often employed to induce radical formation on the membrane surface. Benzophenone is a commonly used photoinitiator and it is typically applied by soaking the membrane in a benzophenone solution immediately before photografting.[281–289,291,293–295] The benzophenone may adsorb to the surface of the membrane polymer or, if the solvent is capable of swelling the membrane, penetrate into the polymer matrix. Ulbricht *et al*. have, for example, promoted penetration of benzophenone into a PP membrane by using *n*-heptane as the benzophenone solvent/carrier. When benzophenone was entrapped within the membrane matrix, the resultant grafted poly(acrylic acid) layer was less dense and had longer chains compared to grafted layers formed when the photoinitiator only was adsorbed to the membrane surface.[284] Other photoinitiators used include benzoyl benzoic acid,[292,294] N-(p-benzoylbenzyl)-N,N,N-triethylammonium bromide,[294] and xanthone.[290]

Photografting by UV irradiation is a robust technique capable of utilizing a variety of vinyl monomers. Acrylic acid is probably the most frequently employed monomer for surface modification by this technique,[281–287,291,292,294] largely due to its hydrophilicity. Other monomers, including methacrylic acid,[290] 2-hydroxyethyl methacrylate,[282] various poly(ethylene glycol) methacrylates,[282,283,285] 3-sulfopropyl acrylate,[283] 2-dimethylamino-ethyl methacrylate,[283,293,295] 2-trimethylammonium-ethyl methacrylate,[283] dimethyl aminoethyl methacrylate,[285] 2-acrylamido-2-methylpropanesulfonic acid,[289,293,295] and D-gluconamidoethyl methacrylate[288] have also been considered. Grafting can be accomplished from either the vapor or liquid phases. To graft from the vapor phase, Ulbricht *et al*. coated PAN membranes with benzophenone initiator and mounted them in a reaction chamber with a glass window. Monomers solutions were placed inside the chamber to saturate the atmosphere. The membranes were then irradiated with UV energy through the window which induced the grafting of vaporized monomers.[281–284] Alternatively, membranes treated with photoinitiator could be directly immersed in monomer solution and irradiated, inducing grafting from the liquid phase.[287,292,294] One limitation of these procedures is that the initiator is capable of abstracting hydrogens (to form radicals) from both the membrane substrate and from the reacted polymer, forming substantial amounts of homopolymer and crosslinked material.[286] To circumvent these issues, Ma, Davis, and Bowman developed a sequential grafting procedure, wherein the membrane surface was activated with photoinitiator before contact with the monomer solution. They demonstrated a four-fold improvement in grafting efficiency over methods in which radical formation on the membrane surface and polymerization occurred simultaneously when acrylic acid was grafted to PP MF membranes.[286]

Hydrophilic monomers have been grafted to several MF and UF membranes in an attempt to improve their fouling resistance. Ulbricht *et al*. aimed to reduce protein adsorption to UF membranes to facilitate their use in protein separations by grafting acrylic acid, 2-

hydroxyethyl methacrylate, and several poly(ethylene glycol) methacrylates to PAN membranes.[282] Hydroxyethyl methacrylate and the PEG methacrylates were effective in reducing protein adsorption to the membrane surface from over 6.5 µg cm^{-2} to less than 3.0 µg cm^{-2}.[282] Ma, Davis, and Bowman photografting several monomers to PP MF membranes, including poly(ethylene glycol) monomethacrylate, acrylic acid, and dimethyl aminoethyl methacrylate, which rendered the respective surfaces hydrophilic. These hydrophilic surface modifications did not greatly improve the fouling performance of the membranes when challenged with bacteria or latex bead suspensions. For example, both unmodified and modified PP membranes had a flux of about 65 L m^{-2} h^{-1} after filtration of an *E. coli* suspension for one hour.[285] However, modified membranes responded to cleaning by backwashing more effectively than unmodified membranes.[285,297] Modified membranes had fluxes ranging from 610 to 670 L m^{-2} h^{-1} after backwashing following *E. coli* filtration, whereas an unmodified membrane had a flux of only 280 L m^{-2} h^{-1} after backwashing.[285] Biofouling reduction was the subject of studies by Hilal *et al*. PES[293] and PVDF[295] MF membranes were photografted with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and quaternary 2-dimethylaminoethylmethacrylate (qDMAEMA) following activation with benzophenone. Membranes modified with qDMAEMA exhibited an antibacterial effect when an *E. coli* suspension was filtered through the membranes.[293,295] Hemocompatability is important for implantable polymeric materials. Ulbricht *et al*. photografted D-gluconamidoethyl methacrylate to form glycopolymer brushes on the surface of PP MF membranes. Glycopolymers are of interest in biomedical applications because they have been shown to exhibit good biocompatibility. Such modification of PP membranes reduced the adhesion of BSA. Unmodified membranes had a flux of 93 kg m^{-2} h^{-1} during filtration of a protein solution, whereas a membrane with 6.03 wt% of D-gluconamidoethyl methacrylate grafted to its surface had a flux of over 450 kg m^{-2} h^{-1}. Furthermore, platelets were observed (by SEM) to adhere less readily to modified membranes than to unmodified membranes, suggesting that the hemocompatability of these membranes may be improved by glycopolymer grafting.[288]

Photografting techniques have also been used to create functional membranes. For example, "smart" polymers, which respond to external stimuli such as changes in temperature or pH, may be grafted to a membrane surface to induce a change in separation characteristics. Ulbricht *et al*. created pH-responsive coatings on PP[284] and PET[294] MF membranes by photografting acrylic acid to their surfaces, similar to the previous work of Ito *et al*., where grafting was accomplished by corona discharge.[270,271] Peng and Cheng prepared pH-sensitive MF membranes by photografting poly(methacrylic acid) to the surface of a PE membrane.[290] By adjusting the feed pH, membrane permeability to water and solutes could be reversibly tuned. Figure 24 shows the dynamic permeability response of a membrane that is subjected to variation in feed pH for a dextran feed solution. When the feed had a pH of 2, the membrane permeability was approximately 4.0 x 10^{-7} cm^2 s^{-1}. When the feed pH was increased to 7.4, the membrane permeability decreased to approximately 7.5 x 10^{-6} cm^2 s^{-1}. At low pH, the methacrylic acid moieties are protonated and uncharged, causing the grafted polymer chains to collapse and permit high water flow. At high pH, the methacrylic acid moieties are deprotonated and negatively charged, causing the polymer chains to spread apart, blocking passage of water through the membrane pores.[290] Similarly, temperature-responsive MF membranes were prepared by photografting poly(*N*-isopropylacrylamide) to the surface of a PE membrane.[298]

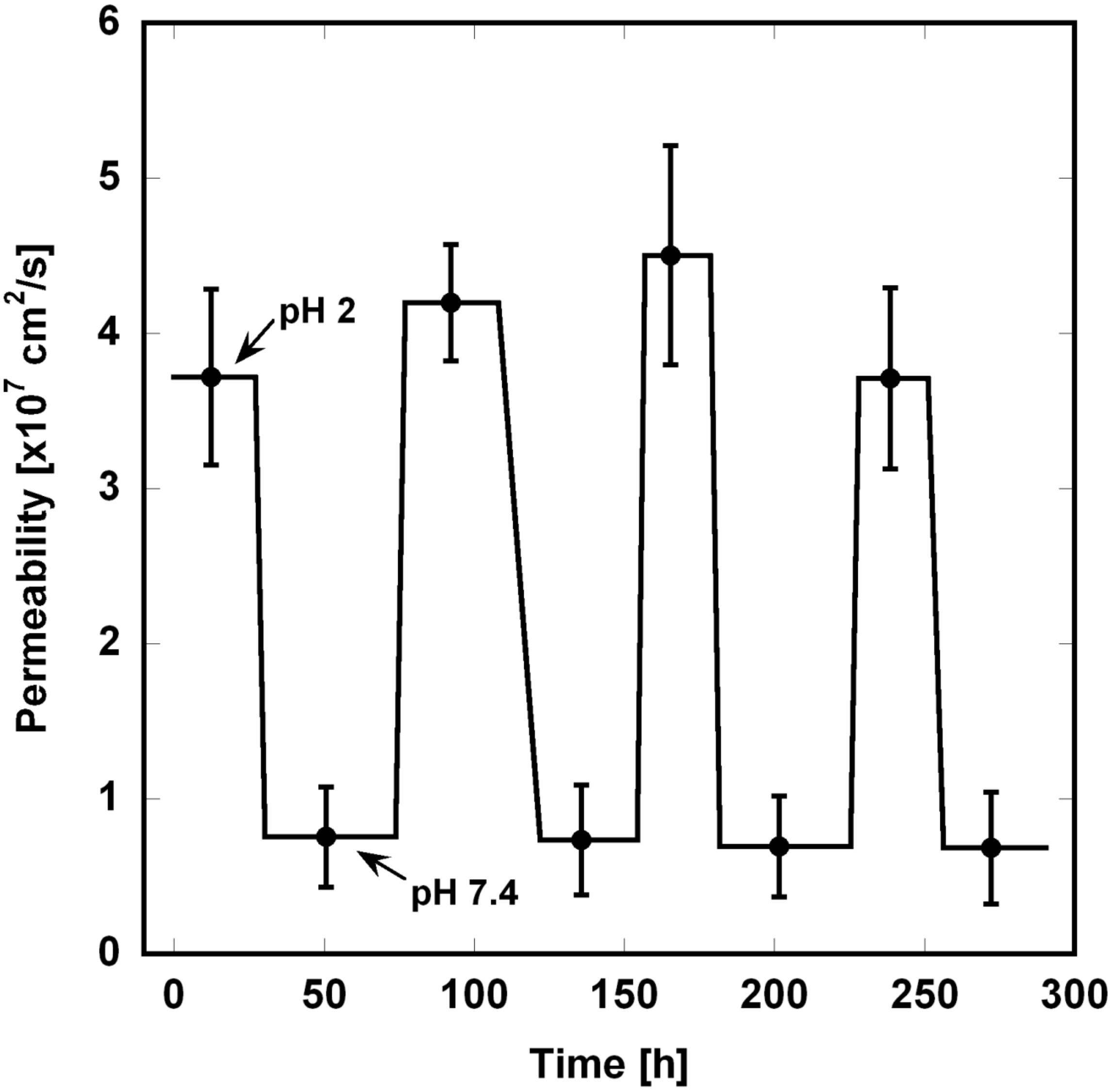


Figure 24. Dynamic permeability response of a PE MF membrane grafted with poly(methyl methacrylic acid).[290] When the feed had a pH of 2, acidic moieties in the polymer were protonated and uncharged. When the feed had a pH of 7.4, the acidic moieties were charged; charge repulsion caused polymer chains to spread apart and block pores, reducing water permeability.

Finally, Ulbricht fabricated molecularly-imprinted membranes by photografting 2-acrylamido-2- methylpropanesulfonic acid with a cross-linker, N,N'-methylenebis(acrylamide), to the surface of PP MF membranes in the presence of a template molecule, desmetryn (an herbicide). The resultant membranes had an affinity for desmetryn and other similar triazine herbicides in water.[289]

All of the studies discussed so far employed an initiator for radical formation on the membrane polymer backbone. Belfort *et al.*, however, demonstrated that poly(aryl sulfone)s are intrinsically photoactive, meaning that radical formation may be induced directly on the surfaces of PES and PSf membranes by UV exposure without a photoinitiator or photosensitizer (cf., Figure 23), thereby simplifying the grafting procedure.[279,299] Therefore, by immersing a membrane in a vinyl monomer solution during UV irradiation, radical polymerization can take place from the membrane surface. Figure 25 shows the proposed pathway for reaction of vinyl monomers with radicals formed on PES backbones.

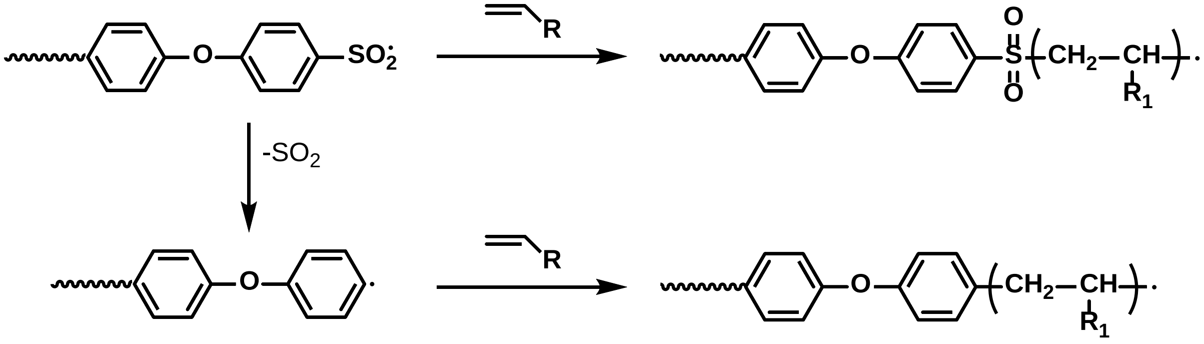


Figure 25. Polymerization of vinyl monomers to radicals formed on the backbone of PES polymer chains. Radical formation was induced by UV irradiation.[279]

Belfort *et al.* explored the effects of reaction conditions, including monomer concentration,[300,301] solvent,[279] irradiation time,[279,302,303] irradiation intensity,[300,301,304,305] UV wavelength,[305] and method of monomer application ("dip" method or "immersion" method)[302,306] on surface grafting of many vinyl monomers to PES and PSf membranes. In the dip method, the membrane was dipped in a monomer solution for 30 minutes, then removed from the monomer solution, secured in a holder, and irradiated in nitrogen atmosphere. In the immersion method, the membranes were irradiated while immersed in monomer solution. Both techniques resulted in membranes of higher hydrophilicity and lower adsorptive protein fouling than that of the unmodified membrane.[302,306] During dip modification, 80-90% of the UV energy reached the membrane surface, causing extensive radical formation and rapid grafting. The high-energy impingement on the membrane surface, however, also caused significant bond cleavage, which reduced protein rejection. An unmodified membrane had protein rejection of 98.3%, while the rejection of a membrane modified by the dip method using 1 wt% monomer and a 60 s irradiation time decreased to 5.1%. In contrast, only 12-18% of the UV energy reached the membrane surface during immersion modification, resulting in reduced radical formation and slower grafting. The reduced impingement of UV energy on the membrane surface also reduced bond cleavage, allowing the immersion-modified membrane to maintain high protein rejection. A membrane modified by the immersion method using 1 wt% monomer and a 60 s irradiation time had a protein rejection of 99.1%.[306] The use of different UV lamps and a liquid benzene filter that eliminated most of the high energy UV light at 254 nm, which was thought to be primarily responsible for PES chain scission, improved protein rejection in dip modified membranes.[305] Generally, water flux was reduced in the case of both dip and immersion modification techniques due to pore blockage by the grafted polymer chains, except in the case of low monomer concentrations (1 wt%) and long irradiation times (≥ 60 s) during dip modification, where prolonged UV exposure caused pore enlargement due to membrane degradation.[306] The incorporation of a chain transfer agent (*e.g.*, 2-mercaptoethanol), which is used to control the degree of polymerization in radical polymerizations, improved the water flux of dip modified membranes, but membranes grafted with the use of a chain transfer agent had reduced protein rejection. For example, a membrane modified by the dip method and a 60 second irradiation time without mercaptoethanol had an invertase rejection of 95%, whereas a membrane modified using 50 mM mercaptoethanol had an invertase rejection of 90%.[304]

Monomer selection was aided by a previously-developed, high-throughput screening protocol focused on assessing protein adhesion to polymeric surfaces.[79,80] Protein adhesion on a membrane surface and within its porous structure contributes to flux reduction during ultrafiltration or microfiltration of protein solutions.[79,299,307] Monomers forming polymeric surfaces resistant to protein adhesion were identified from a library of 66 candidates. Monomers effective in reducing protein fouling on PES and PSf UF membranes included hydroxyethyl methacrylate (HEMA),[296] 2-acrylamido-2-methyl-1-propanesulfonic acid,[300] N-vinyl-2-pyrrolidinone (NVP),[301–303,305,306] 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS),[307] and poly(ethylene glycol)methyl ether methacrylate.[82,83] The addition of grafted polymer chains to the membrane surface typically increased the membrane's mass transfer resistance and protein rejection due to pore plugging. For example, grafting AMPS, one of the largest monomers considered (MW = 206), to the surface of a PES UF membrane increased the resistance to water permeation by a factor of six, even with a degree of grafting less than 0.2.[307] Note that the degree of grafting refers to the mass of grafted chains relative to the mass of substrate membrane, and it is typically defined as:

$$DG = \frac{W_g - W_0}{W_0}$$

where DG is the degree of grafting, W_g is the mass of the grafted membrane, and W_0 is the mass of the ungrafted membrane.[308] In this study,[307] the degree of grafting was determined by monitoring the relative intensities of infrared absorbance peaks on the modified and unmodified membranes, as follows:

$$DG = \frac{H_{X,M}}{H_{1487,M}} - \frac{H_{X,U}}{H_{1487,U}}$$

where $H_{X,M}$ is the peak height at wavenumber X cm^{-1}, corresponding to a carbonyl stretch in the grafted monomer, $H_{1487,M}$ is the peak height at 1487 cm^{-1}, corresponding to a carbon-carbon stretch in an aryl ring of the modified PES or PSf membrane, and $H_{X,M}$ and $H_{1487,M}$ are analogous peak heights for the unmodified membrane.[307] At the same degree of grafting, BSA rejection for an AMPS-modified membrane was near 100%.[307] However, HEMA and NVP dissolved PES membranes, so modified PES membranes with a low degree of grafting exhibited reduced protein rejection; rejection was recovered by increasing the degree of grafting to compensate for pore widening due to PES dissolution.[307]

Interestingly, all tested monomers increased the hydrophilicity of the substrate UF membranes and generally reduced irreversible protein fouling regardless of charge (neutral, strongly charged, or weakly charged).[307] For example, after modification with AMPS (degree of grafting = 0.2), a PES UF membrane suffered virtually no irreversible fouling when challenged with 20 g of 1.0 g L^{-1} BSA solution. The aforementioned monomer screening procedure led Belfort and co-workers to explore monomers not traditionally considered in fouling-resistant materials. For example, several amine-containing vinyl monomers were grafted from binary monomer solutions with poly(ethylene glycol)methyl ether methacrylate; the resultant membranes exhibited improved resistance to protein adhesion relative to membranes grafted with only poly(ethylene glycol)methyl ether methacrylate.[83]

Belfort's studies focused mainly on protein fouling,[79,80,82,83,296,300,301,303–307] but natural organic matter fouling[302,309] was also considered. Some monomers, such as NVP, were successful in mitigating both protein[306] and NOM[302] fouling. However, other monomers, which performed well in protein fouling tests, performed poorly when challenged with NOM.

For example, HEMA grafting produced membranes resistant to protein fouling,[307] but this hydrophilic monomer exacerbated irreversible NOM fouling.[309] Grafting HEMA to the surface of a PES UF membrane, however, reduced the mass transfer resistance due to irreversible fouling by as much as ten-fold when the membrane was challenged with 20 g of a 1.0 g L^{-1} BSA solution.[307] In contrast, when challenged with a NOM feed solution, grafting of HEMA to a PES UF membrane *increased* the mass transfer resistance due to irreversible fouling by nearly a factor of three.[309] Membrane hydrophilicity after grafting correlated well with reduced protein fouling susceptibility. However, membrane hydrophilicity was not a good indicator of susceptibility to NOM fouling,[309] perhaps due to the complex mixture of components (including hydrophilic and charged compounds) in NOM. This result illustrates the complexity of membrane fouling and the importance of testing the membranes under conditions as close as possible to those of interest for any given application.

Ulbricht *et al*. grafted hydrophilic polymers to commercial PES membranes without using a photoinitiator or photosensitizer. Zwitterionic compounds, when immobilized on a surface, reportedly offer resistance to nonspecific protein adsorption.[310] To this end, N,N-dimethyl-N-(2- methacryloyloxyethyl-N-(3-sulfopropyl)ammonium betaine (SPE), a vinyl zwitterionic monomer, was grafted to PES UF membranes by UV irradiation (wavelengths >300 nm to minimize membrane degradation) while immersed in a monomer solution. Membranes were also grafted with PEGMA in a similar manner. Depending upon the degree of grafting, modified membranes (immersed in water) had pendant air bubble contact angle measurements of 37.8º to 42.5º (measured through the water); an unmodified membrane with the same molecular weight cutoff had a contact angle of 61.7º, indicating that it was substantially more hydrophobic than the modified membranes. Furthermore, the zeta potential of modified membranes was less negative than that of an unmodified membrane. Both PEGMA-modified and zwitterion-modified membranes exhibited higher normalized fluxes (approximately 0.60 – 0.85, normalized to the pure water flux) than unmodified PES membranes (0.20 – 0.30) following filtration of 1 g L^{-1} myoglobin solution for 120 min.[280] PES UF membranes grafted with PEGMA were also challenged with feeds containing polysaccharide, alginate, or polysaccharide/protein mixtures; in all cases, the fluxes of the modified membranes were much higher than those of unmodified analogues.[311]

8.3 High Energy Irradiation

Irradiation other than UV irradiation has also been used to induce grafting to polymer surfaces. The use of radiation graft polymerization to prepare membranes, materials used in medical applications, and sorbents has been reviewed elsewhere.[312,313] Many types of high-energy radiation may be employed, such as γ rays, X rays, or electron beams.[313] The use of high energy radiation requires a radiation source. Despite this limitation, the use of high energy radiation is of interest because it can induce graft polymerization at a wide range of conditions, including low temperature and in the solid state, and the degree of grafting may be controlled by appropriate selection of irradiation conditions.[313] Additionally, high energy radiation tends to penetrate more deeply into the polymer substrate than UV radiation or plasma (which is particularly surface-selective).[313] Therefore, grafting can be accomplished within the bulk of the substrate to produce a more nearly homogeneously-modified membrane; one example of high-energy radiation grafting is the preparation of ion exchange membranes with grafted ion-containing polymers throughout the membrane matrix.[313] The use of high energy radiation in ion exchange membrane fabrication has been reviewed elsewhere.[313] Here, we briefly review a few examples of the use of high energy radiation for membrane surface modification.

Both γ ray[314,315] and electron beam[316–318] irradiation have been used to surface-modify porous water purification membranes. For example, Lee *et al.* irradiated porous PP membranes with γ rays from a ^{60}Co source to form peroxides on its surface. The activated membrane was then immersed in a solution of 2-hydroxyethylmethacrylate to initiation polymer chain growth. The degree of grafting could be controlled by radiation exposure time. Reduced fouling by proteins and enhanced response to cleaning was observed with increased grafting density.[314] Fouda *et al.* hydrophilized PES hollow fiber UF membranes by grafting PEG to their inner surfaces. In this study, however, PEG of various molecular weights was "grafted to" the membrane surface by adsorbing the PEG to the membrane before γ irradiation. A modified membrane exhibited a flux approximately 67% higher than the unmodified membrane during filtration of 50 ppm porcine albumin solution at a crossflow velocity of 4.85 m s^{-1}.[315]

Electron beams have been used to treat PE hollow fibers in a series of publications by Saito *et al*.[316–318] In this work, surface grafting was used to introduce reactive groups onto the PE surface for later conjugation with other molecules. For example, the use of glycidyl methacrylate monomer produced epoxide moieties,[316–318] while acrylic acid[317] or vinyl acetate[318] resulted in hydroxyls. Following irradiation, hollow fibers were contacted with monomer in either the liquid[316,317] or vapor[318] phase. Following graft polymerization, a variety of other reactions were performed to produce membranes suitable for different applications. Conversion of epoxides to sulfonic acids was accomplished by reaction with sodium sulfite, resulting in membranes capable of ion exchange.[316] Protein selective membranes were fabricated by coupling phenylalanine, a protein binding ligand, to epoxide or hydroxyl (via reaction with N-hydroxy-succinimide) groups on the grafted surface. The resultant membranes were used for protein chromatography.[317] Finally, protein fouling of membranes grafted with hydrophilic vinyl acetate and glycidyl methacrylate monomers was evaluated. Adsorption of BSA to the hollow fibers was significantly reduced for modified membranes relative to unmodified membranes. The maximum reported adsorption of BSA onto an unmodified membrane was approximately 50 g protein per kg fiber, whereas adsorption onto vinyl acetate and glycidyl methacrylate-grafted fibers was less than 15 g protein per kg fiber.[318]

A series of patents assigned to the Pall Corporation describe the use of ionizing radiation to graft polymers to membrane surfaces.[319–324] These membranes may be incorporated into filtration systems targeted to remove leucocytes from platelet concentrates,[319] removal of proteinaceous material from fluid mixtures,[320,321] removal of impurities from ultrapure water for microelectronics applications,[322] or removal of impurities,[323] particularly viruses,[324] from pharmaceutical solutions. Preferred membranes for modification included PVDF MF,[323,324] polyamide MF,[320,322] and PSf UF[321] membranes. Depending upon the desired membrane properties, a variety of monomers were used for graft polymerization, including hydrophilic (particularly those that would result in a large number of hydroxyl groups on the surface[319–321,324]) and positively charged[322,323] monomers. Examples of monomers employed for grafting include methacrylic acid,[319] hydroxypropyl acrylate,[320,321,324] poly(ethylene glycol) dimethacrylates,[321,323] and diallyldimethylammonium chloride.[322,323]

9. Polydopamine

Recently, there has been significant interest in surface modifications using materials inspired by the adhesive secretions of mussels and other sessile marine organisms.[113,325,326] Able to anchor themselves firmly to nearly any underwater surface, these species have become a subject of interest for chemists, biochemists, and engineers who seek to understand this remarkable underwater adhesive behavior and apply it to synthetic systems.[327] A 2007 report by Messersmith and co-workers described the deposition of polydopamine onto a variety of substrates, including ceramics, metals, and synthetic polymers, from a mild, buffered, aqueous dopamine solution.[113] The homogeneous, conformal coatings of polydopamine were highly hydrophilic and could readily be used as a platform for secondary conjugation of other molecules.[113] A number of publications, as well as several review articles, have appeared describing the wide use of this biocompatible material, including energy, water purification, biomedical, sensing, and other applications.[328,329]

9.1 Application of Polydopamine to Membranes

"Bio-inspired" materials have been widely studied in membrane fabrication or modification applications. For example, Hawes and Akhtar mimicked the phospholipid bilayer structure of the outer membrane of a red blood cell, which has a zwitterionic character. Following plasma treatment (to introduce surface hydroxyl groups), they grafted 2-methacryloyloxyethyl phosphorycholine to PVDF and CA MF membranes. Modified membranes exhibited much higher flux during protein crossflow filtration than unmodified membranes. For example, after filtration of a BSA solution for 2 h, the flux of an unmodified PVDF membrane was approximately 300 L m^{-2} h^{-1}, while a modified membrane had a flux of approximately 3800 L m^{-2} h^{-1}.[330] Xu *et al.* grafted phospholipid-like polymers to MF membrane surfaces by ring-opening polymerization.[331] Huang *et al*. prepared bio-inspired coatings by introducing phospholipid moities/phosphorylcholine onto membrane surfaces by chemical reaction in an effort to make membranes resistant to protein adsorption.[332]

Polydopamine is of interest for water purification membrane surface modification because it provides a facile route to hydrophilization of the (typically hydrophobic) membrane surfaces that often suffer from fouling during water filtration. Polydopamine also addresses many of the disadvantages of other traditional surface modification techniques. For example, due to the non-specificity of polydopamine deposition, no special chemistry is required between the membrane surface and the polydopamine coating. In contrast, many grafting processes depend on the presence of a specific moiety on the membrane surface.[112,142,212] Furthermore, polydopamine modification occurs under mild, aqueous conditions, meaning that the underlying membrane does not suffer degradation, in contrast to chain scission, which is a potential problem in polymeric membrane modification by irradiation-[85,279,306] or plasma-based[107,237,251] methods. Additionally, because the deposition takes place in aqueous solution, the membrane can remain wet during the entire modification process. Unlike modification by corona or plasma treatment, no drying is required; drying can decrease membrane permeability due to pore collapse induced by strong capillary forces that develop during drying.[268] Finally, a common problem with many membrane coating procedures is the inevitable loss in water permeability associated with the coating. While this issue cannot be avoided in all cases with polydopamine, it can be mitigated by controlling the polydopamine deposition thickness. By varying polydopamine deposition time or the concentration of dopamine in the coating solution, the thickness can be controlled over a range of a few to several tens of nanometers.[333–335] Such thin coatings allow a relatively high membrane permeability to be maintained following surface modification.[333,335,336] Because many membrane surface modifications are challenging to implement industrially due to their complexity or specificity, polydopamine may be a useful route to modifying membrane surfaces.[337]

Many commercial membranes, including MF, UF, NF, and RO membranes, have been successfully modified with polydopamine.[333,335,336,338–346] Due to the non-specific nature of polydopamine deposition, polymeric membranes based on many polymers, including polyamides, poly(aryl sulfones), PVDF, PP, and PTFE have been rendered hydrophilic.[333,335,336] Generally, modified membranes are rinsed with an organic solvent such as ethanol to remove weakly-bound polydopamine, after which little leaching from the membrane surface is observed. Modified membranes exhibited an improvement in flux during constant transmembrane pressure crossflow filtration of oil/water emulsions relative to their unmodified counterparts.[335,336] Furthermore, as demonstrated by Messersmith *et al.*, amine- or thiol-containing molecules could be readily conjugated to polydopamine-coated surfaces under similarly mild, aqueous conditions as the polydopamine deposition.[113] PEG-NH_2 was grafted to polydopamine-modified membranes, which generally resulted in further improvements in flux during crossflow filtration of oil/water emulsions. Figure 26 shows flux decline curves for unmodified, polydopamine-modified, and polydopamine-*g*-PEG-modified PSf UF membranes.[336]

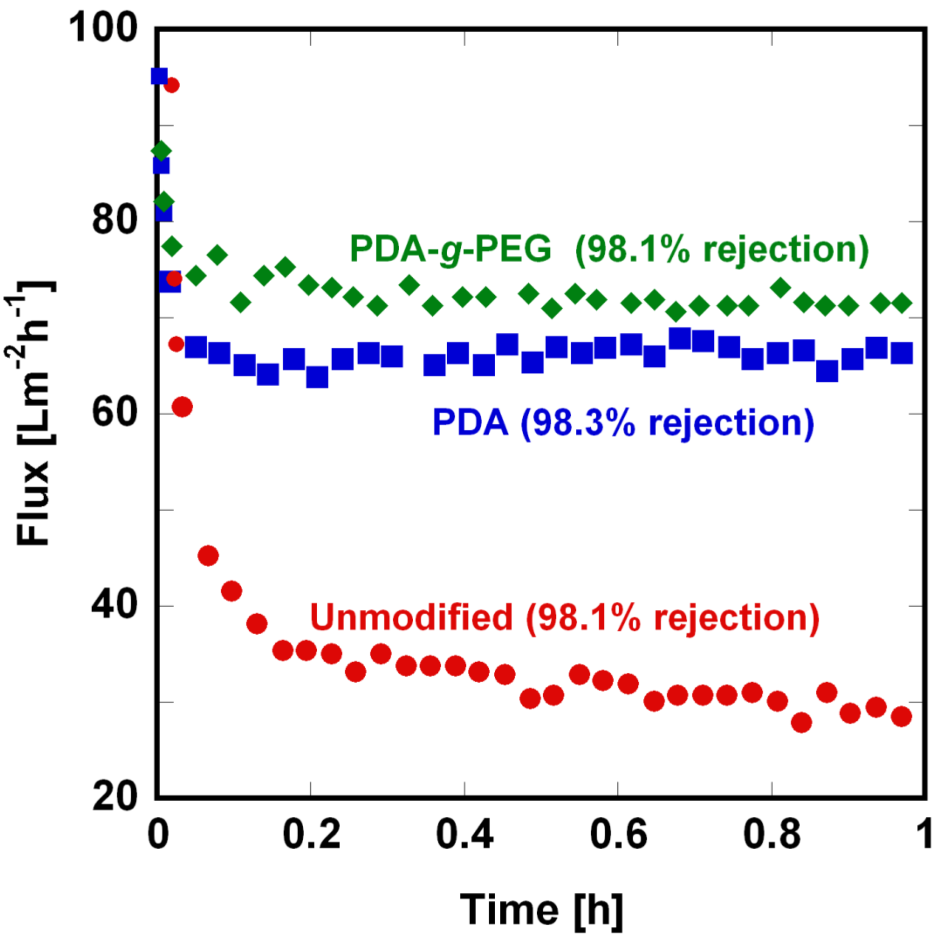


Figure 26. Flux decline during constant transmembrane pressure filtration of emulsified oil by unmodified, polydopamine-modified (PDA), and polydopamine-*g*-PEG-modified (PDA-*g*-PEG) PSf UF membranes. Transmembrane pressure = 2.1 bar, crossflow velocity = 0.18 m/s, 1500 ppm soybean oil emulsion (9:1 oil:nonionic surfactant).[336]

Due to the promising results obtained during constant transmembrane pressure laboratory fouling studies with polydopamine-modified membranes, pilot-scale studies were undertaken. One such study involved purification of flowback water from hydraulic shale fracturing operations in the Barnett Shale region of north Texas.[339] Hydraulic fracturing can require over a million gallons of water per well, and 10-30% of the water used for fracturing often returns to the surface during gas recovery, laden with organics, salts, and other impurities. Reuse of flowback water could reduce strain on freshwater resources, especially in arid regions where such wells are frequently located. However, flowback water must often be desalinated due to incompatibility between salts and certain additives in the fracturing water.[347] A two-stage pilot study was performed; in the first stage, oils and other organics were removed by ultrafiltration, while in the second stage, water was desalinated by reverse osmosis. In the ultrafiltration stage, a polydopamine-*g*-PEG-modified PAN module was run in parallel with an unmodified, but otherwise identical, UF module. The modified module exhibited 50 – 100% higher permeance than the unmodified module.[339] In the RO stage, a train of three polydopamine-modified composite polyamide RO modules was run alongside a train of three unmodified, but otherwise identical, RO modules. No productivity enhancement for the modified RO modules was realized relative to the unmodified modules, but the modified RO modules exhibited higher salt rejection than the unmodified modules. The train of modified RO modules exhibited salt rejection values above 99.5%, whereas the train of unmodified RO modules typically had salt rejections in the range of 96.5 – 99.0% (depending upon feed composition). The polydopamine modification may have improved the salt rejection of the RO membranes by filling tiny imperfections in the polyamide layer that would readily permit salt passage across the membrane.[339] Similar results have been reported for other surface coatings on RO membranes.[142,155]

Polydopamine and polydopamine-related surface modifications were also evaluated for their ability to mitigate biological fouling, including reductions in biofilm formation and blood coagulation. Polymeric MF, UF, and RO membranes were modified with coatings of polydopamine,[333,338,348] polydopamine-*g*-PEG,[333,338] polydopamine-*g*-heparain,[349] and poly(L-DOPA).[350] (Heparin is a blood anticoagulant and L-DOPA is an amino acid closely related to dopamine.) The effect of these modifications on adhesion of proteins, bacteria, and blood platelets to the surfaces was evaluated by contacting them with static protein solutions,[333,350] monoculture bacterial suspensions,[338] or platelet-rich blood plasma[348,349] for up to two hours. In a similar study, medical grade silicone was modified with polydopamine and subsequently grafted with antimicrobial carboxymethyl chitosan and incubated with monoculture suspensions of *Escherichia coli* and *Proteus mirabilis* for 24 hours.[351] Under these static, relatively short-term conditions, the polydopamine modifications universally reduced adhesion of these common foulants.[333,338,348–351] Longer-term biofouling resistance under flow conditions was evaluated using the autochthonous drinking water population. In these experiments, which lasted over a week, PSf UF membranes modified with polydopamine and polydopamine-*g*-PEG exhibited similar biofilm growth on the membrane surface as unmodified membranes.[338,342] Thus, biofouling is a complex problem that may not be solved easily by altering membrane surface properties. Biofilm growth in an industrial environment occurs with a diverse population of organisms under dynamic flow conditions over long periods of time. The effects observed for simple, short-term, static adhesion measurements in the laboratory may not be representative of performance under more realistic operational conditions.[338] Notably, other surface modifications, such as copper or antimicrobial coatings, also failed to prevent long-term biofilm formation.[342]

The effects of polydopamine deposition on membrane transport properties have also been extensively studied. Typically, polydopamine is deposited from dopamine solution buffered within a pH range of 8.5 - 9.0, as reported by Messersmith *et al*.[113] Dopamine polymerization depends on solution pH, as the deposition on surfaces of polyamide RO membranes was not observed from acidic dopamine solutions.[335] Jiang *et al*. assessed the effect of dopamine solution pH on the deposited polydopamine coating. Positron annihilation lifetime spectroscopy suggested an increase in free volume as pH was increased from 7.8 to 9.4.[346,352] The effects of polydopamine deposition time and dopamine concentration in the modification solution on polydopamine layer thickness have also been studied. As polydopamine deposition time or dopamine concentration is increased, the deposited polydopamine film thickness generally increases,[333,334] typically leading to decreases in membrane permeance.[333,340,346,348] Furthermore, using positron annihilation lifetime spectroscopy, Jiang *et al.* observed that polydopamine free volume decreased with increasing dopamine concentration.[352] While membrane permeance generally decreased upon deposition of polydopamine, the permeance of some hydrophobic MF membranes remained the same or increased following deposition of polydopamine.[333] Potentially, the increase in hydrophilicity afforded by polydopamine, which acts to facilitate water passage through the hydrophobic pore structure, counteracts the increased resistance to water transport imposed by application of the coating. Because the pores of MF membranes are relatively large (on the order of tenths of microns or more), the application of a polydopamine coating several nanometers thick did not adversely affect their permeances. In the case of PTFE, PP, and PVDF MF membranes, the pure water permeance after polydopamine application was the same or slightly higher than that of the native membrane.[336]

For membranes with smaller pores, such as poly(aryl sulfone) UF membranes, the effect of polydopamine deposition on permeance was more pronounced. In addition to the constant transmembrane fouling studies mentioned above, the efficacy of polydopamine surface modifications were also studied under constant flux conditions.[340] In this scenario, the transmembrane pressure required to maintain a particular flux is monitored as the membrane fouls. Therefore, although the hydrophilic polydopamine coating nominally imparts some fouling resistance to the membrane, the decreased permeance of the modified membrane results in a higher transmembrane pressure during constant flux fouling for a modified membrane than for an unmodified membrane, as shown in Figure 27a.[340,341] This problem may be circumvented by polydopamine-modifying a membrane with large pores until it has the same permeance as an unmodified membrane with smaller pores. Because the thickness of the polydopamine coating can be easily varied, the permeance of a modified membrane can be tuned simply by adjusting polydopamine deposition time and/or concentration. In cases where a polydopamine-modified UF membrane was compared to an unmodified membrane of the same permeance, modified membranes exhibited substantially lower transmembrane pressures (i.e., lower fouling) than unmodified membranes at the same flux.[340,341]

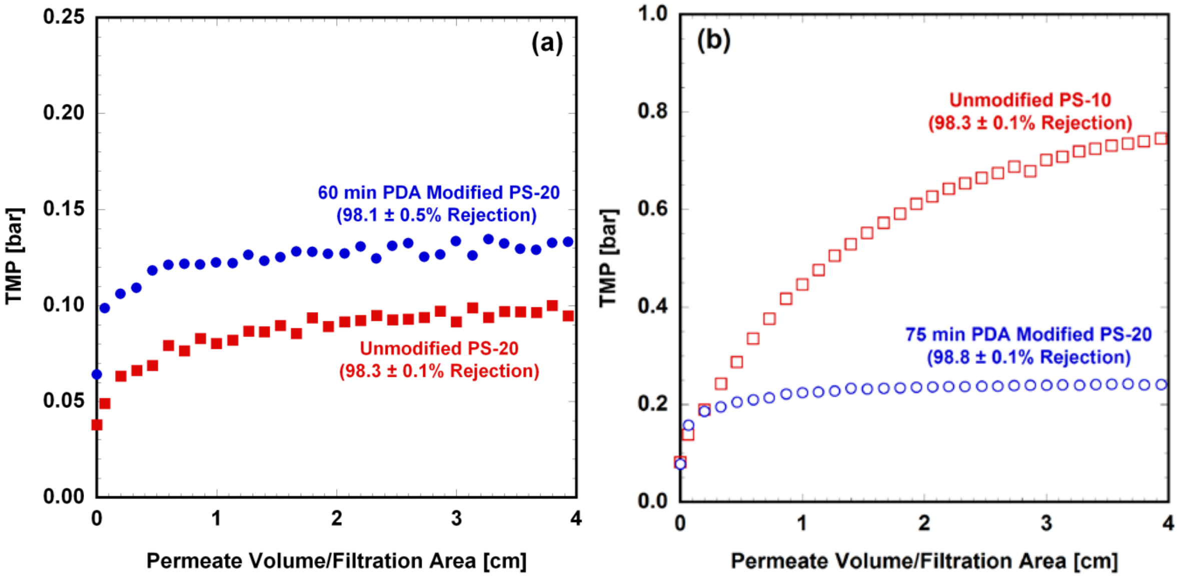


Figure 27. Constant flux fouling of unmodified and polydopamine-modified PSf UF membranes with 1500 ppm soybean oil emulsion at a flux of 40 L m^{-2} h^{-1}. (a) Comparison of unmodified PS-20 UF membrane (pure water permeance = 900 L m^{-2} h^{-1} bar^{-1}) and polydopamine-modified PS-20 UF membrane (60 min polydopamine deposition, pure water permeance = 900 L m^{-2} h^{-1} bar^{-1}). (b) Comparison of unmodified PS-10 UF membrane (pure water permeance = 575 L m^{-2} h^{-1} bar^{-1}) and polydopamine-modified PS-20 UF membrane (75 min polydopamine deposition, pure water permeance = 575 L m^{-2} h^{-1} bar^{-1}).[340]

Polydopamine has also been used to surface-modify a variety of membrane architectures. For example, Zhu *et al*. fabricated NF membranes by applying a thick layer of polydopamine to flat-sheet PSf UF membranes.[345] This thick polydopamine coating was formed using long deposition times (~20 hours) and, in some cases, sequential coating applications. The hydrophilicity of the membrane could be enhanced using two successive coatings. The thick polydopamine coating created a skin layer atop the porous membrane that gave rise to ion selectivity.[345] The rejection of ions followed the trend: $NaCl < Na_2SO_4 < MgSO_4 < MgCl_2 < CaCl_2$, with $CaCl_2$ rejection reaching 68.7%. Composite membranes have also been constructed with polydopamine skin layers atop porous, hollow-fiber poly(sulfone) supports.[346,352] These hollow fibers exhibited strong interfacial adhesion between the polydopamine skin layer and the porous support, as well as promising performance in pervaporation tests.[346,352] Figure 28 shows SEM images of PSf/polydopamine composite hollow fiber membranes.

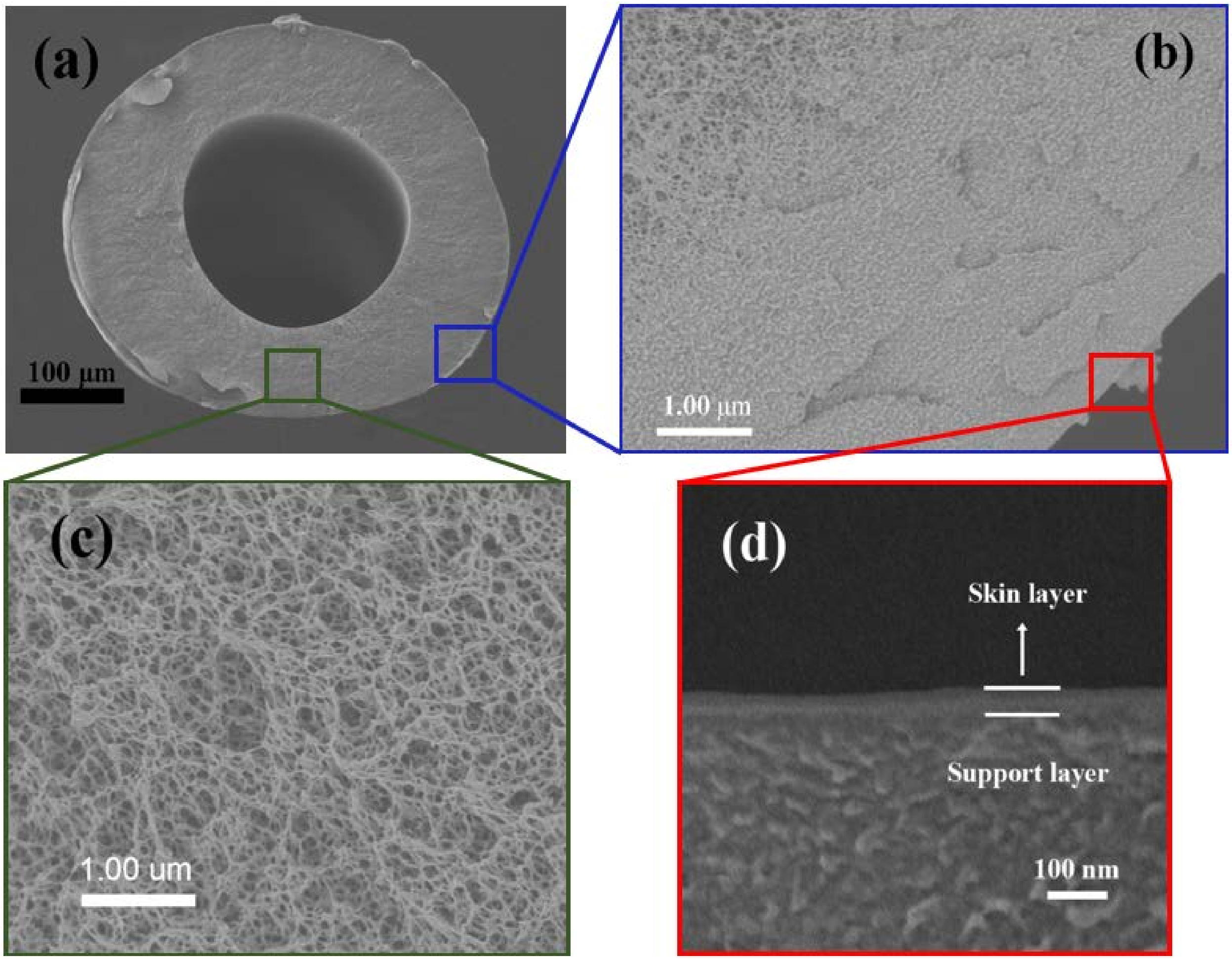


Figure 28. SEM images of PSf/polydopamine composite hollow fiber membranes. (a) Overall cross-section of composite hollow fiber. (b) Cross-section showing thin polydopamine skin layer. (c) Cross-section showing porous PSf support. (d) Close-up cross-section of thin polydopamine skin layer. Reproduced with permission, Elsevier B.V.[346]

Polydopamine has also been used to impart fouling resistance to filtration materials with large pore sizes. For example, Cao *et al*. modified a mesh (nominal pore size ~60 μm) with polydopamine-*g*-*n*-dodecyl mercaptan for oil/water separation. The *n*-dodecyl mercaptan is highly oleophilic, imparting hydrophobic character to the mesh, resulting in high efficiency in filtration of mixtures containing water and hexane, petroleum ether, gasoline, or diesel fuel.[353] The rejection of these organics was greater than 99.7% except for diesel fuel, where the rejection was approximately 98%. Liu *et al*. modified polyester filter fibers (nominal pore size ~100 μm) with polydopamine for fouling reduction.[354] Due to the relatively large pore size in these fibers, the pore size change was minimal upon coating with polydopamine. The polydopamine-modified fibers were compared to unmodified fibers by filtration of membrane bioreactor effluent for more than three weeks. During this study, the modified fibers exhibited less irreversible fouling and a slower transmembrane pressure rise than the unmodified membranes, permitting longer filtration cycles. Over a 25-day filtration period, an unmodified membrane required washing three times (on days 13, 20, and 25), whereas the polydopamine-modified membrane required only a single washing (on day 18).[354]

Engineered osmosis processes, including forward osmosis and pressure retarded osmosis, utilize osmotic pressure gradients to desalinate water or produce energy.[343] These applications demand new, high-performance membranes capable of high water flux and ion rejection. McCutcheon and coworkers have explored the feasibility of using current thin film polyamide composite RO membranes in engineered osmosis applications. A significant limitation in the use of RO membranes in these applications is severe concentration polarization that develops within the porous PSf support structure under the polyamide thin film layer. Polydopamine deposition within the PSf layer hydrophilizes the support membrane, resulting in substantially improved water fluxes in pressure retarded osmosis operation. Figure 29 compares the pure water flux of an unmodified SW30-XLE RO membrane and a SW30-XLE membrane modified with polydopamine in the PSf support layer. To facilitate mass transport in the PSf layer, the nonwoven poly(ethylene terephthalate) (PET) layer was removed before modification.

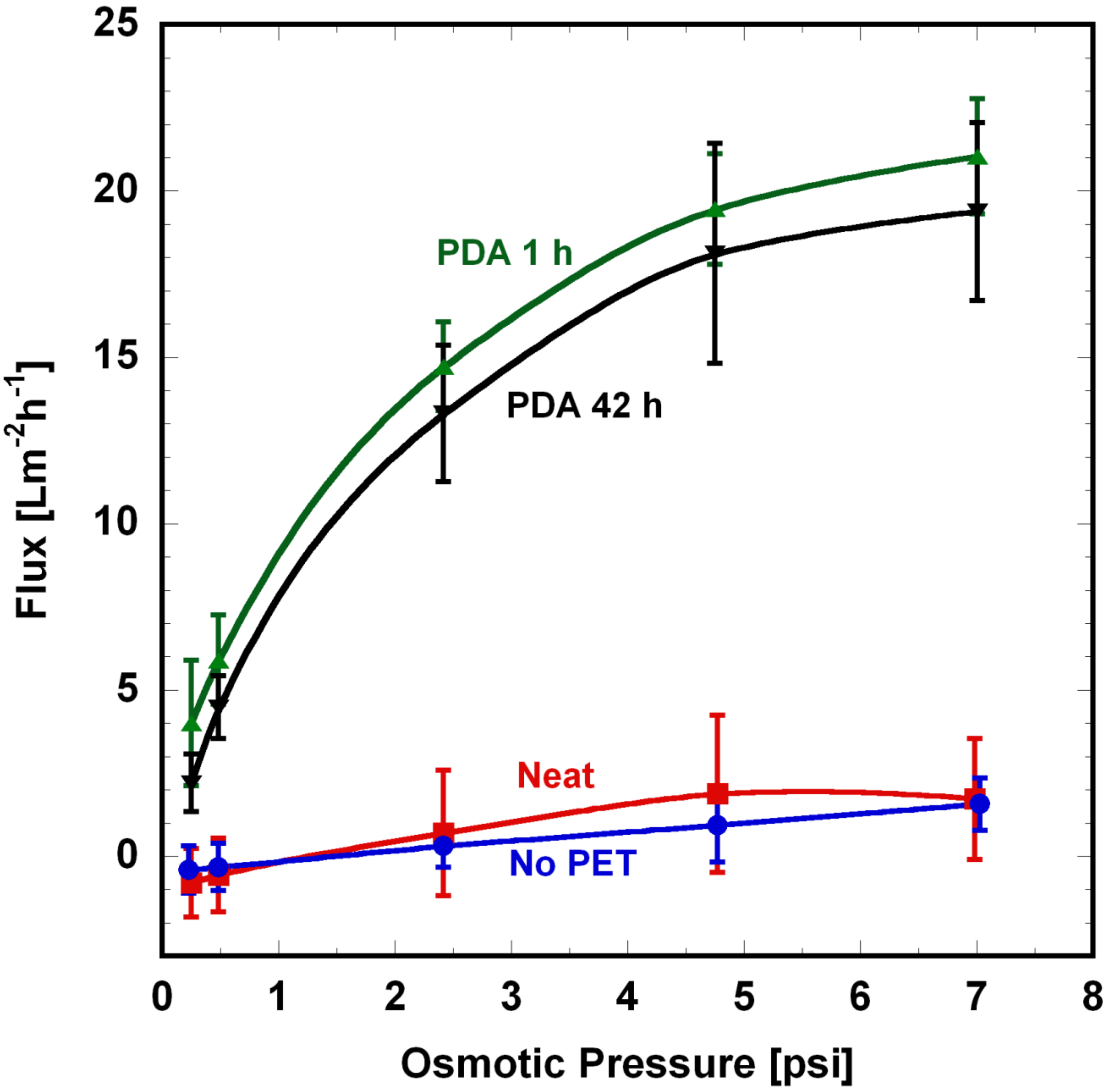


Figure 29. Pure water flux as a function of osmotic pressure for unmodified and polydopamine-modified SW30-XLE RO membranes. As-received (Neat) membranes and membranes with their PET non-woven backing layers removed (No PET) exhibited statistically indistinguishable pure water fluxes, suggesting that the PET backing layer did not contribute resistance to pure water flow. Membranes modified with polydopamine in the PSf support layer for 1 (PDA 1 h) or 42 hours (PDA 42 h) exhibited substantially improved pure water fluxes relative to unmodified membranes.[343]

Polydopamine-modified membranes had salt rejections similar to those of unmodified membranes.[343,355] Engineered osmosis membranes have also been fabricated by first coating a porous support membrane with polydopamine, and then forming the thin polyamide layer atop the modified membrane. Porous PSf,[356] PAN,[357] and polyamide-imide[358] support membranes were all successfully used in this application. In addition to rendering the underlying support membrane hydrophilic, the polydopamine also facilitates formation of the polyamide thin film by reducing the nominal pore size of the support membrane.[356]

A potential advantage of using polydopamine for surface modification is the ability to graft a wide variety of other molecules to the surface. Because polydopamine deposits non-specifically, it provides a broad platform for straightforward conjugation of many amine- or thiol-containing molecules to nearly any surface. Much of the work in this area has involved conjugation of biomolecules to polydopamine-modified surfaces.[113,326,327,359] A few studies have reported the conjugation of biomolecules to membranes surfaces using polydopamine. For example, BSA, a common model globular protein, was coupled to a polydopamine-modified PE MF membrane.[360] In another study, aquaporins were immobilized on PAN MF membranes. Aquaporins are proteins found in biological membranes that exhibit outstanding water permeance and selectivity. Aquaporin Z was incorporated into liposomes, which were subsequently tethered to the surface of a polydopamine-modified PAN microporous membrane such that they spanned the pores and all of the water transport was mediated by the aquaporins.[361,362] Liposomes, which are fragile and may rupture upon immobilization or under water filtration conditions, were stabilized by crosslinking. Ethylene glycol dimethacrylate[361] or acrylate-capped block copolymers[362] were incorporated into liposomes and UV irradiated to form crosslinks. Amine-terminated PEG was explored as a means of tethering the liposomes to the membranes and providing some “cushion” against the membrane surface, making liposome rupture less likely.[361] AquaporinZ-containing membranes were stable when subjected to pressures of 5 bar and to surface shear.[361]

Due to its long history as an anti-fouling material, PEG (and related poly(alkylene oxide)s) are commonly grafted to polydopamine-modified surfaces. Various MF and UF membranes modified with polydopamine and subsequently grafted with PEG exhibited improved flux during filtration of oil/water emulsions relative to their unmodified counterparts.[336] PEG grafting density was found to correlate with polydopamine deposition time.[333] Koelsch and co-workers prepared surfaces with densely-packed poly(ethylene oxide) brushes by tethering amine- or thiol-terminated PEO chains of various lengths to polydopamine-modified surfaces. Adsorption of human serum albumin and fibrinogen were not detectable on polydopamine-*g*-PEO-modified surfaces. The adsorption of lysozyme and human blood plasma decreased with increasing PEO chain length.[363] Similarly, Freeman et al. found that increasing PEG chain length reduced adhesion of BSA to polydopamine-*g*-PEG-modified membranes.[333] PEG has been grafted to polydopamine coatings on many other substrates, including electrophoresis capillaries[364] and catheters,[365] for fouling mitigation.

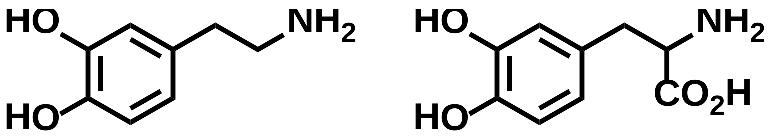
The incorporation of nanomaterials into membranes to improve membrane transport properties is currently of interest. To this end, polydopamine has been used to attach nanomaterials to membrane surfaces. For example, polydopamine enabled facile binding of TiO_2 nanoparticles to polyamide thin film composite membranes.[366] TiO_2 has been targeted due to its promise as an anti-fouling material. The TiO_2 nanoparticles readily conjugated to free hydroxyl moieties on the polydopamine-modified membrane surface without covalent attachment. Compared to traditional self-assembly methods, immobilization with polydopamine resulted in more irreversible binding of TiO_2 nanoparticles to membrane surfaces as evaluated by scanning electron microscopy. Membranes coated with polydopamine before attachment of nanoparticles were also able to maintain a higher water flux than membranes prepared by traditional self-assembly techniques, perhaps suggesting a difference in agglomeration of the nanoparticles that allowed higher water passage for the polydopamine-modified membranes. Finally, the polydopamine modification increased the salt rejection of the membranes. Unmodified membranes rejected 80.3% of $MgSO_4$ from a 2000 ppm feed solution; membranes modified with 2 h of polydopamine deposition and with 2 h of polydopamine deposition followed by TiO_2 deposition from 0.1% w/v TiO_2 suspension had $MgSO_4$ rejections of approximately 87%.[366]

Stimuli-responsive composite membranes have been fabricated by tethering environmentally sensitive polymers to polydopamine-modified membranes. For example, pH-responsive membranes were prepared by grafting poly(acrylic acid) to nylon MF membranes.[367] An ATRP initiator, 2-bromoisobutyryl bromide, was grafted to the surface of the membrane by reaction with free hydroxyl groups on the polydopamine. Surface-initiated ATRP of acrylic acid was then performed. (Surface-initiated ATRP from other polydopamine-modified surfaces has also been reported elsewhere.[368,369]) Grafted membranes exhibited pH-dependent water flux. With a pK_a of 4.3, the acrylic acid swelled significantly as the feed water pH was increased from 3.5 to 5.5, causing flux to decrease.[367] An unmodified nylon membrane had a permeance of 1.0×10^4 L m^{-2} h^{-1} bar^{-1} at pH values from 3 to 8. In contrast, a membrane grafted with poly(acrylic acid) from 6% monomer solution had a permeance of approximately 9.0×10^3 L m^{-2} h^{-1} bar^{-1} at pH 3, but had virtually no permeate flux at pH 8.[367] The use of polymers responsive to two different environmental stimuli permits fabrication of double stimuli-responsive composite membranes.[370] Abetz and co-workers used pH-sensitive block copolymers, polystyrene-*b*-poly(4-vinylpyridine), to prepare porous membrane by a traditional phase inversion process. These membranes were coated with polydopamine, to which an amine-terminated temperature-sensitive polymer, poly(*n*-isopropylacrylamine), was grafted. Changes in feed pH caused swelling or deswelling of the membrane, and changes in temperature caused the grafted poly(*n*-isopropylacrylamine) to undergo a coil-globule transition. In this way, two independent environmental stimuli could be used to control the membrane water flux.[370]

9.2 Polydopamine Chemistry: New Pathways to High Performance Membranes?

The chemistry of polydopamine is complex, however, and there are many outstanding challenges that prevent the realization of synthetic systems that show the same adhesive properties as those produced by nature. Here, the history and development of polydopamine and related compounds is reviewed, and some perspectives on the utility of these materials for various applications, particularly membranes, are offered.

Mussel adhesive secretions are largely comprised of proteins which typically contain a high proportion of lysine and L-3,4-dihydroxyphenylalanine (L-DOPA), compounds that feature free amino and catechol functional groups, respectively. These moieties are believed to be responsible for the protein's solidification and the ensuing adhesion of the mussel to a surface.[113] In organisms, these catecholamine precursors are enzymatically polymerized to afford highly robust, polymeric melanin products.[371] Synthetic melanins have been prepared using a variety of commercially available catechols and catecholamines as analogues of the biological systems, the most common being dopamine (1) and 3,4-dihydroxyphenylalanine (DOPA) (2), shown in Figure 30. Dopamine is a small molecule containing amino and catechol functionalities and has been advanced as a commercially viable analogue of the aforementioned naturally occurring melanins. Upon polymerization in alkaline buffer, dopamine is capable of strong adhesion to a variety of surfaces.[113] Many of the key features (*e.g.*, strong adhesion, intense pigmentation, light absorption, good electrical conductivity, etc.) observed in the biologically derived melanins are typically preserved in the synthetic melanins.[372]



1 **2**

Figure 30. Structures of dopamine (**1)** and DOPA (**2**).

Melanins have a long history in chemistry and biochemistry. Catecholamines and their polymer derivatives are ubiquitous in fields as diverse as nutrition science (*e.g.*, the browning of fruits and vegetables),[373] neuroscience (*e.g.*, the proposed link between catecholamine oxidation and neurodegenerative disease),[374] and botany (*e.g.*, the formation of melanin as a metabolite of catecholamines which can influence stress response and growth).[375] Thus, the vast array of research into melanins provides fertile ground from which to draw insight into the chemistry of related synthetic materials, such as polydopamine. Indeed, no discussion of polydopamine would be complete without addressing the chemistry of melanins.

9.2.1 Terminology

The terminology surrounding the melanins and derivatives thereof can be complex since much of the vernacular stems from antiquated origins. The term "melanin" can be traced back to at least the 19th century in primarily an anthropological context (*e.g.*, human skin pigmentation).[376] Since that time, and as the field of melanin chemistry has become more molecular in nature, the use of the term has broadened to the extent that it is not necessarily obvious whether or not a molecule or macromolecule may appropriately be considered a "melanin."

As of this writing, the IUPAC has yet to precisely define any of the terms below in their Compendium of Chemical Terminology (with the exception of "quinhydrone," as noted). Thus, the following terms are offered to improve the clarity of the accompanying discussions.

- Melanin: a general term used to describe dark pigments in biological systems that are commonly derived from the oxidation of tyrosine,[377] although the molecules themselves can be prepared either naturally or synthetically;[328,378] it has been previously suggested (1953) that melanins share common chemical traits, including "resistance to solvents, bleaching when subjected to the action of oxidants, and the capacity to reduce ammoniacal solutions of silver nitrate"[379]
- Eumelanin: a black-brown subclass of melanins found in skin, hair, fur, and feathers; pheomelanins, in contrast, contain sulfur (from cysteine residues) and are typically yellow or red in color[377,378,380,381]
- Quinhydrone: "[from the IUPAC Compendium] molecular complexes of one equivalent amount of a quinone with one equivalent amount of the corresponding hydroquinone"[382]
- Polydopamine: a synthetic melanin prepared by the oxidative (typically aerobic) polymerization of dopamine (3-hydroxytyramine)

9.2.2 Discovery

Biological pigments have been of interest for many years, but the chemistry underlying these pigments was not the subject of direct investigation until the 19th century. Mammalian pigments were observed by Purkyně in the *substantia nigra* as early as 1838[383] and by Simon in pig embryos in 1841.[384,385] The isolation of these pigments was reported by Berzelius (1840),[386] who is often credited with first application of the term "melanin,"[377] Mörner (1887),[387] and Landholt (1899).[385,388] In 1895, Bourquelot and Bertrand recognized that blackening in various fungi was due to enzymatic action on tyrosine.[389–391] A variety of other plants and animals were found to possess similarly active enzymes, including cephalopods, insects, and amphibians.[376] In the early 20th century, Bloch showed that crude samples of human skin could catalyze the formation of melanin granules upon immersion in a solution of DOPA.[392]

Beginning in 1928, Raper reported studies of the precise enzymatic processes responsible for this behavior,[393] and in 1948 Mason refined these mechanisms.[394] The so-called Raper-Mason mechanism, which has since been widely adopted in understanding the polymerization behavior of catecholamines, will be discussed in greater detail below, but historically this work proved to be seminal in the development of a more molecular understanding of complex pigments and melanic polymers. The understanding of the chemistry and biochemistry displayed by melanin and eumelanin progressed after this time and has branched into several fields of chemistry,[381,395] biology,[396] and medicine.[328,397] Despite this broad importance, surprisingly little is known about melanins, primarily as a result of the difficulties associated with their isolation and characterization. In the sections that follow, a summary of some of the key findings will be presented, with a particular emphasis on those aspects that pertain to polydopamine as a specific and timely example.

9.2.3 Structure and Bonding in Polydopamine and Related Synthetic Melanins

The synthetic approaches applied to melanin formation may be divided into two categories: enzymatic and non-enzymatic. Most of the ongoing development of polydopamine chemistry does not utilize the enzymatic approach, however. Catecholamines of many varieties are known to undergo oxidative polymerization under aerobic conditions.[398] As would be expected, therefore, the polymerization of dopamine can be suppressed under inert atmospheres.[369] Polymerization is readily initiated when dopamine is treated with a base under aerobic conditions. Similar behavior is seen when catechol (*o*-benzenediol) or hydroquinone (*p*-benzenediol) are exposed to alkaline, aerobic media,[399] suggesting the polymerization behavior stems from reaction of the diol moiety (pK_a of catechol = 9.25;[400] observed pK_a of dopamine = 8.89[401]) with the base, rather than the free pendant amine (pK_a of benzeneethaneamine= 10.42[402]).

Aside from molecular oxygen, various solution-based chemical oxidants such as ammonium persulfate ($(NH_4)_2S_2O_8$), sodium periodate ($NaIO_4$), and potassium chlorate ($KClO_3$) can polymerize dopamine as well.[403] These reactions have been shown to exhibit dependence on pH, similar to the aerobic oxidation. At pH < 7.0, dopamine exhibits minimal reactivity with all of the aforementioned chemical oxidants except ammonium persulfate; at pH > 8.5, however, all of the noted oxidants were able to initiate polymerization reactions.[403]

Mechanistically, there are multiple ways of understanding how the oxidative polymerization(s) may proceed, but each of the mechanisms results in products with significantly different structures. As has been the case for melanins over the years, the unique structure of polydopamine remains the subject of much debate. The proposed structures of polydopamine may be divided into two broad categories: those that incorporate covalent linkages between the monomers and those that incorporate non-covalent linkages.

The initial steps of the tyrosinase-catalyzed oxidative polymerization of dopamine and other similar catecholamines are well known and generally accepted to proceed via the so-called Raper-Mason mechanism; the key transformations are shown in Figure 31 using tyrosine as a model compound. Notably, however, the final steps of the process (*i.e.*, the formation and structure of melanochrome and the final melanin product) were not well understood at the time this mechanism was proposed. Unfortunately, these steps are essential for understanding the structure of the final product, and lie at the heart of the present literature debate on the subject.

With respect to the polymerization of dopamine *via* this mechanism,[404] it is worth noting that dopamine lacks the carboxylic moiety present in tyrosine. The resulting inability to decarboxylate dopamine during its polymerization could lead to formation of the saturated indoline derivative, rather than unsaturated indole. Autoxidation of the indoline is possible, but would be anticipated to be slow, given the high stability of indolines to oxidative conditions [405]. The conversion of indolines to indoles typically requires strong oxidants (*e.g.*, hypochlorite and dimethyl sulfide[406]), or the use of metal catalysts (*e.g.*, cobalt,[407] manganese,[408] or gold compounds[409]).

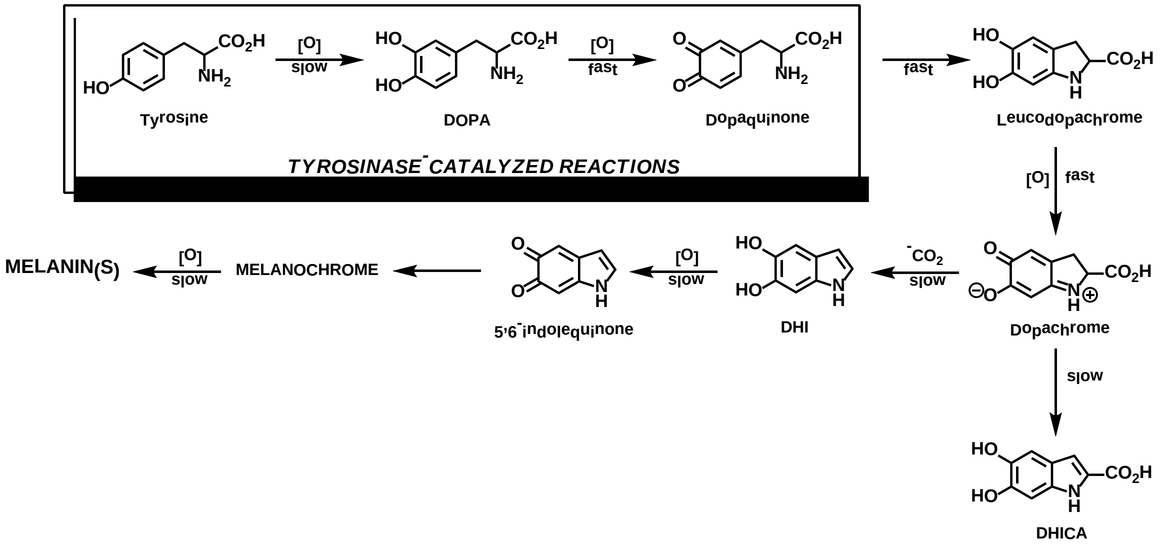


Figure 31. Tyrosinase-catalyzed oxidation and polymerization of tyrosine according to the Raper-Mason mechanism. DHI = 5,6-dihydroxyindole; DHICA = 5,6-dihydroxyindole-2-carboxylic acid.

According to the Raper-Mason mechanism, the key precursor of melanin is 5,6-dihydroxyindole (DHI), and much of the research in the field of DHI chemistry has been described by a team of researchers at the University of Naples. Through meticulous work spanning several decades, the Naples team has used many techniques (*e.g.*, chromatography, mass spectroscopy, and UV-vis spectroscopy)[410] to understand the reaction intermediates, the melanin polymers themselves, and the degradation products produced by reaction of melanin with various chemical agents.

The majority of the structural models of melanin proposed by the Naples team can be understood in terms of the reactivity of DHI with its oxidized form (5,6-indolequinone). In particular, it has been proposed that DHI can act as a nucleophile and the quinone can act as an electrophile (Figure 32),[376,411] affording new covalent linkages upon combination and leading to a variety of structures, including the 2,4', 4,4', 4,7', and 7,7' arrangements. Radical mechanisms have also been suggested as potential sources of these covalent linkages, particularly for the formation of symmetrical species (*e.g.*, the 2,2' dimer).[376]

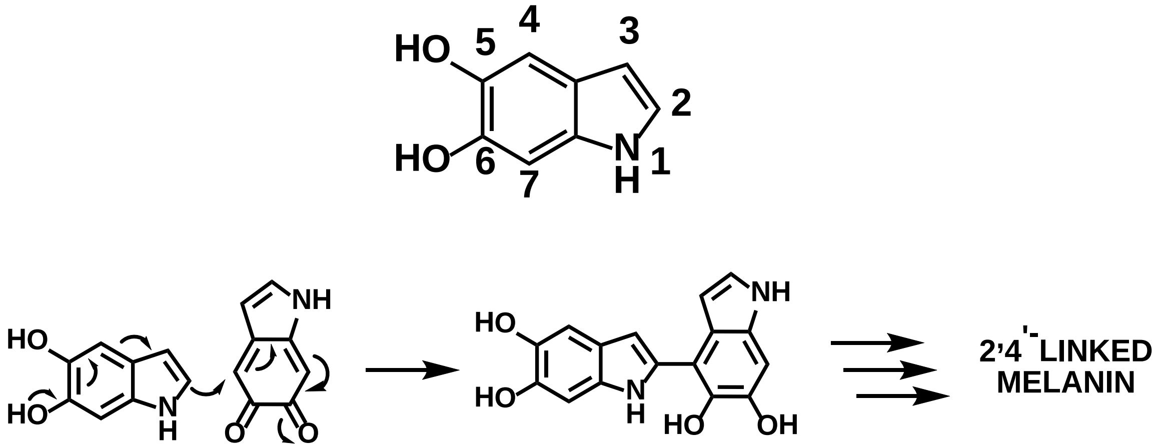


Figure 32. Numbering in DHI (top), and the proposed electron pushing schemes for the conversion of DHI and 5,6-indolequinone to the corresponding 2,4'-linked melanin polymer product (bottom).

The formation of the intermediates along these pathways has also been studied extensively by the Naples group [395]. One key approach employed toward this end has been protection of the catechol functionality *via* acetylation of the melanochrome intermediate(s) (Figure 33),[412] typically achieved using acetic anhydride and a base (*e.g.*, pyridine). Protection of the catechol moiety in this fashion allowed for isolation and characterization of the intermediate(s), as well as postulation about the subsequent reaction pathways leading to the final melanins. Subsequent hydrolysis of the acetylated derivatives under anaerobic conditions resulted in the reformation of the catechols (identified by UV-vis spectroscopy), and further exposure to an oxidizing atmosphere led to polymerization to the corresponding melanin. In sum, covalent linkages in polydopamine are believed to arise as a result of nucleophilic-electrophilic interactions between heterocycles of varying oxidation state, or from radical species generated *in situ*. It has been further proposed that these small bound species undergo further bonding, analogous to a step-growth polymerization, or aggregation to form the final insoluble polymer product (see further discussion below of aggregation phenomena).

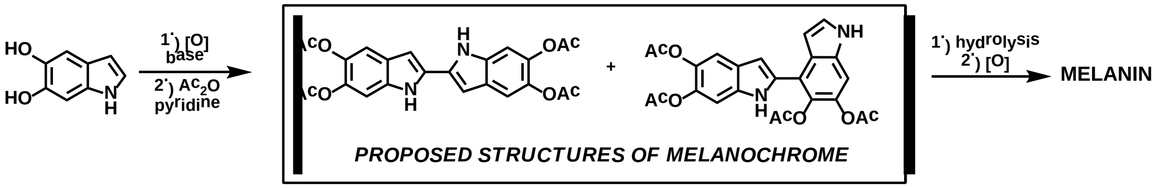


Figure 33. Proposed structures of melanochrome determined *via* isolation and characterization of the acetylated intermediates formed during oxidative polymerization of DHI.

A recent study that investigated the structure of powdered polydopamine samples has reported a non-covalent structural model.[413] Solid state ^{15}N NMR spectroscopy indicated the formation of a cyclized species (*e.g.*, indoline or indole), rather than the free amine, in contrast with some previously proposed models of polydopamine, which suggested to us that the majority of the monomer units remained uncyclized in the polymer product.[376,414] Further analysis of the polymer by ^{13}C NMR spectroscopy revealed several important features, including partial saturation of the bicyclic ring system (indicating the presence of an indoline-type structure rather than an indole) and oxidation (or partial oxidation) of the diol to a dione. The key question of whether or not covalent bonds existed (principally proposed to occur through the benzene moieties, as noted above) was addressed with the use of dopamine isotopically labeled with ^{13}C (99 atom%) only on the arene ring. A standard 1D cross-polarized (CP) spectrum of the sample revealed the presence of protons bound to the benzene core of the molecule. This result appeared to be inconsistent with the predominately covalent models that have been alternatively proposed.

Lacking spectroscopic evidence for the presence of aryl-aryl linkages in the as-prepared polydopamine powder, efforts turned toward investigating the nature of the bonding interaction between the monomers. Powder X-ray diffraction (PXRD) indicated the presence of ordered stacking (d-spacing = 3.8 Å) consistent with a variety of π-stacked structures [415]. Furthermore, analysis of the powder by electron paramagnetic resonance (EPR) spectroscopy showed the presence of stable free radicals present at low concentration in the polymer sample (less than 1 spin per 25 repeat units), consistent with a variety of other melanins (see discussion of radical character below).[416] Collectively, these results suggested to us that the repeating units in polydopamine were held together via non-covalent bonds rather than covalent carbon-carbon bonds, as many of the previous models have proposed (Figure 34). The data indicated that these occur through a mixture of hydrogen bonding interactions (similar to the strong non-covalent interactions believed to be present in quinhydrones[417]), π-stacking, and charge transfer processes. As indicated by polydopamine’s near complete insolubility and the exceptional stability of its coated forms, these non-covalent interactions are very strong (both between the monomer units and the underlying substrate, if present), as has been demonstrated for a variety of natural and synthetic polymer materials.[418] These conclusions regarding a non-covalent model of polydopamine bonding, however, has recently been challenged with data suggesting a covalent bonding model.[419]

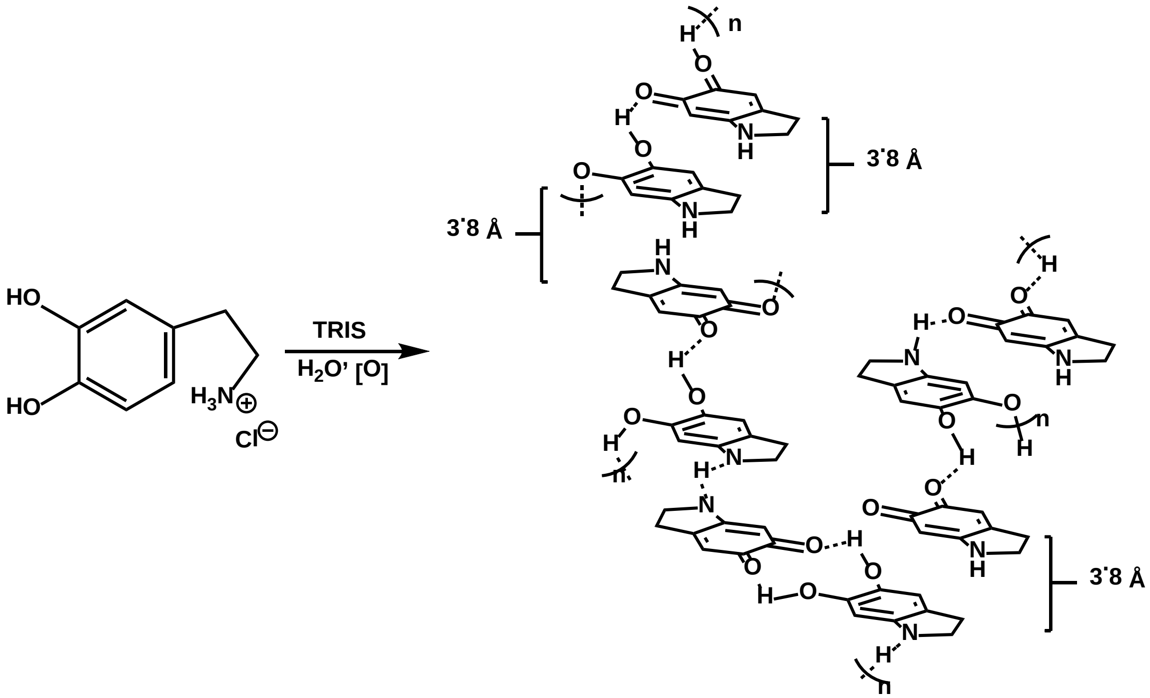


Figure 34. Proposed supramolecular structure of polydopamine, incorporating a combination of non-covalent hydrogen bonding, charge transfer and π-stacking interactions.[413]

It has previously been shown that melanins may be degraded by exposure to hydrogen peroxide, molecular oxygen, peracetic acid (CH_3CO_3H), or alkaline potassium permanganate ($KMnO_4$) through an oxidative bleaching process.[376,420–422] As described above, these degradation products have been a crucial source of information on the structure of the parent polymers. Nicolaus and coworkers have suggested that the primary compound formed by treating sepiomelanin with the aforementioned oxidants is pyrrole-2,3,5-tricarboxylic acid (PTCA, 3) (Figure 35), identified *via* paper chromatography, in addition to trace amounts of the other di-, tri-, and tetracarboxylic acid derivatives of pyrrole.[422] Similarly, polydopamine was found to degrade by either aqueous sodium hypochlorite (NaOCl) or potassium meta-periodate (KIO_4) at room temperature over periods of several hours. The insoluble, darkly colored powder became fully soluble, clear, and nearly colorless as reaction with either of these oxidants proceeded. In accordance with the non-covalent model of polydopamine and supported with FT-IR spectroscopy, this solubilization was proposed to have occurred *via* oxidation of the catechol functional groups, leading to the formation of 2,3-dihydro-indolo-5,6-quinone.

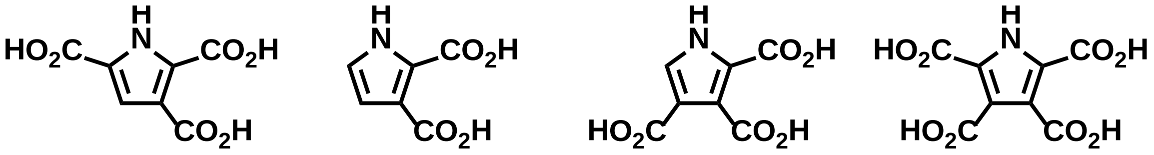


Figure 35. Product mixture obtained by treating sepiomelanin with either peracetic acid or alkaline potassium permanganate. The primary product was found to be pyrrole-2,3,5-tricarboxylic acid (PTCA, **3**), with trace amounts of the other acids (**4–6**).[422]

The proposed structural model of polydopamine differs significantly from the majority of models that have been previously suggested, though other studies have shown that non-covalent, supramolecular interactions are key components of polydopamine’s structure.[378,380] Higher order secondary and tertiary interactions are known to be present in various melanins (similar to protein folding interactions), resulting in complex nanoaggregates and filaments (see Figure 36).[423] The importance of secondary interactions in melanins formation is supported by the work of Tsolakidis and coworkers, who used density functional theory to describe a melanin model in which tetrameric or pentameric protomolecules stacked into supramolecular assemblies.[424]

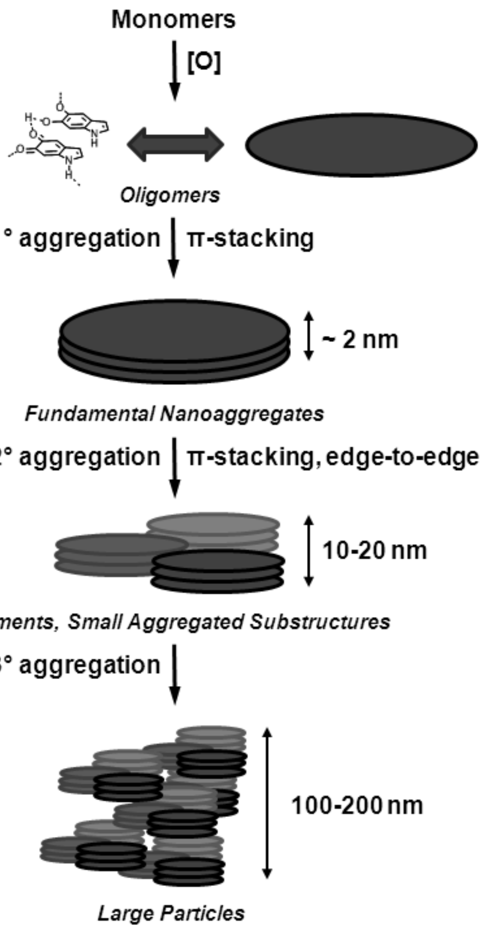


Figure 36. Schematic of primary, secondary, and tertiary ordering in melanins such as polydopamine. Reproduced with permission, John Wiley & Sons, Inc.[425,426]

While the debate surrounding this fundamental question of the material's structure and bonding is likely to continue, the non-covalent model presents a structure that is most consistent with the chemistry seen in other similar molecular architectures (*e.g.*, quinhydrones, supramolecular polymers, proteins, etc.). A proper understanding of the polymer's structure is not merely an academic question: the ability to install orthogonal functionalities (*e.g.*, fluorophores, solubilizing polymers, etc.) into the monomer, while preserving its ability to undergo oxidative polymerization and adhesion, will depend on how the repeat units are linked in the polymer and ultimately determine its properties. While the models that rely on covalent coupling between the monomers suggest that substitution of the monomer at any position, particularly the aryl core, will impede its subsequent polymerization, the non-covalent model suggests that the catechol functionality is the crucial moiety. The non-covalent model also predicts that para substitution of the diol functionality (as in hydroquinone) will afford analogous products; ortho substitution of the diol may not be strictly required for the reaction to proceed. Though the para substituted diol derivative of dopamine is known (*i.e.*, 2,5-dihydroxyphenylethylamine), it has not been applied to polymerizations of the type described herein.

9.2.4 Physicochemical Properties of Polydopamine

The unique structural properties of polydopamine and related melanins, described in the previous sections, endow these materials with a number of distinctive and useful physical properties, particularly for use in membrane-based applications. In addition to those previously discussed (*e.g.*, strong adhesion to a broad range of surfaces), electronic conductivity and broadband absorption of light are of particular interest and importance. Melanins as a broad class of molecules have long been known to exhibit semiconductive properties.[427,428] Arising from the material's unique structure and bonding, the conductivity of polydopamine depends on a variety of factors, including temperature, hydration state, and exposure to light.[428–431] The key semiconductor properties of polydopamine and other melanins are summarized in Table 4.

	Conductivity (T = 293K) σ_{293} (Ω^{-1} cm^{-1})	Thermal Activation Energy ΔEA (eV)	Preexponential Factor σ_o (Ω^{-1} cm^{-1})	Photocurrent Intensity ΔI_{ph} (A)
Polydopamine	$(5.1\pm0.1) \times 10^{-12}$	0.71 ± 0.01	8.0	*
Polyadrenaline	$(1.3 \pm 0.1) \times 10^{-12}$	0.68 ± 0.01	0.6	*
Polyadrenochrome	$(5.2 \pm 0.1) \times 10^{-12}$	0.73 ± 0.01	18.6	*
Polyadrenolutin	$(1.5 \pm 0.1) \times 10^{-10}$	0.62 ± 0.01	7.0	8.0×10^{-9}

* no photocurrent observed

Table 4. Summary of the electronic properties of polydopamine and related melanins prepared from catechol amines.[430]

In addition to semiconductivity, polydopamine strongly absorbs light over a broad range of wavelengths.[380,425] Indeed, it is precisely this trait of melanins that makes them excellent photoprotectants. In addition to the absorption of light, it has also been proposed that the particulate nature of melanins leads to a combination of Rayleigh and Mie scattering, particularly at wavelengths below 300 nm.[432] Contributions of this scattering effect to the total optical attenuation range from < 6% between 210 and 325 nm (no scattering was observed at longer wavelengths in this study[433]) to 12 – 13.5% in the visible range.[434] Due to the broadband, monotonic nature of polydopamine's absorption profile, the determination of the electronic and molecular structure *via* optical spectroscopy has proved challenging. Likewise, efforts to measure the materials' band gap in amorphous samples have led to widely varying values, ranging from 1.3 eV to as much as 3.4 eV.[428,431] As with the semiconductor properties of the materials, however, the measured band gaps show a dependence on preparation method, hydration state and temperature.

While polydopamine has strong absorption properties, as much as 99.9% of the absorbed energy is dissipated non-radiatively, primarily as phonons.[380] As such, synthetic melanin exhibits minimal fluorescence or phosphorescence, displaying quantum yields below 7 ×

10^{-4}.[435] In the many reported studies of melanins' photophysical properties, it is apparent that polymers of this type do not possess a single, well-defined chromophore, but a mixture of light absorbing/emitting species.[380] As noted by Meredith and co-workers, the line shapes in the absorption and emission spectra of melanins do not mirror one another, in violation of the so-called "mirror-image rule" of well-defined organic chromophores.[380] While the absorption profiles for most melanins are broad and monotonic (see Figure 37), as previously described, the emission profiles are typically Gaussian.

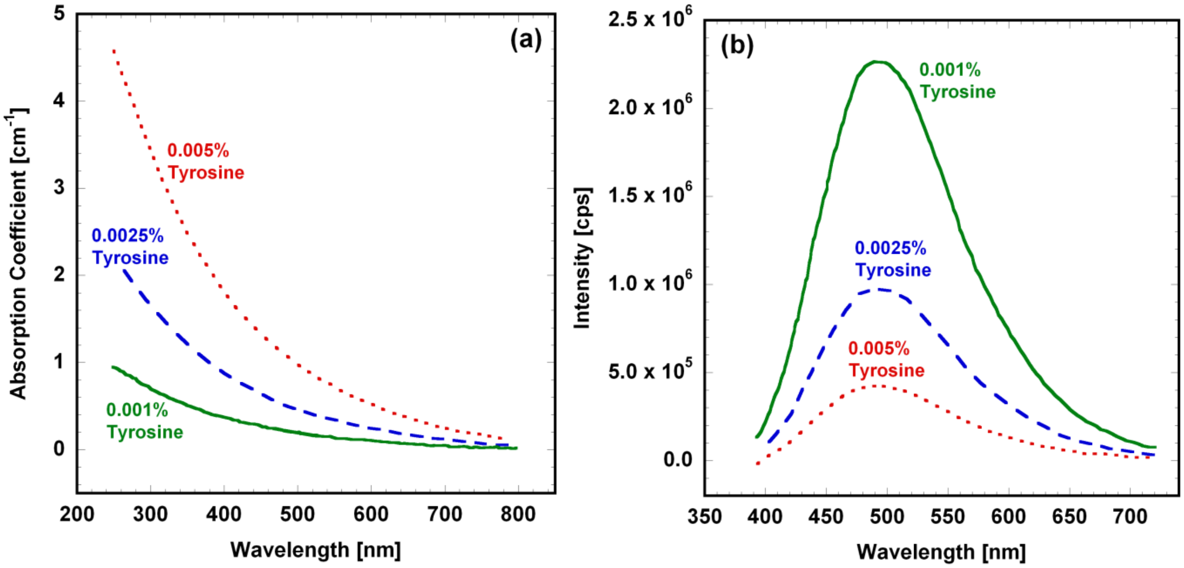


Figure 37. UV-vis absorption profiles (a) and photoluminescence emission profiles (b) for synthetic melanin prepared from tyrosine at three different concentrations: 0.005% (dotted line), 0.0025% (dashed line) and 0.001% (solid line) by weight concentration.[435]

In addition to these desirable physical properties, polydopamine has certain chemical properties that are also remarkable. The most significant of these relate to the polymer's redox properties, which are relevant even in biological systems where eumelanins act as oxygen scavengers.[436] Polydopamine and other melanins can act both as reductants as well as as oxidants.[328] This divergent behavior is believed to stem from the fact that polydopamine possesses both oxidizing quinones and reducing catechols, both of which may participate in electron transfer reactions. For example, polydopamine rapidly oxidizes thiols (and amines to a lesser extent), converting the quinoidal moieties in the polymer to the corresponding catechols.[437] In contrast, polydopamine can electrolessly metallize Ag(0),[438] Au(0),[439] or other metals onto various surfaces by reduction of the corresponding metal salts from aqueous solutions. The reduction of the carbon-based material, graphene oxide, to graphene by the oxidative polymerization of dopamine has also been demonstrated.[440]

Beyond the redox chemistry and its propensity to bind water[441] as well as various metal ions,[327,442] polydopamine is resistant to most other chemical agents, giving rise to the previously described stability of deposited films. Polydopamine coatings may be modified through the attachment of polymers, but these reactions typically occur to relatively minimal extents and often require the presence of orthogonal functional groups. For example, it has been shown that amine-terminated PEG may be conjugated to polydopamine coatings *via* condensation of the terminal amine and the carbonyls present in the quinones in polydopamine.[364,443] Similarly, PEG chains have been conjugated to polydopamine via attachment to the N–H position of the acyclic monomers.[444] In these and other strategies that have been employed, however, the polydopamine coatings themselves remain largely intact, preventing disruption of the desirable adhesion.

The chemical inertness of polydopamine is also manifested by the presence of stable radical species, present both during and after the polymerization reaction.[413] Comprehensive EPR studies performed on poly(DOPA) have suggested the presence of more than one type of radical (*e.g.*, a semiquinone-type species and a species associated with defects in the polymer).[425,445] The steady-state concentrations of radicals in these materials is proposed to be very low; on the order of 10^{17}–10^{18} g^{-1}.[328]

Though polydopamine and other synthetic melanins can be isolated as a bulk powder,[413] this form of the material is intractable and has no known uses other than for fundamental study. This powder is, however, considered representative of the coating material deposited on substrates in contact with alkaline dopamine solution and often used for characterization purposes.[372] Derivatives of polydopamine, such as those with polymers attached to them,[446] can be prepared, and some of these have excellent solubility properties. However, such conjugates still readily deposit, and typically irreversibly, onto myriad surfaces.

In view of polydopamine's minimal to non-existent bulk processability, the majority of polydopamine applications (discussed in greater detail in section 3.5) focus on coatings.[328,447] Upon immersion of either hydrophilic or hydrophobic materials of a variety of shapes into alkaline solutions of dopamine, thin coatings are deposited and later characterized.[113,326,337,448–450] In general, the thickness of polydopamine films has been found to increase with deposition time and temperature.[334] The observed water contact angles of coated substrates have been measured to be nearly uniform (θ = 50–60°), regardless of the underlying material (Figure 38), suggesting that the polydopamine top coat dominated the composite materials' surface properties.[403] Significant conversions of surface hydrophilicity have been reported using polydopamine on hydrophobic surfaces that include PVDF, PTFE, PET, and polyimide.[334] Dopamine solution concentration and deposition time have also shown little effect on the surface hydrophilicity after modification.[334] When silica was used as a substrate, the film growth rate was found to be approximately 3.6 nm h^{-1} (see Figure 39), though decreasing the immersion time from 15 min to 5 min was found to increase the deposition rate to as much as 7 nm h^{-1}.[372] The resulting coatings were highly robust and were resistant to mechanical,[451–453] chemical,[113] and electrochemical degradation.[452,453] To remove these coatings, strongly alkaline or oxidizing solutions were typically required. Polydopamine coatings have shown good corrosion resistance when applied to stainless steel,[449,454] copper,[448] and silicon[452,453] substrates.

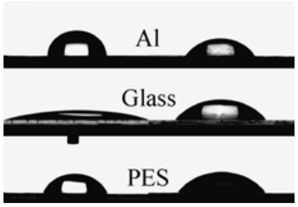


Figure 38. Water contact angles of polydopamine-free aluminum, glass, and poly(ethersulfone) (PES) (left), and the polydopamine-coated substrates (right). Reproduced with permission, Royal Society of Chemistry.[403]

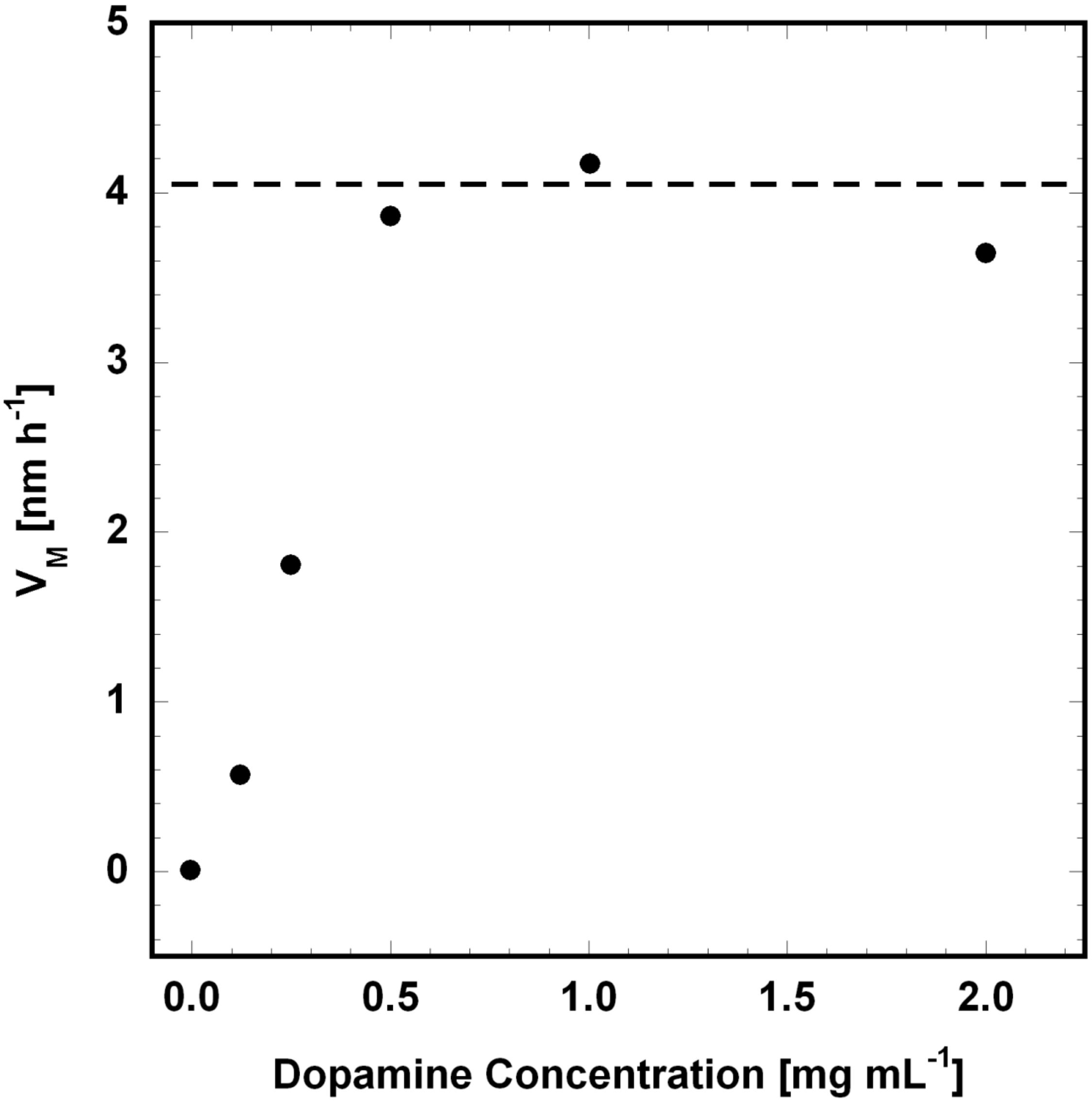


Figure 39. Polydopamine deposition rate (v_M) as a function of the initial buffered aqueous dopamine solution concentration. Performed on silica substrates under normal atmosphere at pH 8.5 and 25°C for immersion times of 15 min. The horizontal line represents an observed plateauing of the deposition rate at higher concentrations.[372]

The surface adhesion of polydopamine is believed to arise through non-covalent interactions (*e.g.*, hydrogen bonding, metal chelation, etc.) between the polymer and the surface onto which it is deposited, similar to other melanins. Using mica or titanium dioxide as a common substrate, it has been shown that the adhesion strength of melanin coatings varies with the number of hydrogen bonding partners. For example, films with a high DOPA content (a derivative of dopamine that contains an additional pendant carboxylic acid moiety; see 2) exhibited increased adhesion work (measured in mJ m^{-2}), as determined by various force measurement apparatus.[455] It is believed that in more complex polymers, such as poly(DOPA), polydentate hydrogen bonding is enabled, allowing for even stronger adhesive properties. Films of this type are susceptible to attack by strong oxidants, however, presumably occurring through oxidative degradation of the repeat units, as well as the bonds that adhere to the polymer to the surface.

10. Conclusions

Water purification membranes offer a low-energy technology to meet the ever-increasing demand for fresh water. However, the polymeric materials typically used to fabricate these membranes often have surface properties that contribute to undesirable phenomena such as fouling. Membranes whose surfaces are hydrophobic, rough, and electrically charged tend to exhibit the most severe fouling. Many surface modification techniques, which aim to alter the undesirable surface properties without compromising the bulk properties that make polymers attractive for membrane fabrication, have been explored. Table 5 summarizes the surface modification techniques presented in this review and their associated advantages and disadvantages. Generally, all of these techniques improve membrane fouling resistance.

Modification Technique	*Membrane Types*	*Advantage(s)*	*Disadvantage(s)*
Additive Blending	MF, UF	modification throughout internal pore channels; low rates of surface modifying macromolecule leaching; little effect on porosity/pure water permeance	surface modifying macromolecule must be miscible in membrane casting solution
Adsorbed Coatings: Uncured	MF, UF, NF, RO	simple modification; may increase rejection	prone to leaching from the surface; may decrease pure water permeance
Adsorbed Coatings: Cured	MF, UF, NF, RO	reduced leaching relative to uncured adsorbed coatings; may increase rejection	may decrease pure water permeance
Chemically Induced Small Molecule Coupling	MF, UF, NF, RO	permanent modification to membrane surface	may require several synthetic steps
Chemically Induced Grafting	MF, UF, NF, RO	permanent modification to membrane surface; may increase rejection	may decrease pure water permeance
Plasma Treatment without Polymer Coupling	MF, UF, NF, RO	rapid, simple modification; applicable to many membranes	requires plasma reactor; membranes may lose hydrophilic character; aggressive treatment may cause membrane damage
Plasma Coating	MF, UF, NF, RO	rapid, simple modification; more permanent than plasma treatment without polymer coupling; applicable to many membranes	requires plasma reactor; aggressive treatment may cause membrane damage
Plasma-Induced Grafting	MF, UF, NF, RO	more permanent than plasma treatment without polymer coupling; applicable to many membranes	requires plasma reactor; aggressive treatment may cause membrane damage
Corona Discharge Treatment	MF, UF	rapid, simple modification; applicable to many membranes	requires corona discharge reactor; aggressive treatment may cause membrane damage
UV Irradiation	MF, UF	rapid, simple modification	may cause membrane damage
UV-Induced Grafting	MF, UF	rapid, simple modification	may cause membrane damage, may reduce rejection
High Energy Irradiation	MF, UF	grafting may be accomplished under many different conditions	requires radiation source; may cause membrane damage

Polydopamine	MF, UF, NF, RO	non-specific deposition on many materials; thin, conformal coatings; all wetted parts in a membrane module may be modified	prone to degradation by strong oxidizers or extreme pH

Table 5. Summary of surface modification strategies presented in this review.

While surface modification of filtration media has been practiced for over 100 years, a few dominant techniques have emerged. UV irradiation and plasma treatment have garnered extensive interest, especially for grafting hydrophilic polymers to a membrane surface. Plasma treatment has found use in commercial manufacture of MF membranes. Dense, hydrogel-like coatings to membranes have also been successfully applied to porous and non-porous membranes. Surface modification is currently practiced commercially to improve fouling resistance of NF and RO membranes, which have fouling-resistant coating layers atop the thin polyamide selective layer.

Polydopamine is an emerging technology in surface modification. The non-specific nature of polydopamine deposition allows it to be applied to many membranes of different architectures and compositions. Because polydopamine coatings can be very thin, the membrane surface may be rendered hydrophilic without severely impacting water transport. While the chemistry governing the aggregation and deposition of polydopamine is still an area of active investigation, it appears that polydopamine bears much in common with that of other small-molecule chatecholamines, which are frequently found in biological systems yet are poised for use in a broad range of membrane-based applications.

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