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Chapter 2

Development of Conventional RO Membranes

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Additional information is available at the end of the chapter

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Abstract

Polymeric RO membranes have dominated commercial applications since the very first RO desalination plant became industrially active. Due to their technological development they offer low-cost fabrication, ease of handling, and improved performance in selectivity and permeability. One of the earliest reviews on polymeric RO membrane materials was reported by Cadotte. It focused on composite RO membranes and covered the period from the inception of composite RO membranes up to approximately 1985. In 1993 Petersen offered a comprehensive review of the same subject, specifically examining the chemistry of the membrane materials. This section will briefly highlight the early development of membrane chemistry and graphical illustrations are used to visualize the performance improvement potential in RO membranes. This chronological description provides the readers with a quick overview of RO membranes formed by different mechanisms and their respective impact on the desalination industry over the years. For a more complete study of the early RO membrane development, readers are advised to further refer to Petersen's work. In general, the development of membrane materials can be divided into two periods according to research activity: (i) the search for a suitable materials (chemical composition) and membrane formation mechanisms (1960s to late 1980s), and (ii) the evolution of more controlled conditions for membrane formulation as a way of enhancing membrane functionality and durability (late 1980s to date).

Keywords: asymmetric, thin-film composite, reverse osmosis, surface modification

1. Introduction

Polymeric RO membranes have dominated commercial applications since the very first RO desalination plant became industrially active. Because of the way they can be technologically developed, they allow for easier handling, lower cost of production, and superior performance capacities when it comes to permeability and selectivity parameters. Cadotte [1] produced one of the earliest reviews of the polymeric RO membrane materials and specifically

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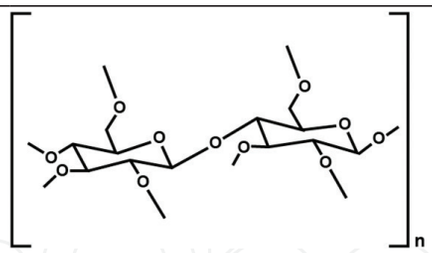
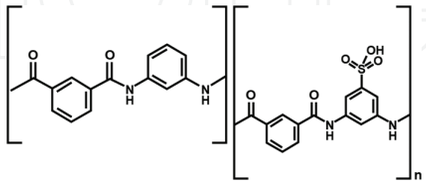
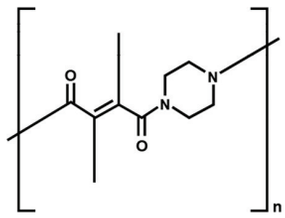
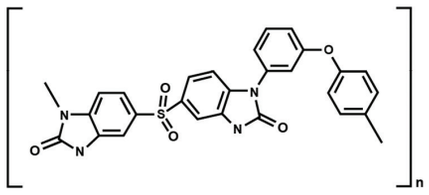
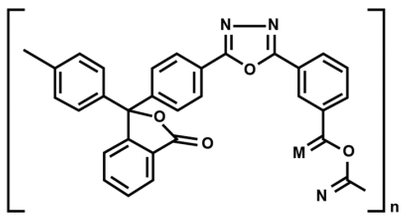
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focused on the composite RO membranes by examining the period from the composite RO membranes' inception until around 1985. At a later period, in 1993, Petersen [2] put together a more in-depth review of the same composite RO membranes, but this time prioritizing the membrane materials' chemistry. The following section will track earlier development and overall analysis of membrane chemistry and its effects, as well as utilize graphical illustrations to reflect and visualize the performance improvement potential that exists in RO membranes. Such a chronology-driven overview offers readers an effective summary of the RO membranes created with various mechanisms and their respective effects on the desalination industry throughout the last several decades. A substantially more rigorous assessment of the early RO membrane development can be found in Petersen's work [2]. Overall, the development of membrane materials may be strategically divided into two key periods that reflect the duality of research directions and activities: (1) the first is shaped by a search for more suitable materials, based on chemical compositions, and membrane formation mechanisms during the period between 1960s and late 1980s [1–4], and (2) the second is shaped by the development of controlled conditions for membrane creation as a method of improving membrane durability and functionality starting in the late 1980s and continuing today [3, 4].

2. Early membranes approaches and the development of asymmetric membranes

The Sea as a Source of Fresh Water report that came out in 1949 was the beginning of a progressive expansion into the salt-rejecting membranes research [5]. While the experimental project that came out of this report was not successful due to its limited membrane focus, it did offer the necessary grounds for future membrane study. Researchers Reid and Breton reported in the late 1950s that a hand-cast thin symmetrical cellulose acetate (CA) membrane was able to retain salt effectively by attaining a 98% rejection rate. The same experiment, however, showed that the critical permeate flux values were highly discouraging, at the order of <10 mL m^{-2} h^{-1} [6]. The development of the Loeb-Sourirajan CA membrane was the next vital step, since it was the first successful effort to create RO in practice [7]. A Loeb-Sourirajan CA asymmetric membrane was then produced, featuring a dense 200-nm thin layer over a thick microporous membrane body. As a result of these experiments, a new morphological approach resulted in water flux values of at least an order of magnitude greater than the initial symmetric membrane [8]. The specific molecular composition of these CA membranes is outlined in **Table 1**.

Figure 1 shows the primary developments in asymmetric RO membranes, starting with the early research initiatives and projects and up to 1980s. During the decade following Loeb-Sourirajan membrane creation, new research focused on CA materials was conducted with the particular intention of refining membrane transport properties, as well as improving its manufacturing process and then introducing this technology for a widespread industrial applications [1]. In the following research projects, the cellulose triacetate (CTA) membrane was created as an effective alternative that allows for increased stability in a much wider range of temperatures and pH values and offers greater resistance potential

Chemical type and description	Chemical structure
1. Cellulose acetate—Loeb-Sourirajan CA [8] Flux: 0.35 m^3 m^{-2} day^{-1} Salt rejection: 99% Test: > 100 bar, 4% NaCl solution	
2. Aromatic polyamide: Polyamide-hydrazide [9] Flux: 0.67 m^3 m^{-2} day^{-1} Salt rejection: 99.5% Test: 30°C, > 100 bar, 3.5% NaCl solution	
3. Polypiperzine-amide [10] Flux: 0.67 m^3 m^{-2} day^{-1} Salt rejection: 97.2% Test: > 80 bar, 0.36% NaCl solution	
4. Polybenzimidazoline [11] Flux: 0.13 m^3 m^{-2} day^{-1} Salt rejection: 95% Test: > 6 bar, 0.105% NaCl solution	
5. Polyoxadiazole [12] Flux: 0.07 m^3 m^{-2} day^{-1} Salt rejection: 92% Test: > 45 bar, 0.5% NaCl solution	

Note: The chemical structures listed represent segments of these membranes. It does not show all possible forms of the structure, for example, the CA structure shown is CDA, rather than CTA or mixed-CA.

Table 1. Asymmetric RO membranes.

of biological and chemical attacks when compared to the membranes composed of earlier cellulose diacetate (CDA) material. On the other hand, CTA membranes are predisposed to being affected by compaction and as a result may experience a substantial decrease in flux even at low operating pressures such as 30 bar or less [13]. The combination of CTA and CDA allowed for greater permeability and selectivity values than the CA membranes. Such a combination also offered greater resistance to the effects of compaction [14]. Additional research studies have been conducted with the aim to control degree of mixed ester substitution for the hydroxyl groups located in cellulose and to assess how well the CA membranes are working [15].

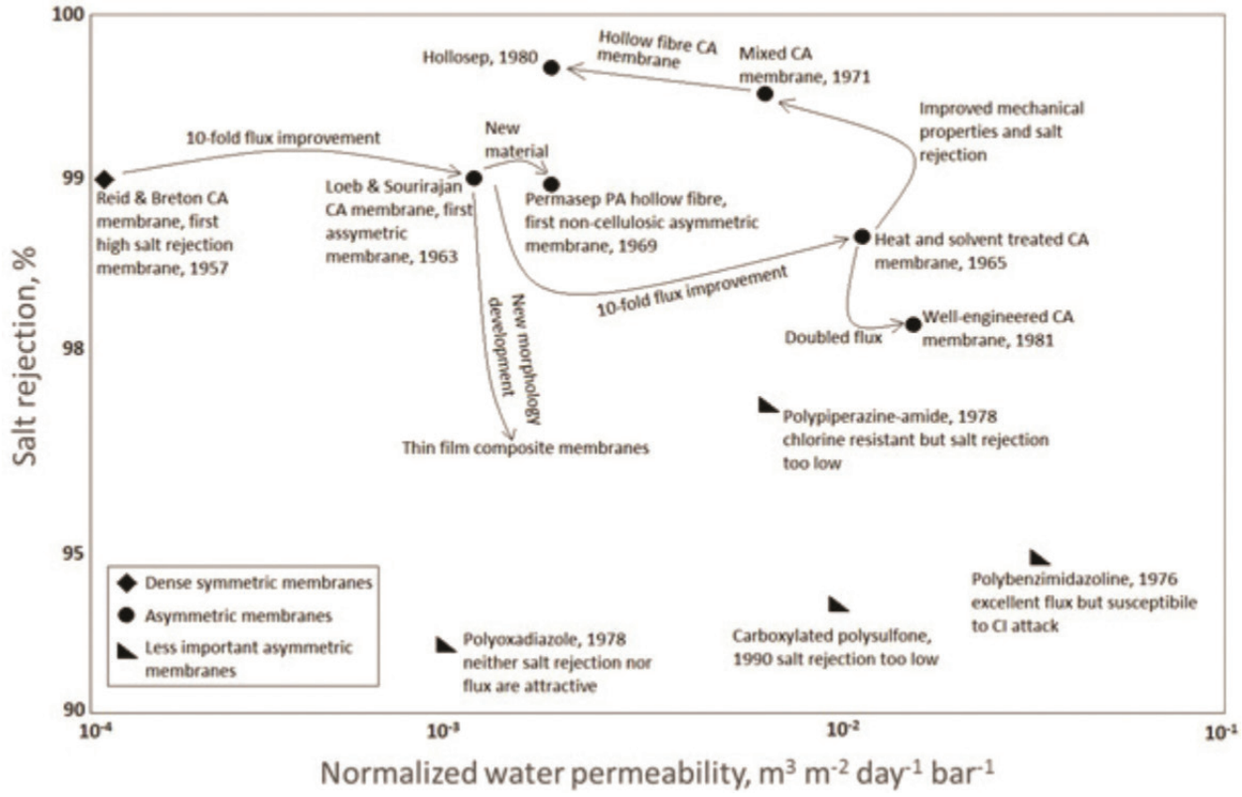


Figure 1. The development of asymmetric RO membranes [1].

The CA was the best available membrane material for the RO up to 1969, despite the extensive search for potential alternatives in membrane polymers. During this period, acetate group's susceptibility to hydrolysis, in both alkaline and acidic environments, and its relative sensitivity to microbial contamination had significantly limited its durability as well as its potential applications [16]. As a consequence, despite multiple alternative polymers examined in 1960s, a substantially sturdier material featuring greater chemical stability was severely needed.

Richter and Hoehn developed the first noncellulosic asymmetric membrane that received attention because it was comprised of an aromatic polyamide (PA) asymmetric hollow-fiber membrane [17]. This type of membrane was then commercialized by Du Pont with the trade name of B-9 Permasep® specifically for application during brackish water desalination processes. Although it features small flux and salt rejection values, it does offer stability, durability, and versatility which surpass those of aromatic polyhydrazides or CA [18]. Even though the low flux was problematic, it experienced relative commercial success due to its effectual packing of hollow fibers that helped it outperform the CA spiral wound elements, with respect to flux per unit module volume values. For a more in-depth discussion of the variation in reactants for the PA, asymmetric membranes refer to sources that specialize in this area [19].

The polyamides' predisposition to being attacked by disinfectants, such as ozone and chlorine (halogens), was noted after prolonged application of the B-9 Permasep® membranes. Subsequently, chlorine-resistant asymmetric membranes based on polypiperazine-amides were developed as a response [10, 20, 21]. These membranes have the permselectivity similar

to the permselectivity of the asymmetric CA membrane. Lower quantities of amidic hydrogen in the membrane likewise improved its overall resistance to chlorine attacks [22]. Despite its advantages, this membrane was not commercialized because of its low salt rejection properties (≤95%) [23]. In this case, the phenyl and sulfonic groups in sulfonated polysulfone were projected to improve permeability, as well as chemical, biological, and mechanical stability; however, the salt rejection potential value was far lower than the acceptable level needed for industrial and commercial applications [24]. Carboxylated polysulfone likewise suffers from an uncompetitive salt rejection potential, even though it has promising flux values [25, 26]. On the other hand, polybenzimidazoline (PBIL) membranes created by Teijin reflect great permselectivity in harsh operating conditions, while at the same time remain susceptible to chlorine attacks and pressure compaction [11, 27, 28]. In another instance, polyoxadiazole has been exhibiting superior thermal and mechanical stability, while its permeability and salt rejection values fail to offer a commercially feasible or attractive option when it comes to industrial RO applications [12, 19].

3. Thin-film composite (TFC) membranes

Research indicates that only a small number of soluble polymers can successfully create asymmetric structures during a one-step casting process. Out of these soluble polymers, only a limited number are commercially attractive when it comes to the right combination of salt rejection capability and permeability potential. Furthermore, the densification in the middle transitional layer of the CA asymmetric membranes tends to occur under pressure [29]. These conditions have led to the creation of a two-step casting method that enables individual optimization of the materials being used for the barrier layer and for the microporous support film, the former for the optimal salt rejection potential and permeate flux and the latter for improved mechanical support. In addition, an extensive number of polymers may be tested for the support layer and barrier layer separately. Such anisotropic types of membranes are currently identified as the composite membranes.

3.1. Early development of TFC membrane

Figure 2 shows that the first TFC membrane was created by float-casting a CA ultrathin film onto the water surface and then followed by the process of laminating and annealing the film onto a preformed CA microporous support [30]. Membranes that were produced with the aid of this particular technique did not receive much commercial interest due to their asymmetric counterparts. An extensive empirical study into commercial membrane application suggested that polysulfone was the ideal material for the support layer because of its reasonable flux value, overall resistance to compaction, and its critical stability in acidic environmental settings. The latter key quality allows for the development of the TFC membrane using interfacial polymerization and acid polycondensation [31].

In order to overcome the scale-up issues in float-casting technology, a dip-coating methodology based on acid polycondensation of low molecular weight hydroxyl-containing compounds was

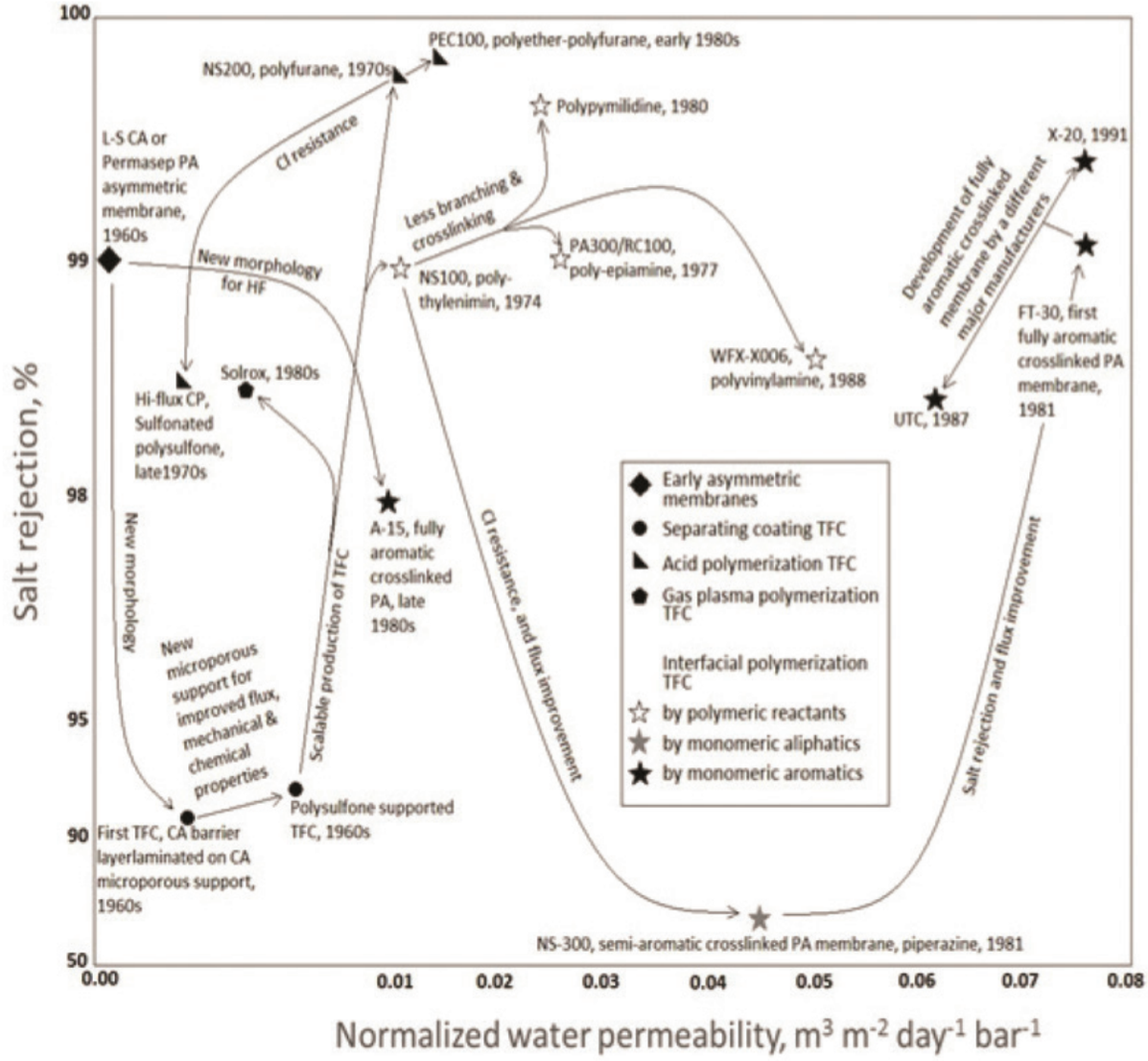
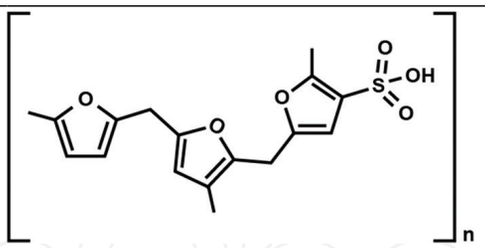
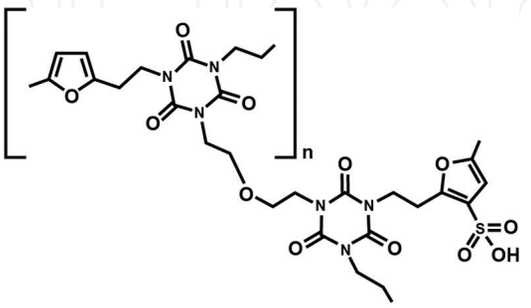
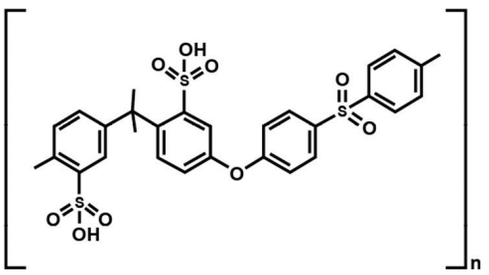
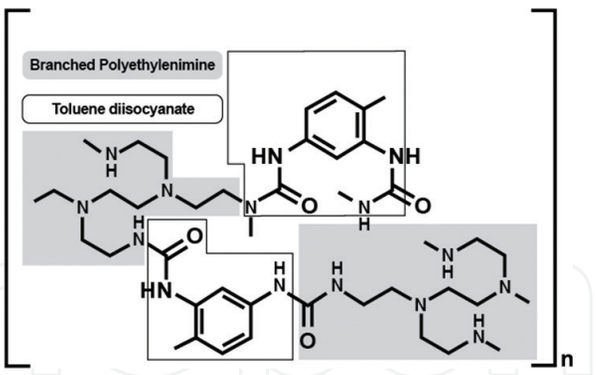
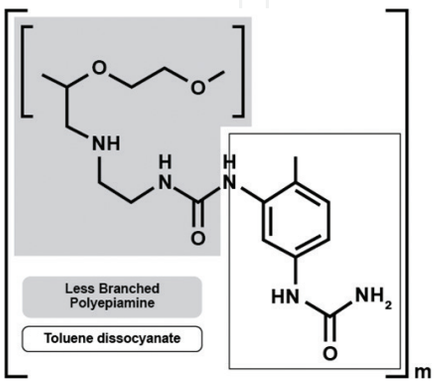
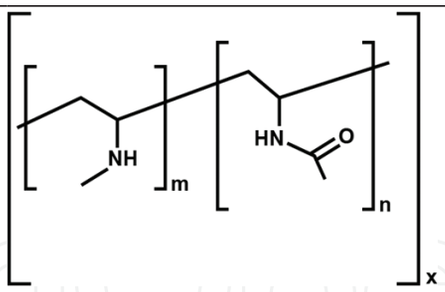
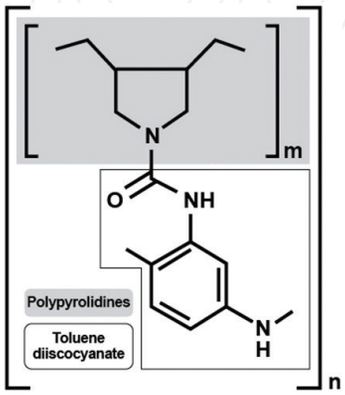
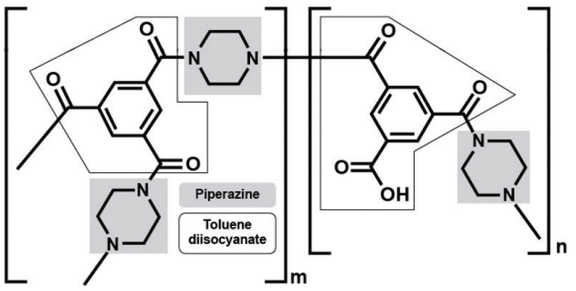
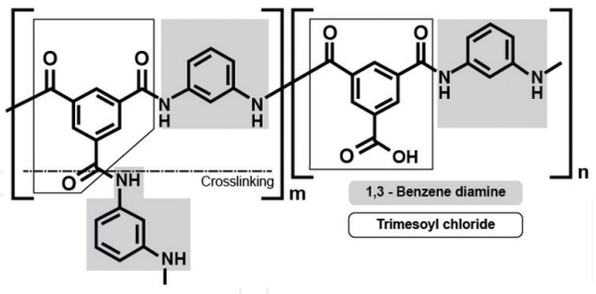
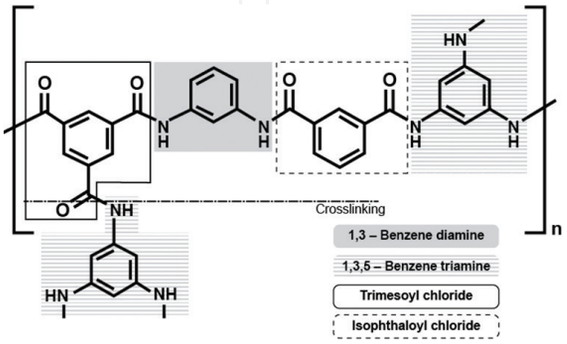


Figure 2. Development of thin-film composite RO membrane [30].

created [19, 32]. The original patented product based on this method was labeled NS-200 and entailed a product caused by the reaction of polyoxyethylene, sulfuric acid, and furfuryl alcohol (**Table 2**) [33]. Although NS-200 offered superior salt rejection capabilities, it was problematized by the irreversible swelling as well as hydrolysis of the sulfate linkage. Another example of the membrane created with the aid of acid polycondensation was the PEC-1000 TFC RO membrane produced by Toray Industries Inc., [34]. This membrane used 1,3,5-tris(hydroxyethyl)isocyanuric acid rather than polyoxyethylene.

While it did show a relatively high salt and organic compound rejection potential with sufficient flux levels, this membrane was vulnerable to chlorine attacks. In the next iteration of research, sulfonated polysulfone membranes were created so as to ensure a more uniform stability values in oxidizing environments [24]. However, substantial Donnan effects were still observed, thus suggesting that the shielding effect of divalent cations may drastically lower the monovalent ion rejection potential. A collective summary of key TFC RO membranes is listed in **Table 2**.

Chemical type and description	Chemical structure
1. Polyfurane Name: NS-200 [33] Flux: 0.8 $m^3\ m^{-2}\ day^{-1}$ Salt rejection: 99.8% Test: > 100 bar, 3.5% NaCl solution	
2. Polyether–Polyfurane Name: PEC-1000 [34] Flux: 0.5 $m^3\ m^{-2}\ day^{-1}$ Salt rejection: 99.9% Test: > 69 bar, 3.5% NaCl solution Excellent organic rejection	
3. Sulfonated polysulfone Name: Hi-flux CP [67] Flux: 0.06 $m^3\ m^{-2}\ day^{-1}$ Salt rejection: 98% Test: > 69 bar, 3.5% NaCl solution Excellent chlorine resistance	
4. Polyamide via polyethylenimine Name: NS-100 [67] Flux: 0.7 $m^3\ m^{-2}\ day^{-1}$ Salt rejection: 99% Test: > 100 bar, 3.5% NaCl solution	
5. Polyamide via polyepiamine Name: PA-300 or RC-100 [45] Flux: 1.0 $m^3\ m^{-2}\ day^{-1}$ Salt rejection: 99.4% Test: >69% bar, 3.5% NaCl solution	

Chemical type and description	Chemical structure
6. Polyvinylamine – Name: WFX-X006 [68] Flux: 2.0 m^3 m^{-2} day^{-1} Salt rejection: 98.7% Test: > 40 bar, Conductivity: 5000 μScm^{-1}	
7. Polypyrrolidine [69] Flux: 0.8 m^3 m^{-2} day^{-1} Salt rejection: 99.7% Test: > 40 bar, 0.5% NaCl solution	
8. Polypiperazine-amine Name: NS-300 [52] Flux: 3.3 m^3 m^{-2} day^{-1} Salt rejection: 68% Test: > 100 bar, 3.5% NaCl solution	
9. Cross-linked fully aromatic Polyamide: 1 Name: FT-30 [54] Flux: 1.0 m^3 m^{-2} day^{-1} Salt rejection: 99% Test: >15 bar, 0.2% NaCl solution	
10. Cross-linked fully aromatic Polyamide: 2 Name: UTC series [70] Flux: 0.8 m^3 m^{-2} day^{-1} Salt rejection: 98.5% Test: > 15 bar, 0.5% NaCl solution	

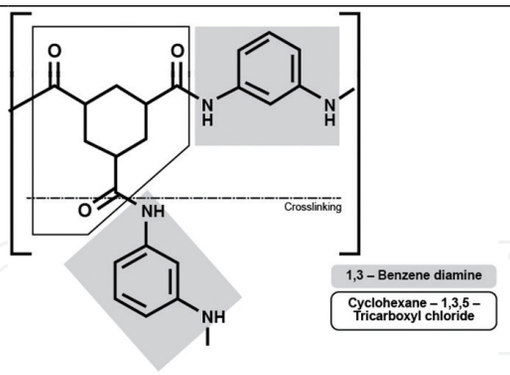
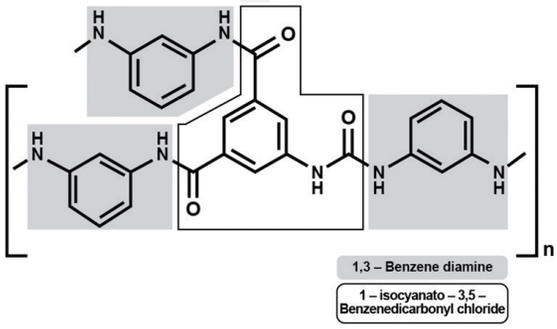
Chemical type and description	Chemical structure
11. Cross-linked aralkyl polymide Name: A-15 [64] Flux: 0.26% m^3 m^{-2} day^{-1} Salt rejection: > 98% Test: > 55 bar, 3.2% NaCl solution	
12. Cross-linked fully aromatic Polyamide: 3 Name: X-20 [71] Flux: 1 m^3 m^{-2} day^{-1} Salt rejection: 99.3% Test: > 15 bar, 0.2% NaCl solution	

Table 2. TFC RO membranes.

The barrier layer may likewise be created using plasma polymerization during which the monomer vapor is incited with the help of the gas plasma method and the monomer's atomic polymerization is brought to the cool surface, frequently in the form of polysulfone support surface.

A variety of polymers have been tested as a part of membrane research, and adequate permselectivity levels have been achieved with vinylene carbonate/acrylonitrile, vinyl acetate/acrylonitrile, acetylene/water/ nitrogen, allylamine, as well as acetylene/water/carbon monoxide arrangements [35–41]. Yasuda's research collective was especially successful in plasma polymerization studies by producing a membrane created using water, acetylene, and nitrogen. This membrane performed exceptionally well during seawater desalination tests and showed 99% salt rejection with a flux of 1.5 m^3 m^{-2} day^{-1} at 100 bar operation parameters. Multiple research groups have conducted experiments with applications in gas separation and plasma-polymerized films [42]; however, only the Solrox membrane type of RO membrane has been successfully commercialized using this method. Plasma-polymerized RO membranes primarily feature low chlorine resistance potentials because of their nitrogen-enriched chemical configuration.

3.2. Interfacial polymerization of TFC membranes

Application of polysulfone as a potential support layer paved the way for production of RO membranes and interfacial polymerization because it could withstand the alkaline condition

created by caustic soda applied as an acid acceptor throughout the interfacial polymerization processes. In the history of RO process, the production of NS-100, that is, polyethylenimine reacting with toluene diisocyanate (**Table 2**), is a critical developmental step in membrane research. In fact, this was the first successful instance of noncellulosic membrane featuring comparable monovalent and flux salt rejection potentials. This membrane likewise showcased improved stability at high temperatures, and advanced organic compound rejection capacity in acidic and alkaline environments [43, 44]. On the other hand, NS-100-type membranes provide very limited resistance to chlorine and show a distinct surface brittleness due to their overly cross-linked configuration. An alternative commercialized membrane product created using interfacial polymerization of polymeric amines is polyepiamine and specifically its two types PA-300 and RC-100 (**Table 2**) [45–47]. The PA-300-type membrane had enhanced permeate flux by 42.8% at about 1 m^3 m^{-2} day^{-1} and with the salt rejection of 99.4% at 70 bar, if compared to the NS-100-type membranes. This noticeable improvement has contributed to the effective installation of PA-300 spiral wound modules at the TFC SWRO plant in Jeddah [48]. RC-100, on the other hand, exhibited high resistance to biofouling and was thus installed at Umm Lujj II as well as other desalination plants [49]. The two other notable interfacially polymerized TFC membranes are polyvinylamine and polypyrrolidone. While polyvinylamine offers higher flux capacity, polypyrrolidone is the type of membrane where the amino/carboxy groups may be controlled in a way that permits variable selectivity and amphotericity properties. Early efforts to use interfacial polymerization of monomeric amines, including aromatic and aliphatic diamines, with terephthaloyl chloride did not help facilitate the creation of membranes with the required salt rejection values [2]. Furthermore, once the polymerization conditions were improved, then the method was able to produce an improved type of membrane in the form of NS-300 [20, 21, 50]. This polypiperazine-amide membrane showed substantial Donnan exclusion effects because of the presence of anionic carboxylic groups at the membrane's surface. Due to this presence, the NS-300 membrane could produce outstanding rejection potential of divalent anions, including sulfate at higher flux values. Such a result makes NS-300 substantially more useful for practical industrial applications based on nanofiltration (NF) (**Table 2**). As a result, a variety of NF membranes based on this chemistry have been effectively commercialized, for example, NTR-7250 by NittoDenko [51], NF-40 series by DOW FILMTECTM [52], and UTC-20 by Toray Industries [53]. Research has shown that membranes with improved permselectivity can be created with the help of monomeric aromatic amines and aromatic acyl halides, while comprised of at least three carbonyl halide groups, with trimesoyl chloride allowing for the best results [54–56]. This method is further unlike other interfacial polymerization approaches since it helps to avoid the use of heat curing. Similarly, surfactants and acid acceptors were not compulsory as both cross-linking and polymerization were quick even when acyl halide was provided at low concentration values. FT-30-type membrane (**Table 2**) was created using the interfacial reaction between trimesoyl chloride and 1,3-benzenediamine and has resulted in distinct surface characteristics. This particular membrane can be defined through a "ridge and valley" configuration, instead of the slightly grainy and smooth surface achieved from the aliphatic amines [20]. Research studies have indicated that the rougher "ridge and valley" type of surface contributed to a larger surface area used specifically for water transport needs and as a consequence for the water flux [57]. During seawater desalination testing, FT-30 membrane produced fluxes of almost

1 m^3 m^{-2} day^{-1} and 99.2% salt rejection rate at 55 bar operation parameter. FT-30's aromatic polyamide structure offers a higher degree of thermal and chemical resistance, resistance to compression, and a much wider pH operating range. While the membrane was not entirely resistant to the effects of a chlorine attack, the FT-30 showed a substantial degree of tolerance to chlorine that proved to be enough to successfully endure accidental exposure to this kind of chemical substance [58]. DOW FILMTECTM has commercialized a number of products based on this membrane and its properties [59]. The commercialization of membrane such as this can have a substantial effect on the cost projections and design involved in RO desalination [60]. In fact, this was the first spiral wound-type membrane element that was able to rival the DuPont asymmetric hollow-fiber polyamide B-9 Permasep® membranes originally produced in 1972. The overall success of FT-30 contributed to the creation of a wide range of comparable membrane products [61], including the UTC-70 by Toray Industries [62] and CPA2 membrane produced by Hydranautics [63]. Furthermore, the Permasep A-15 TFC membrane (**Table 2**) was manufactured using the reaction of 1,3-benzenediamine with a saturated cross-linking agent, cyclohexane-1,3,5-tricarbonyl chloride, and thus facilitated an aralkyl polyamide membrane which offers improved flux capacity [64, 65]. The application of isocyanato aromatic acyl halides (e.g., 1-isocyanato-3,5-benzenedicarbonyl chloride) as cross-linking agents for 1,3-benzenediamine was likewise patented so as to design the type of membrane that includes urea and amide linkages, both of which improve salt rejection and flux properties (**Table 2**) [66]. This particular membrane was labeled as X-20 and has showcased noticeably better resistance to chlorine and fouling because of its stronger polyamide–urea bond linkage and comparatively neutral surface charge [66].

4. Postsynthesis modification and optimization of interfacial Polycondensation reaction

The research and development of innovative polymeric materials for RO membranes has declined drastically after the groundbreaking success that came with the market production of cross-linked fully aromatic polyamide TFC RO membranes. Existing membrane products from RO desalination membranes' major manufacturers are still being designed around the original chemistry developed in 1980s. As a result, current membranes rely on the interfacial polymerization of monomeric aromatic amines [72]. DOW FILMTECTM, as the largest manufacturers of desalination membranes, is currently marketing and selling membrane products based on FT-30. Other companies, like Toray Industries, are using UTC-70, while Hydranautics membranes are based on NCM1, a membrane that is similar to CPA2. Trisep membranes are still using X-20. Alternatively, asymmetric membrane products have remained unchanged and are still based on conventional CA materials. For instance, the Toyobo HollosepTM products use CTA while remaining the primary asymmetric RO membrane presently in usage.

Although there have been no original polymeric membranes commercialized recently, the overall performance of RO membranes was noticeably enhanced over time (**Figure 3**). For example, the water permeability capacity has been doubled and the freshwater recovery potential can be

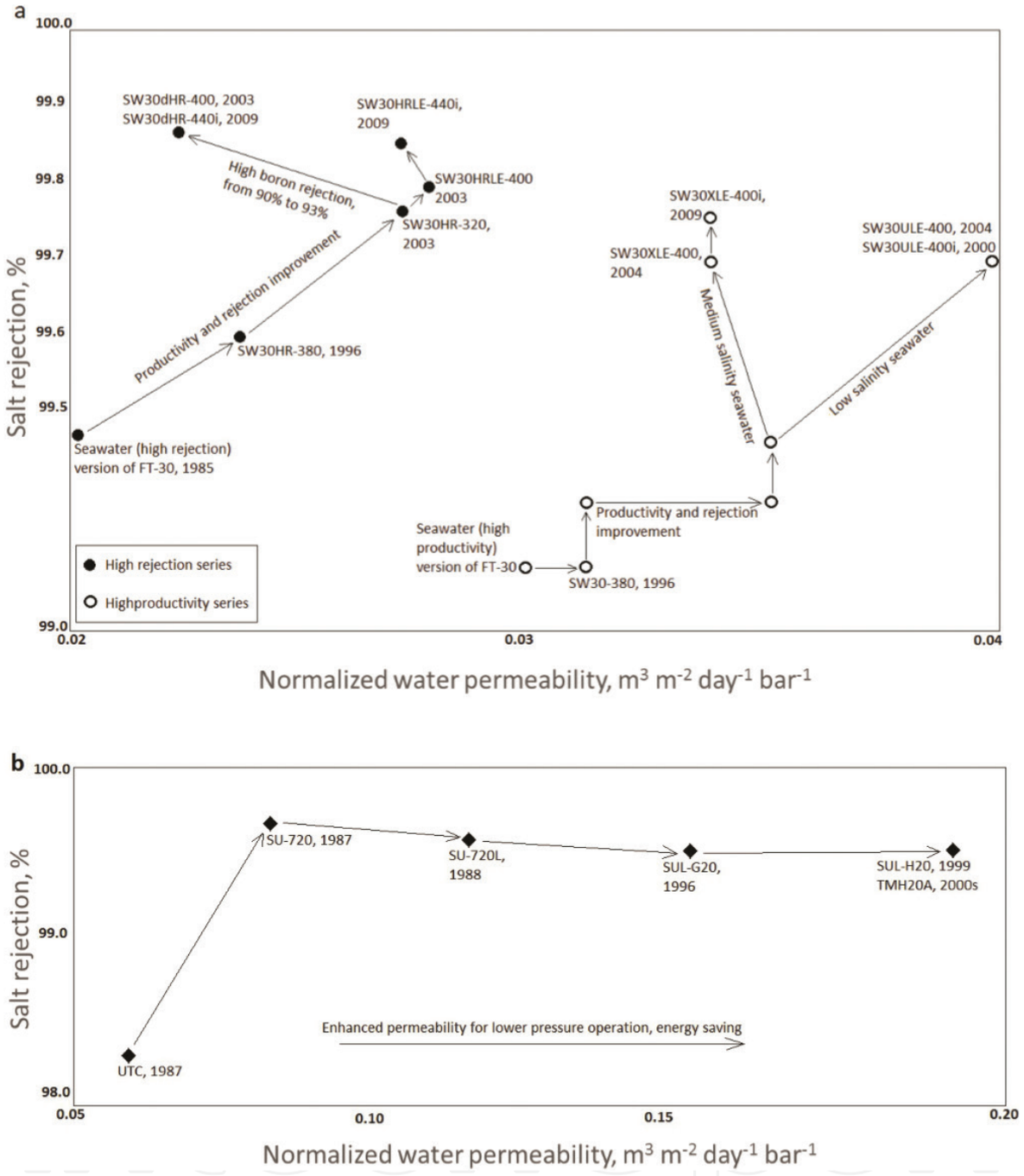


Figure 3. Development of RO membranes by reaction optimization and postsynthesis surface modifications: (a) Dow Filmtec seawater series and (b) Toray brackish water series.

as high as over 60%. Enhancements such as these are caused directly by surface modification as well as closer monitoring of interfacial polymerization reaction parameters. They are also linked to a substantially more effective module structure design [72, 73]. Furthermore, an in-depth research into the membrane structure has led to improvements in membrane characterization techniques [74]. Atomic force microscopy (AFM), for example, has remained a critical tool for

confirming that membrane surface roughness properties may greatly improve permeability while at the same time ensuring higher salt rejection potential due to an increase in the effective membrane surface [75].

Tracking the development of commercially relevant RO membranes after 1990 has been difficult because of the low patenting activity among membrane manufacturers. To share posttreatment and chemical composition data that have been used with commercial RO membranes, researchers have chosen to merge the use of multiple methodologies and analytical techniques. One of these tools is the Rutherford backscattering spectrometry, and it can be used for elemental composition analysis of various layers and physicochemical characterization [76–79]. In order to gain a better understanding of chemical and physical membrane structure characteristics and how these characteristics are connected to the membrane's overall performance, a combination of analytical techniques, ATR-FTIR, XPS, TEM, and streaming potential measurement have likewise been applied [80–82]. The relevance of several analytical tools was also reviewed with respect to membrane characterization [83]. While there is ongoing proactive academic research conducted in the field, this review specialized in the engineering developments that offered the most innovation and were integrated into commercial products with direct industrial applications.

4.1. Surface modification

A key research area focused on membrane postsynthesis encompasses hydrophilization since it may help obtain an increase in chlorine resistance and permeability properties. Currently, the applied monomer reactants are not easily available and their preparation method is overly complex, despite the fact that there was some success in synthesizing membranes using monomer reactants that included hydrophilic groups, like eliminated amide hydrogen and carboxylate [84–87]. As a consequence, the preference is given to posttreatment that chemically modifies the membrane's surface properties, as well as numerous physical and chemical techniques established for this. Water-soluble solvents, including alcohols and acids, have been used for treating the membrane's surface. Mixtures of acid (hydrofluoric and hydrochloric acid) and alcohol (ethanol and isopropanol) in water have likewise been tested as a way to enhance rejection and flux performances because of the skin modification and partial hydrolysis initiated using acid and alcohol [88]. The existence of hydrogen bonds has been argued to instigate interactions between water and acid and thus to incite higher surface charges and enhance water flux and hydrophilicity values. For example, Mickols patented membrane surface posttreatment that includes alkyl or ammonia compounds, such as ethanolamine and ethylenediamine, that improved membrane salt rejection and flux capacity [89]. Specifically, a 70% flux improvement may be obtained when composite membranes are soaked in solutions containing a range of organic species, like sodium lauryl sulfate, triethylamine salt of camphorsulfonic acid, and glycerol [90, 91]. The membrane posttreatment base on an aqueous solution of poly(vinyl alcohol) (PVA) and a buffer solution can help improve the overall flux stability of the membrane as well as abrasion resistance potential [92, 93].

Hydrophilization has been produced by effectively coating the membrane's surface with additional hydrophilic compounds. The process of coating has been a favored method when it comes to addressing various fouling-related issues. A key example of this can be seen in the launch of the Hydranautics LFC series in 1996 [94], as well as the creation of the LFC3-LD membranes in 2005 [95] with the aim of targeting wastewater treatment/reclamation applications. Membranes such as these are neutrally charged and as such are designed to minimize the organic foulant adsorption. The relatively stable performance reported in research over time has been [96] connected to the poly(vinyl alcohol) (PVA) coating located on the surface of conventional fully aromatic polyamide membranes [81]. Coatings with poly(N,N-dimethylaminoethyl methacrylate) and PVA have likewise signaled greater resistance capabilities against chlorine attacks [97]. Recent research suggests that hydrophilic dendritic polymers were able to effectively modify the membrane's surface and enable fouling reduction [98, 99].

Substantial flow improvement was obtained when chemical treatment was used on a FT-30-type membrane. The FT-30 membrane was soaked in a 15% solution of hydrofluoric acid for seven consecutive days, after which period it showcased a slightly higher salt rejection capacity and a fourfold improvement in terms of flux. An analysis of the membrane's surface indicated that the fluorine ratio was higher due to the effects of the treatment. Furthermore, the etching of the surface helped to facilitate a thinner barrier layer [100]. While this method improved flux capacity without changing chemical structure, this approach is undermined over time by the leaching of hydrophilizing components that can cause the loss of any gained flux advantages [101].

Additional surface modification methods currently employed to covalently attach useful monomers onto the membrane's surface may include the applications of free radical-, redox-, radiation-, photochemical-, and plasma-induced grafting. Gas plasma treatment was similarly employed so as to encourage surface modifications. In this case, water permeability was enhanced using oxygen plasma treatment that relies on the addition of hydrophilic carboxylate groups, while the argon plasma treatment improved chlorine resistance potential by increasing the extent of cross-linking at the nitrogen sites [102, 103]. Recent research by Lin et al. suggests that the application of graft polymerization and atmospheric gas plasma surface activation on the conventional polyamide TFC membranes' surface is capable of significantly improving antifouling properties [104]. Once the gas plasma surface activation occurs, a polymeric brush layer will form with the help of the free radical graft polymerization based on acrylamide monomers or methacrylic acid. A brush layer of this type can successfully decrease the foulants' capacity to cling to the membrane's surface. This has been verified during multiple fouling tests, where such a membrane managed to outperform commercial low-fouling membrane LFC1, in particular during the mineral fouling tests. Both, graft polymerization and atmospheric gas plasma treatments can be easily adapted to large-scale membrane industrial applications and manufacturing.

4.2. Optimization of polymerization reactions

Optimization of interfacial polymerization reactions is another critical area of research, and it requires a controlled assessment of parameters such as kinetics, reaction time, reactant diffusion coefficients, solution composition, solvent solubility, polymer molecular weight range, curing time, nucleation rate, and other features of the microporous support [105–109]. Tomaschke and

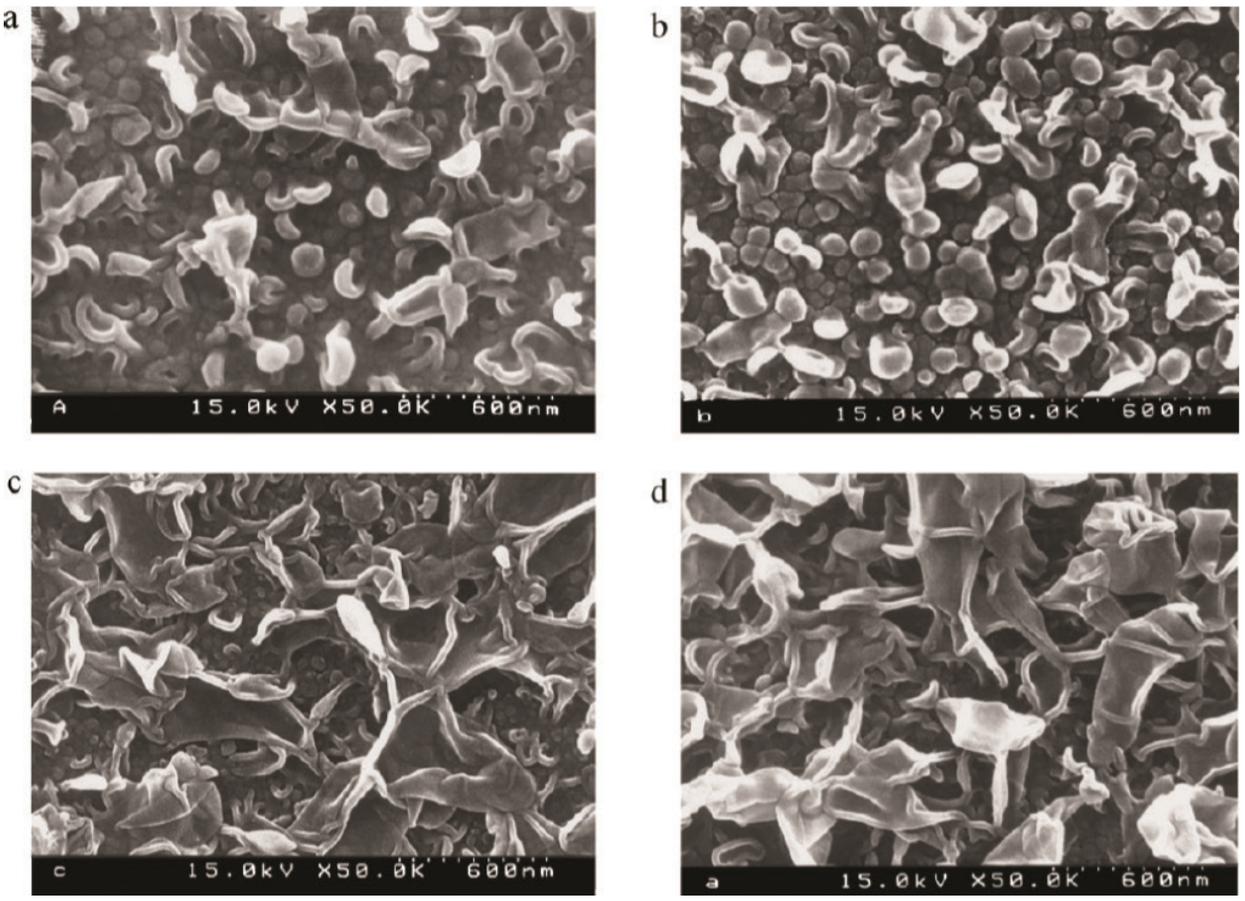


Figure 4. FE-SEM micrographs of RO membrane surface with various permselectivity. (reprinted with permission from Kwak et al., 1999) [117]. (a) Flux: 1.15 m^3 m^{-2} day^{-1}, salt rejection: > 96%. (b) Flux: 1.16 m^3 m^{-2} day^{-1}, salt rejection: > 99.1%. (c) Flux: 1.52 m^3 m^{-2} day^{-1}, salt rejection: > 98.7%. (d) Flux: 1.85 m^3 m^{-2} day^{-1}, salt rejection: > 98.4%. Note: Tested at 20°C, >15 bar for 0.2% NaCl solution. The scale bar is 600 nm for all figures.

Chau obtained early success when they experimented by introducing additives into the casting solution (amine reactants), which then incited extensive research into the application and addition of a range of additives [63, 110]. For instance, the application of amine salts, including the camphorsulfonic acid triethylamine salt, as an additive in an aqueous casting solution allowed for postreaction drying at temperatures greater than 100°C. As a consequence, a substantially more cross-linked membrane was created with improved characteristics in terms of the salt rejection properties and without the loss of flux capacities. Chau's research tried adding polar aprotic solvents, and particularly N,N-dimethylformamide, to the casting solutions. This experimental addition allowed for a greater carboxylate content in the membrane and subsequently improved water permeability.

The method of introducing additives into the casting solution can play a critical role when it comes to adjusting diffusivity, monomer solubility, protonation, and hydrolysis and to aiding the scavenging of reaction-inhibitory by-products [108]. A high number of patents reveal that the introduction of ethers, alcohols, polyhydric alcohol, water soluble polymers, or sulfur-containing compounds to the amine solution may enhance the membrane's overall permeability without substantively affecting its salt rejection capacity [111–115]. For instance, the miscibility of hexane

and water was enhanced by the inclusion of dimethyl sulfoxide into the casting solution. In this case, the diffusion of amine monomers was improved and allowed to create a thinner barrier layer and better water flux potential [116]. **Figure 4** outlines the micrographs of RO membranes fabricated with the aid of various additives and that in turn facilitates diverse permselectivities [117]. Rather than mixing additives directly into the amine reactant solutions, the inclusion of a "complexing agent" into the acyl chloride solution, usually trimesoyl chloride, was patented. Research suggests that the phosphate-containing compounds are the ones used most frequently. These compounds include triphenyl phosphate that has the capacity to modify and reduce the repulsive interaction of acyl chloride with the other compounds by eliminating the halides that were formed during the formation of amide bonds. This minimizes concurrent hydrolysis and ensures that there is a sufficient reaction between amines and acyl halide, which improves membrane formation and helps increase permeate flux potential [118, 119].

Research conducted as part of recent membrane projects indicates that the successful addition of surface-modifying macromolecules into the reactants has been performed. During this method, additives can transfer toward the active surface area during polymerization and as a result change the surface chemistry. For example, the inclusion of hydrophilic surface-modifying macromolecules, like poly(ethylene glycol) end-capped oligomers, in the interfacial polycondensation reaction had overtime enhanced stability of salt rejection and membrane flux potential.

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