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Recent Advances in Thin Film Composite (TFC) Reverse Osmosis and Nanofiltration Membranes for Desalination

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ABSTRACT

Reverse osmosis (RO) by polymeric membranes is known to be among the successful technologies for brackish and seawater desalination. For the development of these polymeric RO membranes, two different techniques have been used - the phase inversion method for asymmetric membranes, such as cellulose acetate membrane and the interfacial polymerization for thin film composite (TFC) membranes. Despite the high quality of the water produced by TFC-RO process, TFC membranes are susceptible to fouling. After a long period of academic and industrial researches, it is generally accepted that hydrophilicity, surface charge, and surface roughness of the TFC membrane surface are the major factors which affect the membrane susceptibility to fouling. As a result, several recent studies have focused on tailoring these properties with the aim of producing TFC membranes with reduced fouling as well as enhanced flux and salt rejection for use in desalination.

In this study, authors present a comprehensive summary of the most recent findings in the literature focusing on the enhancement of TFC RO and nanofiltration membrane performance in desalination applications, by tailoring membrane characteristics. The authors would then present a new concept for the preparation of TFC membranes by interfacial polymerization on porous polysulfone support using novel additives, namely, surface modifying macromolecules (SMMs). Hydrophilic SMMs (LSMMs) were synthesized both ex-situ and in-situ within the organic solvent of the TFC system. The RO performance results showed that the addition of the ex-situ LSMM significantly decreased the salt rejection of the membrane and slightly reduced the flux, while in the case of the in-situ LSMM, salt rejection was improved but the flux declined at different rates for different LSMM concentrations. The membrane prepared by the in-situ LSMM exhibited less flux decay over an extended operational period.

Keywords: Reverse osmosis, thin film composite (TFC) membrane, fouling, desalination

1.0 BACKGROUND

The most common reverse osmosis (RO) membranes used in water treatment and seawater desalination are the thin film composite (TFC) membrane based on aromatic polyamide (PA) [1–5]. TFC membrane is an asymmetric membrane which is comprised of a fabric, a porous support layer made of polysulfone (PS), and a dense ultra thin salt rejection barrier layer [3]. The porous support layer, which is usually made of PS, is made by the phase inversion technique, while the thin layer is made by interfacial polymerization (IP) (polycondensation) [6]. Many routes were described to form the ultrathin barrier layer in the composite membranes. These techniques include [3]: 1) Casting an ultrathin dense layer separately and then cover the microporous support layer with the thin dense layer (lamination), 2) Interfacial polymerization, 3) To dip-coat a polymer solution onto the microporous layer and then dry the coated layer, and 4) To use a gaseous phase monomer plasma to deposit the barrier film

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directly on the microporous support layer (plasma polymerization). Among those methods, IP is the most widely used technique and polyamide TFC membranes are industrially produced by this method [1, 3].

A large number of RO TFC membranes has been successfully prepared from various polymers such as; polyurea, polyamides, polyurea-amides, polyether-amides, polybenzhydrazides, polybenzimidazole, and other polymers. Those TFC membranes have shown excellent salt rejection with low water permeability [4,7,8]. The FT-30 membranes (produced by Dow-Filmtec Co.), which are among the most successful commercial RO TFC membranes, are prepared via interfacial polymerization (polycondensation) reaction between a polyfunctional amine, e.g. 1, 3-phenylenediamine (MPD), and an acid chloride, e.g. 1, 3, 5 benzenetricarbonyl trichloride (TMC), dissolved in water and hydrocarbon solvent, respectively [3, 9]. Since water and the hydrocarbon solvent are immiscible, polymerization reaction takes place at the water/hydrocarbon interface, which results in the formation of a thin skin layer on the surface of the porous substrate membrane [3,6,10]. The low water permeability of membranes formed from different polyamides is due to the rigid cross linked structure [3,7].

Since both the surface chemistry and morphology of the membrane play a crucial role in determining the performance of the membrane, there is a scientific and technological approach behind the importance of controlling membrane surface properties, through the modification of the membrane surface [11,12]. TFC membrane applications could be expanded by improving their performance as well as their resistance to fouling and chlorine attack. As a result, much work in the area of TFC membranes has been focused on developing membranes, with excellent performance (higher flux and separation) and high resistance to fouling and chlorine attack. This could be achieved either by (i) design and development of new polymeric materials to be used in forming the thin films of the TFC-RO membranes or (ii) physical/chemical modification of the thin films [13,14]. Several different procedures have been researched to chemically modify the membrane surface in order to alter membrane surface properties. These procedures may increase the hydrophilicity, change surface chemistry or morphology (e.g., roughness), and/or adjust transport properties [12]. Many methods were reported for membrane surface modification such as grafting, coating [12,15–20], and blending of hydrophilic/hydrophobic surface modifying macromolecules (SMMs) [21]. The chemical modification of the active layer materials by the incorporation of hydrophilic sulfonic acid [22] or carboxylic acid groups [23], or the addition of different polymers with flexible main chain or with bulky group in the side chain such as poly(vinyl alcohol) (PVA) and poly(vinyl phenol) to the aromatic polyamides [24–32], have all been used to enhance water permeability. These modification methods usually improve the TFC membrane water flux but at the same time lessen its salt rejection. Understanding the currently available information on the mechanism of the transport of the solvent through the membrane lead to the conclusion that polymeric materials with hydrophilic group, rigid backbone, and a certain degree of cross-linking, would produce TFC membranes with good performance [13,14].

2.1 Enhancement of TFC Membranes using New Monomers in the IP Reaction

Several attempts were reported in recent literature on TFC membrane development via the selection of monomers used in the IP reaction. Li et al. prepared tri- and tetra-functional biphenyl acid chloride, 3,4',5-biphenyl triacyl chloride (BTRC) and 3,3',5,5'-biphenyl tetraacyl chloride (BTEC), to be used as new monomers for the preparation of TFC-RO membrane via IP. TFC membranes prepared from BTRC and BTEC give higher salt rejection compared to TFC prepared from TMC. This is believed to be due to the highly cross-linked aromatic PA and the presence of the functional acylamide (–CONH–) bonds [13]. PA-urethane prepared from the reaction between a haloformyloxy-substituted acyl chloride with an aromatic polyamine was found to be an excellent performance material for the preparation of the thin active layers of TFC membranes. TFC membrane prepared via the IP of 5-chloroformyloxyisophthaloyl chloride (CFIC) with MPD exhibits excellent solute rejection and permeation properties during the desalination of brackish water [33,34]. Zhou *et al.* [34] prepared TFC membranes via IP between CFIC and MPD. These membranes had dense surface with finely dispersed grainy structure. The near surface region of these membranes contains both urethane and amide functional groups. Compared to MPD/TMC membranes, the MPD/CFIC membranes have higher flux and salt rejection, under the same operating conditions. This was attributed to the presence of amide functional group (-CONH-), urethane functional group (-OCONH-) and hydroxyl functional group (-OH). In a more recent work, Liu et al. also prepared an RO-TFC seawater membrane by the IP of CFIC and MPD, on a PS support, and reported the surface of their membrane to be thick, smooth, and with less cross-linking structure [35]. By adding small concentrations (less than 6%) of isopropyl alcohol to the aqueous phase during the IP reaction, they managed to achieve significant water flux increment and slight increase in salt rejection. Zhou *et al.* prepared TFC membranes using IP between TMC in the organic solution and MPD and *m*-phenylenediamine-5-sulfonic acid (SMPD), both in the aqueous phase. The prepared membranes were found to have a strong correlation between membrane performance and the ratio between (SMPD) and MPD. They reported that as the ratio of SMPD:MPD increased, the NaCl rejection decreased, the flux increased, the linear part with the pendant-COOH in the membrane barrier layer increased, and the surface became smoother [36]. The same team [34] also produced TFC membranes with 5-isocyanate-isophthaloyl chloride (ICIC)/isophthaloyl chloride (IPC) and MPD by IP in PS support film. The membranes produced were dense with finely dispersed grainy structure. They found that increasing the IPC/ICIC mass ratio leads to an increase in permeate flux, but to lower NaCl rejection.

Tang *et al.* [37] prepared nanofiltration (NF) membranes by the IP of triethanolamine and TMC on the PS supporting membrane. The produced membranes, which had rough and dense active layer, exhibited good long term stability and were observed to have amphoteric surface characters. As a result, water flux and rejection of NaCl and other tested salts were found to be strongly dependent on the pH of feed solution.

2.2 Impact of Hydrophilicity on TFC Membrane Performance

In TFC-RO membranes, higher water flux can be achieved mainly due to higher hydrophilicity which appears as a result of the presence of the carboxylic acid structure formed by the hydrolysis of the acyl chloride groups of the aromatic polyamides [38, 39]. The presence of carboxylic acid groups, which increase the negative charges of the PA network, greatly affects water flux as well as salt rejection [38]. Hydrophilicity is a very important membrane characteristic that is believed can overwhelm other important factor that control membrane performance such as film thickness, density, free-volume, polymer chain mobility, and polymer–solvent/polymer–solute interactions. For that reason, controlling the presence of functional groups in the active layer is crucial for the performance of the TFC membranes [38]. Many attempts have been made to increase membrane surface hydrophilicity by surface modification techniques, each having its own advantages and disadvantages. Membrane hydrophilization can be achieved by treating the membrane surface with water soluble solvent (acids, alcohols, and mixtures of both). This method increases the flux without changing the chemical structure but one of its disadvantages is that the water flux decreases with time because of the leaching of the hydrophilizing agent by water permeation [40]. Using a mixture of acid and alcohol in water for the surface treatment can improve the surface properties since acid and alcohol in water cause partial hydrolysis and skin modification, which produces a membrane with a higher flux and higher rejection. It was suggested that the presence of hydrogen bonding on the membrane surface encourages the acid and water to react on these sites producing more charges [40, 41]. Kulkarni *et al.* [40] hydrophilized a TFC-RO membrane by using ethanol, 2-propanol, hydrofluoric acid and hydrochloric acid. They found that there was an increase in hydrophilicity, which led to a remarkable increase in water flux with no loss in salt rejection.

A hydrophilic, charged TFC membrane was also achieved by using radical grafting of two monomers, methacrylic acid and poly(ethylene glycol) methacrylate onto a commercial PA-TFC-RO membrane [42]. It was found that the use of amine containing ethylene glycol blocks enhanced the performance of the membrane and highly improved membrane water permeability by increasing hydrophilicity [43]. Water permeability of PA-TFC-RO membranes could also be increased using an oxygen plasma treatment, which introduces surface carboxylic groups that increases the hydrophilicity of the treated membrane [44]. Karikov *et al.* [45] introduced a hydrophilization technique for both the pore mouth of the TFC active membrane layer as well as the hydrophobic support. Their technique involved pre-wetting the membrane with acetone, followed by oxidation with a hot chromic acid solution.

Liu *et al.* [46] tailored separation performance and surface properties of TFC polyamide membranes, prepared through IP of TMC, ICIC, or CFIC with MPD. They reported that the introduction of the isocyanato group into polyacyl chloride improves the hydrophilicity, water permeability and surface smoothness of the TFC membrane, but reduces the chlorine stability, while the introduction of chloroformyloxy group increases the salt rejection rate and the surface roughness of the composite membrane, but lowers the water permeability. The hydrophilicity of the produced membranes was in the order of MPD-ICIC>MPD-TMC>MPD-CFIC, while the order is reversed for surface roughness. Using similar monomers, Reddy *et al.* [47] prepared TFC NF membranes containing negatively charged and/or neutral hydrophilic surface functional groups by surface modifications of the membranes by in-situ redox polymerization of the acrylate monomers. They found that the hydrophilicity of the produced membranes was also in the order of MPD-ICIC>MPD-TMC>MPD-CFIC, which was the same order for water permeability and salt rejection in feed water containing calcium and sulphate salts. They further reported that the MPD-CFIC membrane was less chlorine-resistant than the MPD-ICIC or MPD-TMC, due to the existence of the urea bond and the pendant -NHCOOH groups. Recently, Jin *et al.* [48] found that more pendant (free) acid groups are present in the PA film at higher TMC concentrations or lower MPD concentrations, longer polymerization reaction times, or lower reaction temperature, which they explained on the basis of monomer diffusion in the IP process. As a result, these free acid groups were shown to have pronounced effects on the hydrophilicity of the PA thin film. Finally, Chena and coworkers [14] synthesized and used sulfonated cardo poly(arylene ether sulfone) (SPES-NH_2) for the preparation of TFC membrane via IP. The SPES-NH_2 was mixed with the MPD in the aqueous phase. The formed membrane was found to have high flux and high salt rejection due to the rigid polymer backbone and the presence of strong hydrophilic sulfonic group.

2.3 The Emergence of Nanotechnology in Making TFC Membranes

Recently, nanotechnology has emerged in producing a new generation of functional groups material, which application in water desalination and water purification still needs to be explored more. Many studies on filtration and desalination using membranes prepared from carbon nanotubes [49–51] and zeolite films [52–54] present exciting new potential. Those mixed matrix or nanocomposite membranes bring together the excellent characteristics of both polymeric materials and nanoparticles. Also mixed matrix membranes can exhibit enhanced chemical, mechanical, and thermal stability as well as improved separation, and sorption capacity [55]. It was found that the water flux of TFC-RO membranes could be doubled without affecting the salt rejection by incorporating zeolite nanoparticles in the thin layer of the TFC-RO membranes [56]. Others reported that biofouling could be hindered using a new type of anti-fouling membranes, developed by introducing TiO_2 nanoparticles into TFC membranes in order to reduce the loss of RO permeability [57, 58].

Jadav and Singh [59] synthesized nano-composite membrane films by incorporating two types of silica nanoparticles (3 nm and 16 nm in size) *in situ* into the PA films. The produced nano-composite membranes were reported to exhibit superior thermal stability than the pure

PA membranes, and in both nano-composite membranes, the best membrane performance in terms of separation efficiency and flux productivity was reported at a certain amount of silica loading. Higher silica loading into the polymer were reported to induce thicker membrane film formation with relatively large pore sizes and higher pore number density.

2.4 Performance Enhancement using Chemical Additives in TFC Membranes

Several researchers attempted to use various chemical additives before, during, and after the IP reaction in the TFC membrane fabrication process, with the aim of enhancing membrane performance. Soaking the freshly prepared TFC membranes in solutions containing various organic species, including glycerol, sodium lauryl sulphate and the salt of triethylamine with camphorsulfonic acid can increase the TFC flux in RO applications by 30–70% [17]. TFC physical properties (abrasion resistance) and flux stability were also improved by applying an aqueous solution composed of PVA and a buffer solution as a post treatment step during the preparation of the TFC membranes [18,19]. More recently, it was reported that using PVA-based amine compound having a side chain amino group as the aqueous phase monomer, instead of MPD, can produce high flux TFC membranes for low pressure applications [20]. Addition of alcohols, ethers, sulfur-containing compounds, and monohydric aromatic compounds and more specifically dimethyl sulfoxide (DMSO) in the aqueous phase can produce TFC membranes with an excellent performance [60–63]. For example, addition of DMSO to the IP system can produce TFC membranes with water flux five times greater than the normal TFC water flux with no considerable loss in rejection [63]. More recently, Yoon *et al.* [64] used electrospun polyacrylonitrile nanofibrous scaffold as a mid-layer support in thin film nanofibrous composite (TFNC) membranes for NF applications. They produced a barrier layer by IP of polyamides containing different ratios of piperazine (PIP) and bipiperidine. Upon comparing the TFNC membranes with conventional TFC membranes, they reported that the TFNC membranes exhibited over 2.4 times more permeate flux than TFC membranes with the same chemical compositions, while maintaining the same rejection rate (ca. 98%), which they attributed to a larger open pore structure and a lower hydraulic resistance of the nanofibrous support in the TFNC membranes. In another attempt, Wu *et al.* [65] prepared thermally stable composite NF membranes by interfacial polymerization of PIP and TMC on a poly(phthalazinone ether amide) ultrafiltration membrane. They reported that, as the immersion time in the aqueous phase during the IP reaction was prolonged, the rejection of Na_2SO_4 was enhanced, but the permeate flux declined. Finally, Louie *et al.* [66] demonstrated that it is possible to reduce gas flux (O_2, N_2, and H_2) through the membrane surface during water RO process by treating the TFC membrane with n-butanol followed by drying.

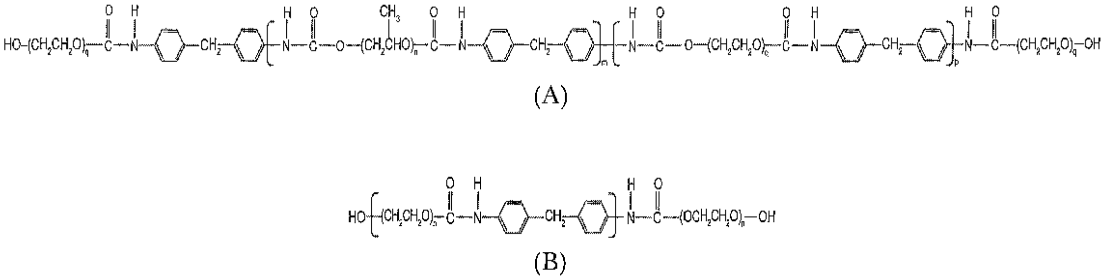
On the other hand, the chlorine resistance of the TFC-RO membrane can be enhanced using chemical treatment, for example, using an argon plasma treatment which causes the cross-linking to take place at the nitrogen sites on the TFC membrane surface [5, 44]. Lang *et al.* produced an excellent chlorine-resistant PVA RO-TFC membrane using malic acid as a cross-linking agent and acetic acid as a catalyst [67]. Similarly, poly(ethylene glycol) (PEG) and its derivatives have also been used for surface modification, to produce TFC membrane resistant to fouling. This was done by grafting PEG chains onto the TFC-RO membranes [16,17]. Louie *et al.* [68], on the other hand, coated the surface of commercial TFC-RO membranes with a solution of polyether-polyamide (PEBAX 1657) to produce anti-fouling membranes.

2.5 The use of Surface Modifying Macromolecules (SMMs) in TFC Membranes

Another alternative and less common approach for the membrane surface modification is the introduction of an active additive. The basis of this technique is the idea that those additives can move toward the top film surface during membrane formation and alter membrane surface chemistry while keeping bulk properties unchanged.

According to this method, only small quantity of the additives is enough to change the surface chemistry of the membranes [69,70]. Blending is a conventional technique used for membrane surface modification, and recently much attention has been given to utilize this technique, in which hydrophobic SMMs are blended to a base polymer for membrane surface modification [71]. Abu Tarboush *et al.* [21] improved flux stability of PA-TFC-RO membrane by using hydrophilic SMMs (LSMMs) formed by in-situ polymerization reaction at the same time as the polycondensation reaction takes place within the organic solvent of the TFC system.

A new concept for the preparation of TFC RO membrane by IP on porous PS support using LSMMs was presented. Scanning electron micrographs depicted that heterogeneity of the surface increases for TFC membranes compared to the control PS membrane, and that higher concentrations of LSMM provided smoother surface. Those LSMMs were synthesized either before (ex-situ) or during (in-situ) the IP reaction, as shown in Figures 1–A and Figures 1–B, respectively. From their experimental results, Abu Tarboush *et al.* [21] concluded that both LSMMs could be incorporated in the aromatic PA layer of the TFC membrane effectively. The NaCl separation was found to increase while the flux decreased as the hydrophobicity of the solvent was increased in a series of solvents, including either esters or hydrocarbons. The performance of the membrane was better for the in-situ LSMM incorporated membrane than for the ex-situ LSMM incorporated membrane. It was reported that the in-situ incorporation of LSMM increased the stability of membrane desalination performance considerably. The membrane prepared with the in-situ LSMM exhibited less flux decay over an extended operational period.


(A)

(B)

Figure 1 LSMM formula. (A): LSMM made ex-situ, (B) chemical block for LSMM made in-situ [21]

4.0 CONCLUSIONS

In the last half century, an extensive research has been conducted on the production of drinking water using reverse osmosis (RO) and nano-filtration (NF) processes. One of the most successful commercial RO membranes, under the trade name FT-30, was developed by Dow-Filmtec Co. The membrane typically of a polyamide (PA) thin film is made by interfacial polymerization (IP) of *m*-phenylenediamine (MPD) in aqueous phase and trimesoyl chloride (TMC) in organic phase. Many research groups around the world have synthesized the PA layer by using various monomers of di-amine (aromatic, aliphatic, alicyclic, etc) and tri-chloride (aromatic, aliphatic, alicyclic, etc). Nevertheless, it needs further steps of improvement by using other monomers. Polymeric and/or small molecular chemical compounds were added during IP to improve the thin-film-composite (TFC) membrane performance. For example, polyethylene glycol is used to reduce fouling, whereas malic acid acts as a cross-linking agent to increase chlorine resistant. Moreover, a recent trend is to make high flux RO/NF membranes through addition of nano-particles, e.g., carbon nano-tubes (CNTs), titanium dioxide (TiO_2), alumina (Al_2O_3), zeolite, metallic silver (Ag), etc. In particular, high flux RO/NF membranes were fabricated by the addition of CNTs. Regarding membrane bio-fouling, the addition of Ag nano-particles has been widely accepted to reduce the growth of micro-organisms on the membrane surface.

A new method by which hydrophilic surface modifying macromolecules (iLSMMs) can be synthesized in the organic phase of in-situ polymerization, enables the incorporation of iLSMM at the PA skin layer of the TFC membrane. Most recently, PA coating was applied upon the surface of electro-spun nano-fiber membrane which acted as a supporting material. The ultimate goal of this research is to develop RO/NF membranes with reduced fouling as well as high chlorine resistance. Indeed, more fundamental research on the TFC RO and NF membranes need to be performed to envisage the next-generation RO/NF membranes with high flux and reduced fouling.

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