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## A recent progress in thin film composite membrane: A review

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### ABSTRACT

The major breakthrough in the preparation of thin film composite (TFC) membrane via interfacial polymerization technique has resulted in tremendous achievements in producing a membrane with a right combination of flux and salt rejection, and generating huge interest in industrial sectors. Over the past decade, there have been intensive and continuous efforts in the development of TFC membrane, both from the industry and academia with the interests to further improve the membrane productivity and selectivity as well as its tolerance against chlorine, solvent, fouling, etc. On basis of a brief introduction of the development history of TFC membranes, this paper reviews the recent research progress of the TFC membrane science and technology, particularly in the fields of water-related separation processes. Reviewing the research progress is imperative and necessary in order to provide an insight for the future development and perhaps open a door to extend the applications to other more challenging areas.

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### 1. Introduction

Thin film composite (TFC) membranes have experienced tremendous development since the concept of interfacial polymerization (IP) was first introduced by Mogan in 1965 [1]. It is generally acknowledged that the scientific breakthrough in developing ultrathin film onto microporous substrate is equivalent to the historic announcement of Loeb–Sourirajan asymmetric membrane in nineteen sixty.

Owing to ultrathin selective layer, reverse osmosis (RO) and nanofiltration (NF) membranes prepared using this coating technique have emerged as excellent candidates in a wide variety of separation applications, particularly in the water and wastewater treatment processes [2–5]. Despite TFC membranes have been well received in industry, there is still an interest among membrane scientists in making asymmetric membranes via single-step fabrication process [6–10]. It is generally agreed that asymmetric membranes can tolerate fairly high level of feed water chlorine in comparison to composite membranes prepared from polyamide (PA) [11]. Several key advantages of TFC membranes however have kept them much competitive in the commercial market. It must be mentioned that each layer (i.e. top selective layer and bottom porous substrate) of TFC membrane can be independently controlled and optimized to achieve desired selectivity and permeability while offering excellent mechanical strength and compression resistance.

Apart from IP technique, coating techniques such as photo-grafting, dip-coating, electron beam irradiations and plasma-initiated polymerization are also introduced to apply an ultrathin barrier layer upon a support membrane. Of these, IP is of particular interest in composite membrane preparation by taking into account a considerable amount of research work that has been conducted so far. These include several relevant review papers [12–15] and a book of NF published in 2003 [11].

A wide variety of research and general information on TFC membrane preparation and characterization is available; however, a recent review on TFC membrane technology and science is necessary to highlight the trend and progress in the development of TFC membranes. This review paper aims to give an overview of the development of TFC membrane technology over the past 10 years, from the top active layer improvement to the application of various polymeric substrates and eventually the state-of-the art approach on IP process. This updated information is of great importance to provide good insights to composite membrane research and development, particularly in the preparation of new types of TFC RO and NF membranes with improved performance.

### 2. Chronicles of thin film composite membrane development

In the early development of composite membrane, Mogan was the very first researcher to propose the use of interfacial polycondensation approach to form a thin polymeric layer onto a substrate [1]. The approach however did not succeed in industrial fabrication until Cadotte and his co-workers discovered that through the optimization of formation conditions, a series of composite membranes with surprisingly high flux could be made by interfacial crosslinking of piperazine with trimesoyl chloride/isophthaloyl chloride mixture [16,17]. Besides high flux production, these membranes also exhibited

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high rejection to aqueous sulfate ions but low selectivity of aqueous chloride ions. The contribution of this approach, which is widely known as Interfacial Polymerization is so significant to membrane science and technology and marks a quantum leap towards production of high flux/low pressure membrane with a good combination of salt removal.

Using the method invented by Cadotte et al. [16,17], many companies succeeded in developing a variety of TFC membranes, allowing the application of membranes for many industrial separation processes. It is well acknowledged that by employing IP technique, the properties of both bottom substrate and top barrier film can be individually tailored and optimized to achieve desired water permeation and solute separation rate. Nevertheless, we must point out that this aspect is not fully investigated yet because based on the literature, efforts have been devoted more to top thin active layer development, whether in the present or past. Properties of substrate are paid less attention during TFC membrane preparation, possibly because substrate plays no role in solute separation and fouling reduction as top selective layer does. The effect of sub-layer properties is therefore generally ignored or rarely reported by researchers during composite membrane preparation. Until lately, several research groups have started to address this issue with the purpose of gaining better understanding on the formation mechanisms between top active layer and supporting substrate made of different structural properties. The research outcomes from their investigations will be reviewed in the following sections.

### 3. Recent progress in thin film composite membrane development

This section does not intend to provide an exhaustive review of all the composite membranes developed to date because a comprehensive review on composite NF and RO membranes was published by Petersen in 1993, covering the structure and composition of composite membranes which have found commercial use up to 1992 [12]. The following section will instead focus on the recent research activities on the improvements of TFC membrane properties with respect to permeability/selectivity, chlorine tolerance, solvent stability, fouling resistance, etc.

#### 3.1. Effects of aqueous and hydrocarbon solution properties on TFC membrane performances

##### 3.1.1. Monomer

As membrane performances are mainly determined by film structure (i.e. pore dimension, thickness, roughness and hydrophilicity) and its chemical properties (i.e. crosslinking, functional groups and bonds), fundamental understanding on the effects of different monomers on composite membrane properties is necessary in order to tailor desired membrane structure and separation performance. Table 1 shows the organic structures of commonly used and newly reported monomers in the thin film formation together with their molecular weights. The commonly used reactive monomers are aliphatic/aromatic diamine such as piperazine (PIP), *m*-phenylenediamine (MPD) and *p*-phenylenediamine (PPD) and acid chloride monomers such as trimesoyl chloride (TMC), isophthaloyl chloride (IPC) and 5-isocyanato-isophthaloyl chloride (ICIC). Among these materials, the cross-linked aromatic polyamide composite membrane produced by interfacial polymerization of MPD and TMC is the most successful commercial products in the past and present. Fig. 1 shows a synthetic pathway used to prepare standard commercial MPD/TMC polyamide membrane with good desalination properties.


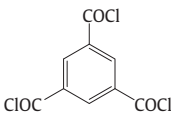
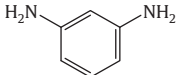
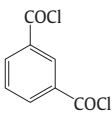
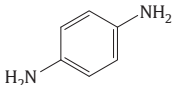
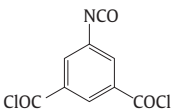
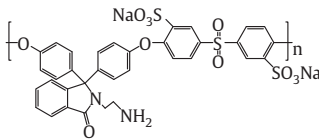
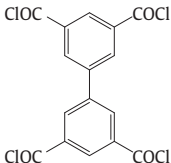
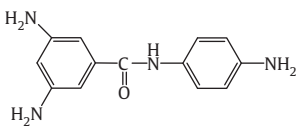
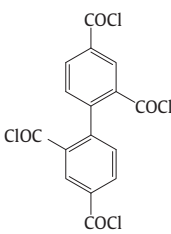
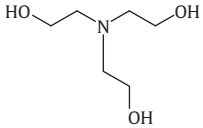
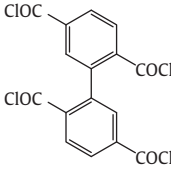
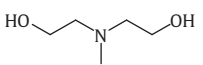
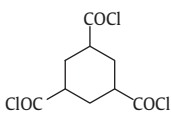
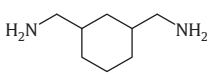
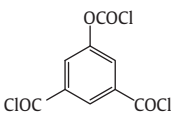
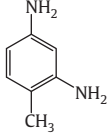
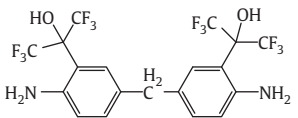
Despite the high performance of composite membrane compared to the asymmetric membrane in water separation processes, the research on how to further improve the properties of top active skin layer still remains as high-priority domain over the years. Newly synthesized monomer used to become the topic of study among the

community of membrane scientists. In the recent past, Li et al. [18] synthesized a series of isomeric biphenyl tetraacyl chloride (BTEC) for the preparation of TFC membrane with MPD as amine monomer in aqueous solution. According to the authors, the organic phase reactant is likely to have greater impact on membrane performance compared to aqueous phase reactant because IP process is generally diffusion-controlled in the organic layer. The experimental results showed that the membrane prepared from *op*-BTEC demonstrated the highest permeability ( $54.2 \text{ l/m}^2 \cdot \text{h}$ ) followed by membranes prepared from *om*-BTEC ( $50.0 \text{ l/m}^2 \cdot \text{h}$ ) and *mm*-BTEC ( $31.7 \text{ l/m}^2 \cdot \text{h}$ ) when tested using 2000 ppm NaCl solution at 2 MPa. The reason for the flux enhancement might be due to the rougher and larger surface area of *op*-BTEC membrane produced which led to greater contact with water molecules. Very interestingly, the membrane of *op*-BTEC did not suffer from a drawback of the “trade-off” between permeability and selectivity as NaCl rejection remained almost the same (>97%). Similar results were also reported in the work of Chen et al. [19] in which the incorporation of water soluble amine reactants – sulfonated cardo poly(arylene ether sulfone) (SPES-NH<sub>2</sub>) into aqueous solution containing MPD could overcome the trade-off effect between membrane permeability and selectivity. Under the optimum preparation conditions, the TFC membranes prepared from SPES-NH<sub>2</sub> showed remarkable increase in water permeability ( $51.2 \text{ l/m}^2 \cdot \text{h}$ ) with slightly decrease in salt rejection (97.5% at 2000 ppm NaCl, 2 MPa) compared to membranes prepared without SPES-NH<sub>2</sub> ( $37.4 \text{ l/m}^2 \cdot \text{h}$  and 99%). The improved results are attributed to the incorporation of hydrophilic SPES-NH<sub>2</sub> to polyamides and/or higher degree of cross-linking formed in the thin selective layer.

In view of the importance of hydrophilicity on the TFC membrane performance, a novel amine monomer – 3,5-diamino-N-(4-aminophenyl) benzamide (DABA) with three amino groups was synthesized and used together with diamines (MPD) in TFC membrane preparation [20]. With increasing the DABA content in aqueous phase from 0 to 0.25% (w/v), the membranes showed increase in water flux from  $37.5$  to  $55.4 \text{ l/m}^2 \cdot \text{h}$  and maintained a high salt rejection (~98%) in filtering salt solution containing 2000 ppm NaCl at 2 MPa. Membrane characterizations revealed that the top membrane surface became more hydrophilic, smoother and thinner as DABA concentration was increased in amine solution. On the other hand, an environmentally friendly yet economical monomer – triethanolamine (TEOA) was utilized by Tang et al. [21] to enhance membrane performance of TFC–NF membrane. It is of great interest to use TEOA as active monomer because the tertiary amino group in its molecule can be flexibly transferred into quaternary ammonium group through variation of feed pH. Moreover, this polyester composite membrane prepared from TEOA and TMC is found to be particularly suitable for treating acidic solution because water flux increased with lowering pH feed due to the fact that amino group on membrane surface can change into  $\text{R}_3\text{HN}^+$ , resulting in increased hydrophilicity at lower pH feed. As an extension of this study, they prepared aromatic PA composite membranes with the use of another alcohol amine, i.e. methyl-diethanolamine (MDEOA) [22]. With the presence of LiBr in aqueous phase solution, it is found that the membranes so prepared exhibited different separation properties compared to the membranes prepared from TEOA monomer. The change in separation performance was explained by the different mechanisms involved between these two monomers and the additive LiBr added.

A key limitation to commercial polyamide membranes is membrane degradation through contact with chlorine – one of the common disinfectants used in water and wastewater treatment. Previous studies have revealed that the changes in chemical nature of PA upon exposure to chlorine can affect membrane performance, shortening lifespan of membrane [23–25]. In order to overcome this limitation, Buch et al. [26] made an attempt to develop chlorine stability of NF by interfacial polymerization of 1,3-cyclohexanebis(methylamine) (CHMA) in water with TMC in hexane under different

**Table 1**  
The commonly used monomers and newly reported monomers for thin film composite membrane preparation.

Amine monomer (abbreviation)	Chemical structure	Molecular weight	Acyl chloride monomer (abbreviation)	Chemical structure	Molecular weight
Piperazine (PIP)		86.14	Trimesoyl chloride (TMC)		265.48
m-Phenylenediamine (MPD)		108.10	Isophthaloyl chloride (IPC)		203.02
p-Phenylenediamine (PPD)		108.10	5-isocyanato-isophthaloyl chloride (ICIC)		244.04
Sulfonated cardo poly(arylene ether sulfone) (SPES-NH <sub>2</sub> ) [19]		774.71	<i>mm</i> -Biphenyl tetraacyl chloride ( <i>mm</i> -BTEC) [18]		404.03
3,5-diamino-N-(4-aminophenyl) benzamide (DABA) [20]		242.27	<i>om</i> -Biphenyl tetraacyl chloride ( <i>om</i> -BTEC) [18]		404.03
Triethanolamine (TEOA) [21]		149.19	<i>op</i> -Biphenyl tetraacyl chloride ( <i>op</i> -BTEC) [18]		404.03
Methyl-diethanolamine (MDEOA) [22]		119.16	Cyclohexane-1,3,5-tricarboxyl chloride (HTC) [27]		271.53
1,3-cyclohexanebis (methylamine) (CHMA) [26]		142.24	5-chloroformyloxy-isophthaloyl chloride (CFIC) [28]		281.48
m-phenylenediamine-4-methyl (MMPD) [27]		122.17			
Hexafluoroalcohol-m-Phenylenediamine (HFA-MPD) [29]		530.31			

conditions. The composite membranes with aromatic–cycloaliphatic PA top layer were then exposed to NaOCl–NaCl mixed solution of various NaOCl concentrations to ascertain the impact of chlorine on

membrane properties. The composite membranes however failed to retain performances as both water flux and salt rejection decreased considerably upon chlorine exposure of 24 h and 1 ppm. It is elucidated

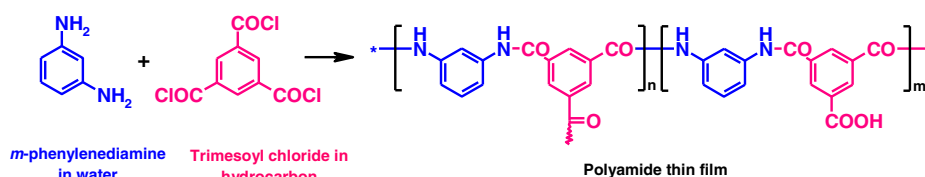


Fig. 1. Standard commercial polyamide membrane derived from *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) via interfacial polymerization.

that the conversion of amide N-H group to N-Cl group upon chlorine exposure is the main factor causing the hydrophobic character of PA layer to increase, leading to remarkable flux deterioration. Compared to the membrane CHMA-TMC, aromatic-cycloaliphatic PA membranes developed from *m*-phenylenediamine-4-methyl (MMPD) and cyclohexane-1,3,5-tricarboxyl chloride (HTC) showed attractive chlorine resistance of more than 3000 ppm-h Cl [27]. The very significant improvement on the stability of the membrane MMPD-HTC is attributed to the use of aromatic diamine compound with a mono CH<sub>3</sub> substituent at the *ortho* position which is believed can minimize the attack by chlorine present in the water (see Table 1). Apart from the high chlorine resistance, the membrane MMPD-HTC also exhibited greater water permeation following a higher degree of pendant group COOH formed on PA skin layer, as shown in XPS results.

In the recent past, Liu et al. [28] fabricated TFC RO membranes through the interfacial polymerization of MPD with TMC, ICIC and CFIC, separately in an effort to assessing the influence of polyacyl chloride structure on the chlorine stability of composite membranes prepared. The results indicated that membrane MPD-CFIC possessed the highest degree of resistant to chlorine attack, followed by membrane MPD-TMC and MPD-ICIC after hypochlorite exposure (up to 2500 ppm-h Cl) at pH 8.5. It is reported that N-chlorination reaction is much easier to be taken place in membrane MPD-ICIC due to the existence of urea (—NHCONH—) bond and pendant group of —NHCOOH. More recently in 2010, novel polyamide TFC membranes with highly tolerant to chlorine were prepared via interfacial polymerization of high MW of hexafluoroalcohol (HFA)-substituted aromatic diamines and TMC [29]. As HFA is an electron withdrawing group and sterically bulky, both electronic and steric factors could play key role in protecting amide linkages and benzene rings against chlorine attack. Results obtained from NMR spectroscopic showed that HFA-PA composite membrane suffered only minor changes in the spectrum after 17 h exposure of 500 ppm hypochlorous acid at pH 5.5. In comparison, the reference PA membrane was severely attacked by chlorine with more than 50% chlorination recorded after the chlorine treatment process, causing irreversible damage to the membrane structure. In this case, protons on benzene ring of reference PA membrane are substituted by Cl via Orton rearrangement upon chlorine exposure.

Polyamide membranes in general also found suitable for the treatment of non-aqueous solutions, though little data on their performance in organic solvents have been published [11]. A general solvent stable composite membrane (including the support) is one that is non-swelling in many solvent categories. In 2006, a solvent stable composite hollow fiber membrane which is found stable in 70% ethanol solution over the 10 weeks studied period has been successfully prepared from the monomer system of poly(ethyleneimine) (PEI) and IPC [30]. In order to improve adhesion between the selective layer and the support (lumen side of hollow fibers), the authors kept the organic monomer solution within the fiber (up to 10 min) instead of passing the solution through the fiber, creating a condition similar to that of the coating on flat films. Prior to this work on PEI/IPC monomer system, reaction of PEI and a diisocyanate was also found useful in the production of stable composite membranes for polar aprotic solvents. Further description on this work can be found in the U.S. patent filed by Black [31].

With respect to fouling resistance, Hilal and his co-workers [32,33] reported that the TFC membranes with improved antifouling

properties could be developed by means of interfacial polymerization between bisphenol A (BPA) and TMC. Though PA composite membrane has been continuously explored since 1970s, a polyester composite membrane with a highly charged surface seems to be necessary to overcome the limitations of composite membrane, i.e. fouling propensity. The highly negative charge of composite membrane coupled with uniform top polyester layer is reported demonstrating lower fouling factor against negative charge of humic acid molecules. In addition to BPA, the use of polyvinyl alcohol (PVA) as co-additive in aqueous PIP solution during interfacial polymerization was also recently conducted by An et al. [34] to improve antifouling performance of composite membranes produced. The introduction of hydrophilic PVA chain into PA active layer has shown positive effects on producing smoother surface and increasing membrane hydrophilicity which were found very effective to resist the fouling of protein, leading to higher productivity over a long run. As flux degradation due to fouling problem is unavoidable in composite membranes of water separation processes, control of membrane fouling will undoubtedly remain as high-priority research domain in the years to come. The state-of-the art approaches to tackle the fouling phenomena of TFC membrane with the addition of various antifouling materials such as silver salts and nanoparticles will be further discussed in the following section (see further in Section 3.1.3).

### 3.1.2. Surfactant

Studies on the use of surfactants as additives in asymmetric membrane preparation have been previously conducted for gas separation and pervaporation processes [35–37]. However, only few articles reporting the impacts of the surfactants on TFC membrane performance are available [39,40]. As surfactant is capable of altering polymerization efficiency of PA layer formation by helping monomer in the water phase move into the organic layer, improved property of composite membrane is thus able to be produced. In certain cases, surfactant is added to improve wettability of the top surface of the supporting layer so that a greater efficiency of polymerization can take place [41].

In the 2002 study of Jegal et al. [38], three different types of surfactants were used for synthesizing PA layer. Among the surfactants used, it is found that only triethyl benzyl ammonium bromide (TEBAB) could enhance the properties of resultant composite membrane, achieving 40% increase in the water flux upon 0.2 wt.% TEBAB added. The use of other surfactants such as trimethyl benzyl ammonium bromide (TMBAB) and triethyl benzyl ammonium chloride (TEBAC) played no role in modifying interfacial properties, revealing that not all surfactants displayed positive influence on membrane performance. Recently in 2009, Mansourpanah et al. [39] made an attempt to modify thin layer characteristics by adding different charge properties of surfactants in organic phase. The results showed that the presence of anionic sodium dodecyl sulfate (SDS) in organic solution could form defects and cracks on the thin layer surface while cationic cetyl trimethyl ammonium bromide (CTAB) and non-ionic Triton X-100 produced denser skin layer, owing to increase in amine monomer diffusion across the interface toward organic phase. It is interesting to note that the overall performance of composite membranes containing surfactant was still superior compared with the membranes prepared without surfactant addition.



Saha and Joshi [40] on the other hand experienced a variation in the characteristics of resultant membranes by increasing the surfactant concentration of sodium lauryl sulfate (SLS) from 0.1 to 0.5 wt.%. At low concentration of SLS added, the performance of membrane remained unchanged. Further increasing the concentration from 0.125 to 0.5 wt.% caused the NaCl rejection to decrease from 48 to 10% when the experiments were conducted at 1.03 MPa using 2000 ppm salt solution. No detailed explanation was given by the authors on the changes, but it is believed that the presence of surfactant plays a role in decreasing interfacial tension which facilitates the mass transfer of amine molecules to the organic phase to react with hydrochloride.

In the earlier literature, the addition of surfactants used to be recommended as necessary component for preparation of good PA membranes. However, it is lack of comprehensive studies – to what extent the presence of different properties of surfactant during IP process might really improve the properties of PA thin layer and what underlying mechanisms involved in the changes. It is difficult to draw a general conclusion based on the limited resources. Extensive work on this subject is certainly needed to provide a better level of understanding on how the surfactant governs the efficiency of interfacial polymerization process.

### 3.1.3. Additive

Most of research studies have focused on improving properties of interfacially polymerized film and subsequently the membrane separation properties by optimizing preparation parameters such as monomer concentration in aqueous/organic solution, monomer ratios, reaction time and post-treatment [11–14]. The presence of additives in aqueous/organic solution in fact is also as important as aforementioned parameters in altering the structure of film.

Recently, attention was devoted by Tang et al. [22] to the preparation of polyester composite NF membrane by adding inorganic salt–LiBr into aqueous phase solution during IP process. Surface of composite membrane became smoother as the LiBr content increased from zero to 3% (w/v). Rougher surface however was observed at greater amount of LiBr (i.e. 5 and 7%). With respect to membrane performance, asynchronous change in pure water flux and salt rejection was experienced with increasing LiBr content. This is mainly due to the unique interaction of LiBr with both alcohol amine and carbonyl of TMC.  $\text{Li}^+$  ion is generally known to be able to interact with the hydroxyl oxygen atom of alcohol amine, increasing the density and reactivity of OH groups in aqueous solution; as a result, a dense layer of composite membrane is formed. Formation of loose surface layer is also possible to occur following the interaction between  $\text{Li}^+$  ion and carbonyl of TMC because acid chloride group of TMC is preferable to hydrolyze in the existence of  $\text{Li}^+$  ion in aqueous solution.

Fig. 2 shows the chemical structure of synthesized hydrophilic surface modifying macromolecules (LSMMs). Attempt has been made by Matsuura and his co-workers to render the TFC membrane surface more hydrophilic by incorporating additive LSMMs onto the active PA layer [42]. It is observed that LSMMs synthesized during in situ polymerization could migrate toward the top air-polymer interface rendering membrane hydrophilic and produce best performing composite membrane with improved flux stability in comparison to LSMMs-free composite membrane. The improved stability is ascribed to the well-dispersed LSMMs in PA layer which increases the mechanical strength of thin film layer formed. With respect to salt rejection behavior, this newly fabricated membrane always showed

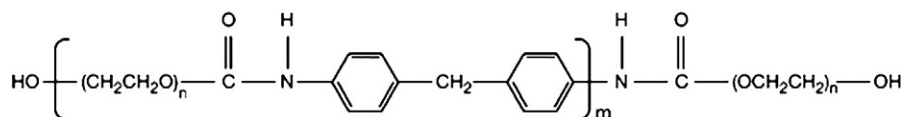


Fig. 2. Chemical structure of hydrophilic surface modifying macromolecules [42].

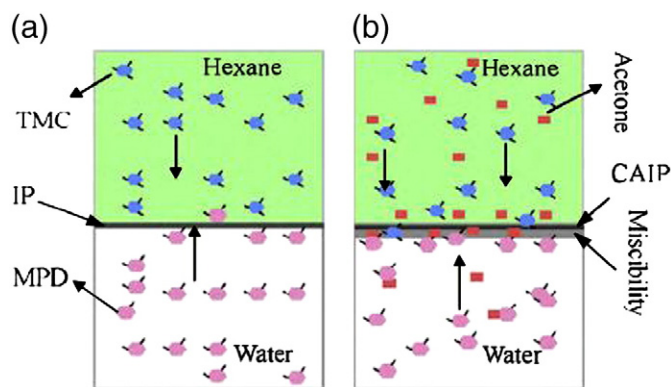


Fig. 3. Schematic diagram of (a) conventional IP technique and (b) novel co-solvent assisted IP (CAIP) technique [44].

higher separation efficiency (~96% vs ~91% of LSMMs-free membrane at 35,000 ppm NaCl, 5.5 MPa) and performed stably throughout the studied period. As an extension of this study, Matsuura et al. [43] incorporated silver salts simultaneously with LSMM into PA layer to mitigate biofouling effects due to various foulants. The results obtained confirmed the antibiofouling effect of silver salts in which silver nitrate demonstrated the highest antimicrobial fouling intensity in desalination of salty solution, followed by silver lactate and silver citrate hydrate.

Kong et al. [44] recently introduced a new concept for synthesis of TFC-NF membranes with controllable active layer thickness and effective “nanopores” through the addition of co-solvent (acetone) into organic phase. Fig. 3 illustrates that the presence of acetone could eliminate the great immiscibility gap between water and hexane, causing the IP reaction zone controllable. This as a consequence led to the production of composite membranes with extremely high flux ( $8.0 \times 10^{-12} \text{ m}^3/\text{m}^2 \cdot \text{Pa} \cdot \text{s}$ ) and no considerable salt rejection loss as compared with the membranes prepared from conventional IP procedure ( $2.1 \times 10^{-12} \text{ m}^3/\text{m}^2 \cdot \text{Pa} \cdot \text{s}$ ). It is also noted that with appropriate addition of co-solvent content, a composite membrane with thinner denser layer and smoother top surface could be produced, reducing the permeation water resistance which in turn enhancing water permeability. Significant flux enhancement on composite RO membrane was also reported elsewhere with the use of solvent dimethyl sulfoxide (DMSO) in the IP process [45]. Similar to acetone, DMSO also plays an influential role in reducing the solubility difference of two immiscible solutions. It increases penetration of diamine molecules into the organic phase, leading to formation of higher degree of cross-linking PA layer.

Most recently in 2010, hexamethyl phosphoramide (HMPA) was first reported that could be utilized as an additive in aqueous solution for PA thin film formation [41]. As HMPA is capable of facilitating diffusion rate of amine monomer into organic phase, it might create a thicker zone of reaction. In comparison to non-additive membrane, composite membrane prepared from 3 wt.% HMPA showed dramatic increase in water flux (>70%) while maintaining a good NaCl rejection. The considerable flux enhancement is resulted from the combination effects of enhanced hydrophilicity of membrane surface coupled with increased cross-linking extent of PA skin layer upon HMPA addition.

Another important development in TFC membrane technology is the incorporation of nanoscale particles into composite membrane

structure. This sort of nanotechnology is currently being used for a wide variety of applications to make complete, highly advanced products. In membrane-based separation technology, Lee et al. [46] considered adding titanium oxide ( $\text{TiO}_2$ ) nanoparticles into PA thin film composite membrane for water treatment process. The top thin layer of PA- $\text{TiO}_2$  was prepared by interfacial reaction between MPD and TMC in the presence of  $\text{TiO}_2$  nanoparticles in the organic phase solution. Results revealed that membrane water flux enhanced with increasing  $\text{TiO}_2$  concentration as a result of increasing surface hydrophilicity. The rejection of  $\text{MgSO}_4$  however was reported to decrease sharply upon  $\text{TiO}_2$  addition. The significant changes in salt rejection can be explained by the significant reaction interference of  $\text{TiO}_2$  in the polymerization process, leading to a lower degree of polymerization. Self-assembly of  $\text{TiO}_2$  nanoparticles on the TFC membrane was also investigated to reduce membrane biofouling [47]. It is little probable that  $\text{TiO}_2$  might wash away from membrane surface during operation, owing to the bidentate coordination of carboxylate to  $\text{Ti}^{4+}$  and H-bonding interaction between COOH functional group and  $\text{TiO}_2$  nanoparticles, as shown in Fig. 4. As  $\text{TiO}_2$  could be hybridized with membrane top structure by simply dipping the neat composite membrane in the  $\text{TiO}_2$  colloidal solution, a new type of TFC membrane demonstrating great potential on microbial fouling prevention could be easily produced.

Apart from  $\text{TiO}_2$  addition, there have been other attempts to modify transport properties of RO membranes by employing different types of molecular sieve nanoparticles in PA film [48,49]. Fig. 5 depicts the new concept of embedding molecular sieve nanoparticles in the top selective layer in the preparation of thin film nanocomposite (TFN) membrane. The new concept was first started by Hoek et al. [48] in early 2007. In their pioneering work, it is experienced that the super-hydrophilic and negatively charged zeolite-A embedded throughout PA thin film was able to dramatically improve the permeability of the TFN membrane and remained equivalent salt rejection when compared with the pure PA composite membrane. Since the size of the zeolite particles is designed to match the PA film thickness, it thus provides a favorable flow path through each particle incorporated into membrane, leading to high water permeation [49]. This improved membrane water process is just as effective as current technology but more energy efficient and potentially less expensive. In order to further enhance water molecules transport rate, Fathizadeh et al. [50] in year 2011 impregnated bigger pore size of zeolite NaX (7.4 Å) in the thin film layer with the aims of creating larger molecular tunnels for water to flow. It is found that this particular pore size of zeolite offers preferential flow paths for water molecules of 2.7 Å in diameter but restricts the permeation of hydrated sodium and chloride ions (8–9 Å). Instead of differences in particles' size, controllable design in interfacial chemistry of membrane is also possible using other type of molecular sieves, owing to their tunable functionality with respect to hydrophilicity, charge density and antimicrobial capability. It was recently reported by Kim and Deng [51] that hydrophilized ordered mesoporous carbons (H-OMCs) modified from pristine OMCs were possible to be used as nano-filler in making thin-film polymer matrix of improved properties. According to them, the plasma treated H-OMCs could be well dispersed in the aqueous solution which were likely to minimize large

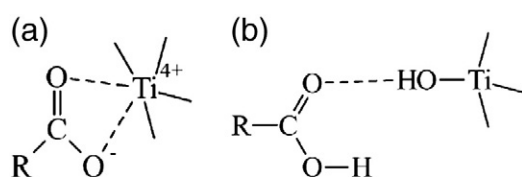


Fig. 4. Mechanisms of self-assembly of  $\text{TiO}_2$  nanoparticles onto thin film layer, (a) by a bidentate coordination of carboxylate to  $\text{Ti}^{4+}$  and (b) by a H-bond between carbonyl group and surface hydroxyl group of  $\text{TiO}_2$  [47].

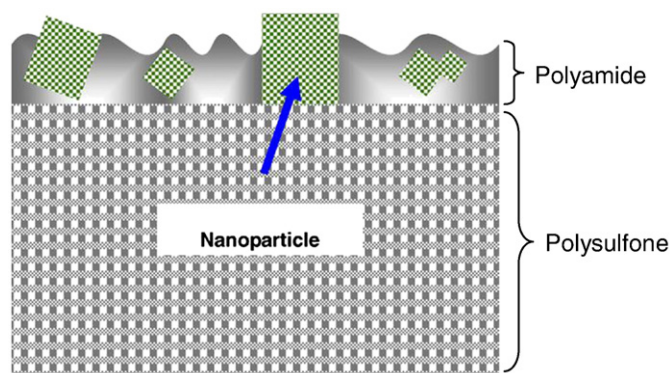


Fig. 5. Conceptual illustration of zeolite-A nanoparticles embedded in the thin film structure of composite membrane [48].

aggregate particles which appeared on the substrate surface during IP process, leading to high quality of thin film layer formed and considerably improved membrane performances with respect to water permeability and bovine serum albumin adsorption. Attempt was also made by Jadav and Singh [52] by incorporating very small size of silica particles (<20 nm) into PA film in an effort to develop TFN membrane with improved separation performance and enhanced thermal stability. Both water permeability and solute selectivity were reported to increase upon the addition of 1–2 wt.% silica. As experienced by the authors, proper control of particle loading is necessary because membranes prepared at high silica loading tend to display thicker top film, accompanied with larger pore size and higher pore number density.

The incorporation of multiwall carbon nanotubes (MWNTs) throughout the superselective thin film layer was also explored as a facile approach to produce superior hydrophilic membrane with fast water molecules transport [53]. As MWNTs were not well-dispersed in the nonpolar solvent of organic phase, a modified IP process was proposed by immersing support membrane into organic phase first prior to the conventional IP process. The TFN membranes have shown to increase both permeability and selectivity ( $\sim 4.5 \text{ l/m}^2 \cdot \text{h}$  at 0.6 MPa,  $\sim 78\%$  at 5 mmol/l  $\text{Na}_2\text{SO}_4$ ) when compared with TFC membrane without MWNTs ( $\sim 1.6 \text{ l/m}^2 \cdot \text{h}$ ,  $\sim 70\%$ ) and TFN membrane prepared by the conventional IP ( $\sim 2.6 \text{ l/m}^2 \cdot \text{h}$ ,  $\sim 74\%$ ). The authors explained that the promising separation is not only caused by the low degree of cross-linking thin layer produced but also the presence of high amount of hydrophilic and negatively charged carboxyl groups on top surface, as evidenced from XPS results.

### 3.2. Applications of different substrates on TFC membranes

A vast variety of polymers has been successfully used as porous supports for TFC membrane fabrication over the years. Among all the polymers used polysulfone (PSF) still remains a mainstay in commercial composite membrane until the present. PSF in general is well accepted as the support film, but it is not without drawbacks being composite membrane support. Its hydrophobic properties and solvent sensitivity are the main concerns to many particularly when the composite membranes are used in separation process of solvent-based solution [12]. Furthermore, these PSF membranes could hardly be used at temperature higher than  $50^\circ\text{C}$  [54]. In light of this, studies have been made on substrate membrane to modify its properties with the objectives of developing chemically and thermally stable polymeric substrates which can withstand harsh environments without compromising water permeability and rejection efficiency.

Generally, thermally stable polymeric substrate is highly desired for many industrial processes. For instance, in pulp and paper industry, a temperature of around  $70\text{--}90^\circ\text{C}$  is required in an integrated mill process which most commercial membranes cannot withstand such

high temperature [11]. In year 2010, Ba and Economy [55] developed a poly(pyromellitic dianhydride-co-4,4'-oxydianiline) (PMDA/ODA PI)-based substrate from precursor polyamic acid (PAA) in the presence of zinc chloride ( $ZnCl_2$ ) in the casting solution. Interaction between zinc ions and carboxylic groups of PAA is found to be able to creating ionic cross-linking structure, facilitating the formation of supporting layer with improved surface properties. In comparison to commercial PSF-based composite membranes, this thermally stable composite membrane provided feasible way to improve significantly water permeability without any drop in salt rejection at elevated operating temperature up to 95 °C. The promising results can be explained by the fact that the high mechanical strength of substrate produced, which resists pore expansion as temperature increases. Kim et al. [56] on the other hand proposed to use superior modified polyvinylidene fluoride (PVDF) as replacement for support layer because fluorinated polymers demonstrated relatively high mechanical strength and good resistance to chemical compared to PSF-based support substrate. Prior to IP process, plasma treatment on the PVDF membrane surface was conducted to improve its hydrophilicity so as it was suitable for fabrication of a PA-PVDF TFC membrane. It is found that under 180 s plasma exposure using oxygen/methane gas mixture, a TFC membrane with outstanding performance was able to be produced, resulting in approximately 37% enhancement in pure water flux and slightly increase in salt rejection compared to the membrane prepared using PSF-based support layer ( $0.19\text{ l/m}^2 \cdot \text{h} \cdot \text{psi}$  and 96% at 2000 ppm NaCl, 2.1 MPa).

Using a novel synthesized poly(phthalazinone ether amide) (PPEA) as substrate material, a thermally stable composite membrane was successfully fabricated by Wu et al. [57]. The resultant composite membrane has shown superior performance in removing dyes from a dye-salt mixed solution at 1.0 MPa, 80 °C. The relative stability of the flux and dye rejection during 5 h of experiment at 80 °C testified the thermal stability of the PPEA-based composite membrane. In addition to this, a supporting membrane made from a novel copolymer – poly(phthalazinone ether sulfone ketone) (PPESK) was also reported exhibiting higher upper temperature limit and better thermal stability than those of typical PSF substrates [58]. Even the PPESK-based substrate was operated at temperature >80 °C, there was no significant sign on pore expansion, proving its extraordinary resistance against thermal attack.

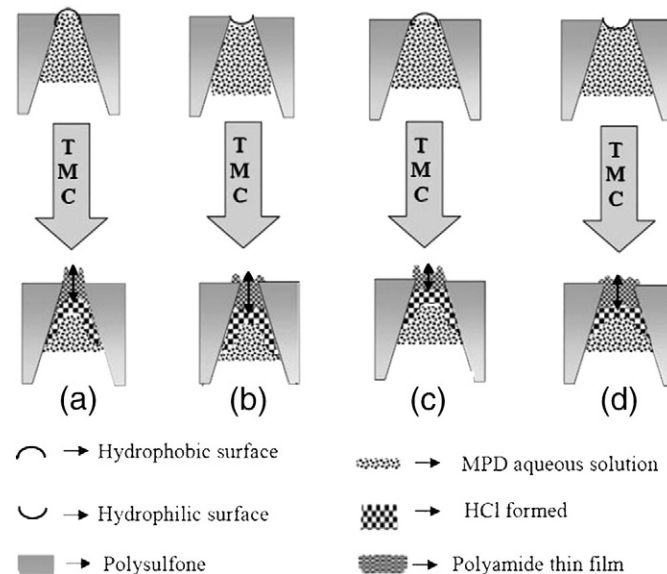
It is also very attractive to apply polypropylene (PP) as support for TFC membrane preparation, owing to its high durability and resistance to chemical, pH variation and a wide range of solvents. As PP is relatively hydrophobic, hydrophilization of substrate is highly recommended prior to IP process. Korikov et al. [30] modified the wettability of PP surface through a chemical surface oxidation method in an effort to improve the adhesion between PA selective layer and supporting layer. Kosaraju and Sirkar [59] on the other hand also utilized PP membrane as supporting substrate in making composite membranes of flat film and hollow fiber. The composite membranes prepared were proved to be stable in methanol permeation and brilliant blue rejection even after 10 weeks of exposure to toluene solution, showing the great potential of PP-based composite membranes in handling a solution consisting of solvent. Other than the polymers mentioned here, alternative polymeric substrates reported with outstanding properties for TFC membrane fabrication include polyacrylonitrile (PAN) [60,61], sulfonated poly(phthalazinone ether sulfone ketone) (SPPEK) [62] and poly(tetrafluoroethylene) (PTFE) [63]. As substrate membranes can be prepared from various polymer materials, the selection of a stable substrate for TFC membrane preparation is therefore subject to the area of industrial applications as well as the cost of polymer material itself. Nevertheless, it must be pointed out that advances in development of stable substrates will offer opportunities to expand application area of membranes particularly to chemical industry of harsh conditions, e.g. petrochemical industry and vegetable oil industry.

Apart from developing substrate membranes with high resistance properties, fundamental studies on the interaction between the ultra

thin selective barrier layer and non-selective microporous substrate should also be focused on. It is true that applications of TFC membranes are well established in industrial activity, but PA-substrate interactions are generally not well documented and understood. In view of this, development of idealized surface properties of support layer for TFC membrane fabrication is an interesting subject to explore. It is worthy to describe how the idealized substrate properties such as pore dimension, porosity, roughness, charge, etc. would match perfectly an idealized PA active layer and form a strong adhesion between layers.

In the literature, only several research works have been reported on the interaction between ultrathin barrier layer and the surface of the underlying microporous support with respect to characteristics of support layer [60,64–66]. In 2001, Oh et al. [60] modified the polyacrylonitrile substrate with NaOH to create a covalent or ionic bond with the PA layer and because of this; higher stability of performance was resulted due to the improved adhesion extent. Similar observation was experienced by Liu et al. [63] where formation of covalent linkages between PTFE substrate film and PA layer led to good layer compatibility and thus greater membrane stability. Singh et al. [64] on the other hand related the changes in PA layer properties to the different pore size distribution of PSF substrate. Smaller pore size distributions of substrate ( $0.07\ \mu\text{m}$ ) is found to have superior salt rejection efficiency compared to bigger pore size distribution ( $0.15\ \mu\text{m}$ ), mainly due to significant increase in skin layer thickness following a reduced penetration of PA into pore of substrate. More recently in 2009, Gosh and Hoek [66] performed a comprehensive investigation on the impacts of PSF support properties on the PA-PSF interfacial composite membranes by producing a wide range of support properties. In order to give clear understanding on the interaction between these layers, conceptual models, as illustrated in Fig. 6 were proposed to explain four different scenarios based on the observations from support membranes with pore size in the range 30–70 nm, water contact angles between 60° and 80° and RMS roughness of 5–10 nm. As can be seen from the figure, it is noticed that thin film layers with different water permeability and structure were possibly produced through a variation in structure and chemistry of PSF-based membrane.

The properties of microporous non-selective layer indeed play an influential role in modifying the characteristics of PA thin film. It could



**Fig. 6.** The impacts of PSF support membrane structure and chemistry in producing MPD-TMC thin film composite membrane with (a) greater permeability and rougher surface, (b) relatively impermeability and intermediate surface roughness, (c) the most permeability and the highest roughness, and (d) the least permeability and intermediate surface roughness [66].



be very attractive to designing commercial TFC membranes with easy-controllable properties using this method but more investigation is needed to find out what is the upper limit of supporting substrate properties for optimized TFC membrane preparation.

### 3.3. Novel/modified IP approach on composite membranes preparation

Concerted efforts have been continuously devoted to modify the procedure of interfacial polymerization process since it was first introduced in the 1960s. It is realized that the modified IP procedure developed to date is mainly focused on improving the interfacial properties of TFC flat sheet membranes and/or forming a defect-free PA skin on a hollow fiber substrate.

Recently, concern was raised on the excessive unreacted polyfunctional acid chloride monomers on the surface of active skin layer following the growing PA film which acts as barrier, restricting the diffusion of amine monomers on the organic phase side. To tackle this problem, Zou et al. [67] used amino monomer to react again with the unreacted acyl chloride groups by placing the membrane in aqueous solution for second time. The membranes prepared using this modified approach yielded a larger amount of amino groups ( $-NH_2$ ) on skin surface and demonstrated better antifouling properties than that of membranes prepared by typical IP approach. According to the authors, multifunctional TFC membranes are possible to be fabricated via this approach by using different polyfunctional amine monomers in the third phase.

Unlike composite membrane in plate and frame or spiral wound configurations, fabrication of composite hollow fiber membrane via IP technique is experiencing a very slow growth, primarily due to the differences in geometry and handling of solution flow. One of the earliest mentions of the TFC hollow fiber membrane was disclosed by Tadros and Trehu in a U.S. patent in 1990 [68]. It is realized that a defect-free PA film is almost impossible to form onto the surface of hollow fiber substrate without modification on IP technique. Due to this difficulty, very little work has been published in this regard; though hollow fiber membrane always offer unique benefit of much higher packing densities than any other membrane configurations.

It is well understood that forming a perfect PA film onto hollow fiber outer surface is much more challenging than forming a thin film onto its lumen surface as coating on outer diameter of hollow fibers could make the neighboring fibers stick to each other, leading to non-reproducibility of TFC hollow fiber membranes. Due to this reason, research work on preparation of interfacially-synthesized PA layer onto the lumen surface of hollow fiber is rather easy to carry out and has therefore gained some attention from several research groups [30,69–71]. Verissimo et al. [69] previously applied an intermediate organic solvent between the aqueous amine solution and the organic acid chloride solution so as to reduce not only the pin-holes on PA layer but also create a stronger adhesion between PA layer and hollow fiber support. In 2007, Yang et al. [71] adopted an easier method to remove the excess PIP solution and droplets by flushing nitrogen gas slowly through the lumen side of the fibers. Results showed that this modified IP procedure is able to produce composite hollow fiber membrane with better stability for long term running, most likely due to the good compatibility between PA active layer and substrate membrane. Korikov et al. [30] on the other hand pointed out that only the appropriate combination of all controlling factors (i.e. hydrophilization of fiber, concentration of monomer and reaction time, degree of removal of excess monomer from lumen side and heat treatment of PA layer formed) during IP process could lead to intact coating in the lumen side of hydrophobic PP hollow fibers. They recommended to use acetone as pre-wetting solution followed by continuous circulation of hot chromic acid solution to hydrophilize pores of PP fibers prior to conventional IP coating process in order to ensure a perfect interfacially film formed [30].

From the standpoint of commercial large-scale production, the current technology of composite hollow fiber membrane preparation is still far from maturity to compete with commercially available composite membranes of flat film and spiral wound format, owing to low reproducibility of the resultant composite hollow fiber. However, from the angle of membrane development, this area is one of the subjects deserving a focused research attention in order to make full use of hollow fiber membrane prepared via IP approach.

## 4. Concluding remarks

The concept of interfacial polymerization has been known for more than 45 years since it was first introduced by Mogan in 1965. Through this concept, an ultrathin selective layer formed by interfacial cross-linking between reactive monomers could be easily established upon a porous supporting membrane, leading to excellent selectivity to divalent ion without sacrificing water productivity. Currently, the use of TFC membranes is found dominating the applications of NF and RO and has showed huge potential to be further used in applications involving gas separation, pervaporation, hydrocarbon fractionations, etc. It is too early to conclude that this technology has already reached the maturity while many opportunities still exist. Efforts should continue on the development of high flux/low pressure composite membrane with enhanced salt rejection as well as improved resistances of fouling, chlorine, solvent, etc. More attention should be paid on the interaction between PA top active layer and underlying supporting membrane. This area deserves intensive studies as no one has conducted comprehensive investigation to describe what kind of idealized substrate surface properties (e.g. pore dimension, surface roughness, hydrophilicity, porosity, etc.) could match perfectly with interfacially synthesized PA layer. Also, development of a strong adhesion between active layer and support is of practical importance to overcome the swelling problem which might limit the operations of composite membranes to certain applications. Continuous improvements in TFC membrane performances with respect to permeability, selectivity and stability perhaps in the future will widen the applications of membranes to new areas.

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