Composite Polyamide Reverse Osmosis (RO) Membranes – Recent Developments and Future Directions

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Abstract

Thin Film Composite – Polyamide (TFC-PA) are commonly used reverse osmosis (RO) membranes in water desalination and waste water applications. Their poor chlorine tolerance and fouling characteristics constrain the life and performance leading to stringent chemical pretreatment requirements. In this context, development of fouling resistant and chlorine tolerant RO membranes would be relevant to reduce the cost of pretreatment in aqueous based separations. In this article, we briefly review the commercially available polymeric RO membranes and then discuss our views on current proposals for fouling resistant RO membranes mostly based on nano-composite material chemistry. In addition, development of similar RO membranes in Desalination Division, BARC is also discussed.

Keywords: Polyamide, composite membrane, reverse osmosis, fouling resistant, chlorine resistant

Introduction

Reverse Osmosis (RO) membrane technology is one of the mature separation technology tools used in various industries for separation either as unit separation process or as combination with other processes. The productive RO membrane should offer simultaneously high solute rejection, water permeability, chemical stability and good chlorine resistance particularly for aqueous separations. Cellulose acetate and aromatic polyamide group of polymers are known as two best polymer materials for reverse osmosis (RO) applications till date [1]. Cellulose acetate (CA), cellulose triacetate (CTA) and cellulose acetate-cellulose triacetate blend (CAB) membranes are prepared generally in asymmetric form and hence give relatively lower flux compared to the new generation thin-film composite (TFC) membranes. In addition, CA based membranes are susceptible to microbiological attack, undergo compaction at higher pressures, and limited chemically stability. On the other hand, polyamide membranes exhibit more flux at a given applied pressure, less microorganism susceptible and are more stable over a wider range of pH values than CA membranes. Thus, polyamide TFC membranes are currently the most widely used desalination membranes. TFC-RO membranes comprise of ultra-thin polyamide film formed in situ by polycondensation reaction of polyfunctional amine and acid chloride monomers over a porous polysulfone support membrane [2]. However, their poor chlorine tolerance (chlorine is inexpensive and effective biocide widely used in water pretreatment) constrains their life and performance characteristics leading to stringent pretreatment requirements. High feed pressures applied for RO applications damage polymeric membranes internally due to physical compaction of the porous support membrane and hence irreversible, internal fouling remains a serious concern for RO membranes till date. Apart from the internal fouling, surface fouling due to
scaling and deposition of organic materials, bioorganisms etc. also is a serious problem limiting the life of RO membranes. Hence development of fouling and chlorine resistant RO membrane with better water flux is a thrust area of membrane research. In this article, we discuss the present status of composite polyamide RO membranes and future direction of research towards development of more fouling resistant and chlorine resistant RO membranes keeping salt rejection and water permeability intact or better than the present membranes.

**Strategies for synthesis of high flux fouling resistant and chlorine resistant polyamide membrane**

More than 30 years, water flux and solute rejection of polyamide TFC membranes have continually improved but still these membranes are not fouling resistant. Internal fouling due to compaction can be managed to certain extent if macrovoids in support membrane can be lesser number and/or by using higher molecular weight polymer. Similarly, organic and biofouling resistant membrane needs to be such that the foulants should not attach to the surface of the membrane easily. In most of the studies so far, only one type of fouling can be solved at a time. For example, if higher molecular weight polymer is used, internal fouling due to compaction can be solved by certain extent but it does not give surface fouling resistant membranes. On the other hand, in surface functionalization by chemical modification of polymer to get surface fouling resistant membrane, chain breakage or degradation of polymer results in low compaction resistant membranes. Similarly, blending of functional polymer with base polymer can also used for preparation of organic and biofouling resistant membranes but very few polymers are compatible with commonly used membrane polymers. However, concept of a mixed-matrix membrane (a small filler material is dispersed throughout a larger polymeric matrix) has brought new degrees of freedom to the development of advanced membrane materials with improved mechanical, chemical, and thermal stability, as well as enhanced separation capacity [3]. And flux can also be increased by using porous nanomaterials in mixed-matrix membrane which opens a preferential flow path for pure water to flow from the feed side to the permeate side of the membrane.

For preparation of chlorine resistant polyamide composite membrane, correlation between the chemical structure of polyamides and membrane chlorine interaction need to be known. In case of polyamides synthesized from aromatic primary diamines compounds, N-chlorination followed by chlorination of aromatic ring by Orton Rearrangement is responsible for changing chemical property of polyamide [4]. The Orton rearrangement takes place only when amide linkage is directly connected with benzene ring (especially from amine side). Aliphatic polyamides, on reaction with chlorine yield N-chlorinated amide which can be regenerated to the initial amide by treatment with reducing agent [4]. Tertiary polyamides are inactive towards oxidative chlorine. So, the strategies for better chlorine resistance are: (a) by protecting active sites on aromatic rings, (b) by synthesizing polymers with tertiary amide groups, (c) by incorporating aliphatic secondary and tertiary amide linkage not directly connected with aromatic rings. Other than polyamides, polysulfone has much better chlorine resistance as it has chemically strong bonds between carbon, sulfur, and oxygen. But polysulfone is hydrophobic and hence RO types of membrane cannot be prepared unless chemical structure of polysulfone is altered by introduction of controlled levels of hydrophilicity while retaining its physical properties. Sulfonated polysulfone has been reported for making nanofiltration (NF) and loose RO membranes that are found highly tolerant to aqueous chlorine solution [5]. However, these are asymmetric membranes and hence flux is expected to be less
than that of TFC membranes. Some of the nanomaterials like carbon nanotube (CNT) can have certain extent of chlorine tolerance and hence can be embedded onto the membrane surface to make it chlorine resistant.

**Discussions**

*Present status in developments of thin film composite (TFC) RO membranes*

The present RO membrane market is dominated by thin film composite (TFC) polyamide membranes consisting of three layers: a polyester nonwoven fabric act as structural support (~100μm thick), a microporous interlayer support of polymer like polysulfone (~40-50 μm thick), and an ultra-thin polyamide barrier layer on the top surface (~0.2-0.25μm thick). However, some of the other polymeric materials other than polyamide also work as very good TFC RO membranes. Table 1 shows details of some of the commercially available TFC RO membranes and similar membranes developed in our division in terms of polymer used as thin film as well as membrane performance in RO testing condition [2, 6]. The membrane preparation machines used for TFC RO membrane making in two steps are shown in Fig.1. The processes and exact chemistries for producing most of the successful commercially available RO membranes

![Fig. 1: Pictures of (a) support membrane casting machine and (b) thin-film polyamide coating machine](image)

**Table 1: Details of the some of the commercially available TFC RO membranes**

<table>
<thead>
<tr>
<th>RO membrane</th>
<th>Material</th>
<th>Testing condition (Pressure, Feed solution)</th>
<th>Permeate flux (m². m⁻². day⁻¹)</th>
<th>Salt rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-200</td>
<td>Sulfonated polyfuran</td>
<td>&gt; 100 bar, 3.5% NaCl</td>
<td>0.8</td>
<td>99.8</td>
</tr>
<tr>
<td>PES-1000</td>
<td>Polyether-polyfuran</td>
<td>&gt; 69 bar, 3.5% NaCl</td>
<td>0.5</td>
<td>99.9</td>
</tr>
<tr>
<td>CP</td>
<td>Sulfonated polysulfone</td>
<td>&gt; 69 bar, 3.5% NaCl</td>
<td>0.06</td>
<td>98</td>
</tr>
<tr>
<td>NS-100</td>
<td>Polyamide (aliphatic-aromatic)</td>
<td>&gt; 100 bar, 3.5% NaCl</td>
<td>0.7</td>
<td>99</td>
</tr>
<tr>
<td>PA-300/RC-100</td>
<td>Polyamide (via polyepiamine)</td>
<td>&gt; 69 bar, 3.5% NaCl</td>
<td>1</td>
<td>99.4</td>
</tr>
<tr>
<td>NS-300</td>
<td>Polypiperazine-amide</td>
<td>&gt; 100 bar, 3.5% NaCl</td>
<td>3.3</td>
<td>68</td>
</tr>
<tr>
<td>FT-30</td>
<td>Fully aromatic polyamide</td>
<td>&gt; 15 bar, 0.2% NaCl</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>UTC series</td>
<td>Fully aromatic polyamide</td>
<td>&gt; 15 bar, 0.5% NaCl</td>
<td>0.8</td>
<td>98.5</td>
</tr>
<tr>
<td>BARC-TFC1</td>
<td>Polyamide (aliphatic-aromatic)</td>
<td>10 bar, 0.2% NaCl</td>
<td>0.45</td>
<td>92.0</td>
</tr>
<tr>
<td>BARC-TFC2</td>
<td>Fully aromatic polyamide</td>
<td>10 bar, 0.2% NaCl</td>
<td>0.55</td>
<td>97.0</td>
</tr>
</tbody>
</table>
are still proprietary. A recent study substantially revealed the physicochemical properties of some of the commercially successful RO membranes [7]. The membrane samples studied included two high pressure seawater RO membranes (SWC4 and SW30HR) and six brackish water RO membranes (LFC1, LFC3, ESPA3, LE, XLE, and BW30). Membranes SW30HR, BW30, LE, and XLE are Dow FilmTec (Minneapolis, MN, USA) membrane and SWC4, LFC1, LFC3, and ESPA3 are Hydranautics (Oceanside, CA, USA) membrane. It was found that the uncoated fully aromatic RO membranes had surface elemental compositions very close to the predicted values for polyamide based on the classical interfacial polymerization chemistry of meta-phenylenediamine and trimesoyl chloride but the coated membranes had higher oxygen and lower nitrogen content. The presence of -OH groups in coating layer was further confirmed by high resolution XPS scans. Streaming potential measurements showed the zeta potential of coated membranes was significantly less negative than that of uncoated ones, consistent with ATR-FTIR and XPS results. The uncoated membranes are ESPA3, SWC4, LE, XLE and probably the polyvinyl alcohol (PVA) coated membranes are LFC1, LFC3, BW30, and SW30HR. So far the best commercially successful TFC polyamide RO membrane has the ultra-thin barrier layer made of cross-linked aromatic polyamide prepared via interfacial polymerization of meta-phenylenediamine and trimesoyl chloride (as given in Fig. 2). From Table-1, it can be seen that BARC-TFC1 and BARC-TFC2 are typically brackish water RO membranes. BARC-TFC2 membrane that is prepared using meta-phenylenediamine - trimesoyl chloride system gives better flux membranes with higher salt rejection than that of prepared using polyethylene imine (PEI) – isophthaloyl chloride (IPC) system (BARC-TFC1). However, the application areas where upto 92% solute rejection with moderate product permeation is acceptable, BARC-TFC1 is more preferable than BARC-TFC2 membrane because stability of raw materials used in former membrane is better than that used in later membrane. Polyethylene imine (PEI) is a very stable chemical and it gives more stable aqueous solution (does not oxidize or change color in presence of air and light) than meta-phenylenediamine. Hence, PEI aqueous solution is used repeatedly and it gives obvious economic advantage. In addition, isophthaloyl chloride (IPC) is easy to purify by simple recrystallization from hexane unlike trimesoyl chloride. But for application where high salt rejection is desired, BARC-TFC2 type membranes need to be used. So, both the reagents (meta-phenylenediamine and trimesoyl chloride) either need to be prepared fresh or need purification just before use to make high salt rejecting TFC RO membranes.

Commercially available TFC polyamide membranes are not fully fouling resistant though they show excellent permeability and selectivity. By membrane surface hydrophilization in post-treatment, different researchers attempted to increase further the permeability and organic fouling resistance upto a certain extent but problem of physical

**Novel composite polyamide RO membranes**

![Fig. 2: Fully aromatic polyamide prepared via interfacial polymerization of meta-phenylenediamine and trimesoyl chloride.](image-url)
Compaction, biofouling and chlorine tolerance was still not satisfactory. In this section, we limited our discussions only on development of fouling resistant TFC polyamide membranes using nanocomposite materials chemistry and of chlorine resistant TFC polyamide membranes using polycondensation reaction of easily synthesized new reactants.

*Thin film nanocomposite (TFN) RO membranes with enhanced permeability and fouling resistance*

It is known that the rejection of monovalent ion in a mixed ion solution is lower than that for a pure solution of monovalent salt. So, the filtration mechanism is not only dependent on size exclusion, but also on Donnan exclusion due to the charged double layer induced by adsorbed ions on the pore or the intercrystalline walls. But ions can be completely excluded by membranes with pore sizes smaller than the size of the hydrated ions in feed solution. Nanoparticles like LTA-type zeolite nanoparticle exhibits 0.4nm pores and MFI-type has 0.56 nm pores which are lower than the size of the common ions presents in contaminated water but bigger than the size of a water molecule (0.278nm). So, LTA-type zeolite particles in the size range of 50–150nm with a Si/Al ratio of 1.5 are taken to make inorganic-organic thin film nanocomposite (TFN) membranes with assumption that nanoparticles will create a straight path for flowing of pure water only retaining salt ions from salt water. Moreover, these particles are very hydrophilic (contact angle $< 5^\circ$), with negative charge which are highly repulsive to anions. The zeolite nanoparticles are dispersed in hexane solution of trimesoyl chloride before the interfacial polycondensation reaction takes place. TFN RO membranes are prepared with various zeolite loadings, size and consequent changes in membrane characteristics have been reported [8, 9].

TFN membranes are smoother, more hydrophilic and more negatively charged than normal TFC membranes prepared under identical condition. Hence TFN membranes have less fouling tendency than the TFC membrane. Also TFN membrane exhibits two times more flux and a slight improvement in salt rejection relative to the hand cast TFC membrane without zeolite nano-particles. Fig. 3 gives conceptual illustration of TFC and TFN membrane structures. Fig. 4 illustrates the membrane separation performance as a result of variation in zeolite nanoparticle loading.
In another study, the compaction behavior of hand-cast polysulfone-nanocomposite supported polyamide composite membranes relative to pure polysulfone supported polyamide composite membranes are evaluated to control irreversible, internal fouling of RO membranes by physical compaction [10]. Nanocomposite support membranes are prepared using silica particles in the size range of approximately 34 to 130 nm and zeolite particles with size range of approximately 250 to 300 nm. Cross-sectional SEM images of uncompacted (as-cast) and compacted at two different pressures namely, 1724 kPa and 3448 kPa are shown in Fig. 5. The figure suggests that membranes containing nanoparticles underwent less compaction, while the pure polymer based membrane experienced a drastic change in thickness and support structure.

A recent study suggests that membranes comprising sub-nanometer diameter CNT can desalt water when used as RO membranes [11]. The narrow pores reject ions extremely well, but conduct water at 5-1000 times (depending on the loading of nanotubes) the rate of commercially available TFC RO membranes. The primary causes of salt rejection and water transport in these studies is the narrow, smooth, nonpolar nature of the CNTs; hence, separation performance may not be specific to chirality of concentric walls. To get photocatalytic reactivity and antibiofouling properties in TFC membrane, anatase TiO$_2$ nano-particles (<10 nm) are dip-coated onto...

Fig. 5: SEM cross-section images of TFC (a1-uncompacted, a2-compacted at 1724 kPa, a3-compacted at 3448 kPa) and ST50 silica-TFC (b1-uncompacted, b2-compacted at 1724 kPa, b3-compacted at 3448 kPa) membranes
an interfacially polymerized TFC polyamide membrane with a surface layer functionalized with carboxylate groups [12]. These membranes have been tested with E. coli-containing feed water and confirmed superior anti-biofouling properties in particular with the aid of UV excitation, without compromising the flux and salt rejection of the original membrane.

**Chlorine tolerant TFC and TFN membranes**

The chlorine resistant polyamide membranes reported so far are either prepared from aliphatic polyimides or from some complicated polymeric systems where water flux is less. Moreover, aliphatic polyimides can not be used at higher pressure due to compaction problem. In order to get high flux chlorine resistant polyamide membrane, the membrane polymer should have benzene ring to give structural rigidity and mechanical strength, secondary aliphatic amide groups not directly connected with benzene ring for chlorine resistivity and substituted hydrophilic group in benzene ring for higher hydrophilicity. To get the polymers with above characteristics, the following system can be tried.

For TFC polyamide membrane preparation, amine part can be poly (enamine)-graft-poly (m- nitrostyrene) and acid part can be oxalic acid. So, poly (enamine)-graft-poly (m-nitrostyrene) need to be synthesized first from graft copolymerization of enamine over poly (m-nitrostyrene) polymer. Reaction of this graft copolymer with oxalic acid over support membrane gives cross linked polyamide TFC membrane. In this TFC membrane, both amide group and aromatic rings are present but amide linkage is not connected directly with aromatic ring.

1st Step: Synthesis of crosslinked copolymer of Poly(enamine)-grafted-poly(nitrostyrene)

Graft copolymerization of poly (meta-nitrostyrene) with enamine could be followed procedure similar to graft copolymerization of polyvinylidene difluoride (PVDF) with N-isopropylacrylamide as reported in literature [13].

For sake of simplicity in writing the chemical equation, the following notation is used in the second step of the reaction.
2nd Step: In situ polycondensation of Poly (enamine)-grafted-poly (nitrostyrene) with oxalic acid.

In this case, oxalic acid is water soluble but difficulties may arise if poly(enamine)-graft-poly (m-nitrostyrene) copolymer is not soluble in a water immiscible organic solvent. In case suitable water immiscible organic solvent is not found, then the target polymer can be synthesized by solution polymerization technique and the synthesized polyamide polymer can be used for making asymmetric membranes.

Recently, it was reported that nanocomposite TFC RO membranes containing multi-walled carbon nanotube (MWCNT) has enhanced chlorine tolerance than normal TFC membranes [14]. In the MWCNT loading range of 0.1–1% (w/v), chlorine resistance of organic/inorganic nanocomposite RO membranes was improved as the amount of MWCNT increased.

In BARC, we have already perfected silver and silver-copper based nanocomposite biofouling resistant ultrafiltration (UF) membranes [15]. Nanocomposite UF membranes are generally more compaction resistant than corresponding pure polymer
membrane. So, using these compaction and biofouling resistant support membranes (silver and silver-copper based polysulfone nanocomposite), preparations of CNT and porous silica based thin film nanocomposite (TFN) membranes are on progress to get high flux, fouling resistant and chlorine tolerant membranes. A conceptual picture of a probable fouling resistant nanocomposite membrane is given in Fig.6.

Conclusions
More resistance to physical compaction, chemical, biological and chlorine attack is most desirable to make significant reductions in both capital investment and operating costs of desalination by RO. Incorporation of nano-technology in membrane preparation could offer an attractive alternative to prepare real fouling resistant membranes and hence many scientists believe that nanotechnology would bring revolutionary advancements to the desalination industry. Among others, zeolite, silica based thin film nano-composite membranes and carbon nano-tube membranes are two most likely novel materials for enhanced RO desalination performance in the future but still a number of challenges remain with regard to their practical implementation. The major practical challenges are (a) high cost of nanomaterials, (b) the extra energy required to effectively disperse the nano-particles into the barrier layer, (c) health and safety issues for use of nanomaterials in the domestic water industry as sometime these are toxic and (d) the difficulty in scaling up nano composite membrane manufacturing processes for commercial use. However, zeolite and silica based thin film nanocomposite membranes appear to be more readily adaptable to commercial use due to their similarity to current commercial RO membranes than carbon nano-tube based membranes where alignment of CNT into the polymer matrix is still a challenge. However, for nanocomposite chlorine tolerant membrane, low concentration of CNTs can be used in which at least few CNTs remain aligned and others give chlorine tolerances.

References