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Unique roles of aminosilane in developing anti-fouling thin film composite (TFC) membranes for pressure retarded osmosis (PRO)

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HIGHLIGHTS

- This work intends to develop anti-fouling membranes for PRO process.
- Aminosilane was used as a grafting agent for PEI TFC PRO membranes.
- Aminosilane can modify the support and the selective layers of PRO membranes.
- The modified membrane had remarkably enhanced hydrophilicity to reduce fouling.

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ABSTRACT

Pressure retarded osmosis (PRO) has been identified as a promising technology to harvest the salinity gradient energy. For practical applications of PRO process, membrane fouling is a challenging issue as it leads to severe decline of PRO performance in terms of water flux and power density. It is imperative to develop anti-fouling membranes for PRO process. The current study demonstrated the unique roles and the great potential of aminosilane in developing anti-fouling thin film composite (TFC) PRO membranes. Experimental results revealed that aminosilane as a grafting agent can modify both the support layer (interior) and the selective layer of PRO membranes with remarkably enhanced hydrophilicity via a very simple grafting procedure. In the grafting, aminosilane was able to minimize the pore-blocking issue with almost no increase in the membrane structural parameter (S). Meanwhile, the membrane mechanical strength was well maintained with the grafting due to the capability of aminosilane as a cross-linker. With enhanced hydrophilicity, it was interestingly found that the water permeability (A) was doubled, while the salt rejection was maintained nearly unchanged. The combination of these effects brought in remarkably enhanced water flux, power density and anti-fouling property to the resultant membrane.

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1. Introduction

Salinity gradients available from salt concentration difference between fresh water and salty water have been identified as one of the renewable and clean energy resources for sustainable development [1,2]. Pressure retarded osmosis (PRO) proposed by Loeb [3] is one of the most promising technologies for harvesting the salinity-gradient energy and has attracted increasing attention for its great potential in addressing the water and energy related issues [1,2,4–6]. In PRO, water from a low salinity stream (feed water) permeates through a semi-permeable membrane to a pressurized high salinity stream (draw solution) that can further drive a turbine for power generation [7].

In practical applications, membrane fouling has been recognized to be one of the major factors limiting the PRO performance [8–13]. Compared to the fouling in conventional pressure-driven processes such as reverse osmosis (RO), membrane fouling in PRO is more complicated and its control is more challenging, given the fact that the PRO is typically operated with the membrane support layer facing the feed water [8–13]. In this membrane orientation, the foulants in the feed water can penetrate into the porous support layer, which would further cause severe internal fouling when the foulants clog the pores of the support layer and/or deposit on the back surface of the active layer [10,11,13]. To mitigate the internal fouling within the support layer of PRO membrane, one of feasible strategies is to modify the properties of PRO membrane support layer to reduce its affinity with the foulant [13]. However, there were limited relevant works reported in the literature [14].

In general, a membrane with greater hydrophilicity is less prone to fouling due to stronger repulsive foulant-membrane interaction [13,

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15–19]. In this regard, improving the hydrophilicity of the PRO membrane (particularly the support layer) could be of great help to improve the membrane anti-fouling properties, for which grafting has been demonstrated to be a useful technique [14,15,20–23]. When using the grafting technique for PRO membrane modification/fabrication, several issues must be further addressed. Firstly, the hydrophilic treatment via grafting should be applied on the interior of membrane support in addition to the membrane surface, since the internal membrane fouling is a major concern in PRO process. Secondly, grafting within the membrane support layer may cause a potential problem of pore-blocking, resulting in an increase in the structural parameter of the membrane support. Thirdly, grafting usually involves a complicated multi-step procedure and is not easy to operate in practice. To overcome above issues, it is essential to select a suitable grafting agent, which (1) can offer a hydrophilic nature after grafting, (2) possesses a small size to minimize pore blocking, and (3) has simple and direct reaction with both membrane support and active layer.

Considering the above, aminosilane such as 3-aminopropyltrimethoxysilane (APTMS) is of interest to us. Aminosilane consists of both alkoxy and aminoalkyl groups connected to the Si atom, initially known as a precursor in the process of silanization and then extensively used in composites and adhesive formulations [24]. The hydrolysis of the alkoxy groups of aminosilane can lead to the generation of hydroxyl groups that offer a hydrophilic nature. Meanwhile, the active aminoalkyl groups of aminosilane give its potential to be grafted with membranes containing aromatic imide groups by a simple reaction such as aminolysis. For example, imide ring-opening reaction has been well reported as an efficient grafting method for fabricating functional membranes based on aromatic imide polymers [25,26]. Coincidentally, aromatic imide polymers such as Ultem® 1000 polyetherimide (PEI) [27,28], Torlon® 4000T-MV poly(amide-imide) (PAI) [29] and Matrimid® 5218 polyimide (PI) [30] are widely used for the fabrication of PRO membranes. All of these suggest that aminosilane can be a suitable grafting agent in developing anti-fouling thin film composite (TFC) PRO membranes via grafting technique.

In the current study, APTMS-grafted PEI TFC PRO hollow fiber membrane was fabricated and evaluated to demonstrate the unique roles and great potential of aminosilane in the development of anti-fouling membranes for PRO application.

2. Experimental

2.1. Materials and chemicals

The commercially available aromatic imide polymer, Ultem® 1000 polyetherimide (PEI, General Electric Plastics) was selected as the polymeric material for membrane fabrication. The commercially available aminosilane, 3-aminopropyltrimethoxysilane (APTMS, >97%, CAS#13822-56-5, Sigma-Aldrich) was selected as the grafting precursor. *N*-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck) was used as a solvent for dope preparation. Lithium chloride (LiCl, >99%, CAS#7447-41-8, Sigma-Aldrich) was used as a pore-former. Trimesoyl chloride (TMC, >99%, CAS#4422-95-1, Sigma-Aldrich) and *m*-phenylenediamine (MPD, >99%, CAS#108-45-2, Sigma-Aldrich) were used as monomers for the interfacial polymerization. Cyclohexane (CAS#110-82-7, Sigma-Aldrich) was used as a solvent for TMC. Glycerol (CAS#56-81-5, Merck) and Isopropyl alcohol (IPA, CAS#67-63-0, Merck) were used as wetting solvents. Dextran $(C_6H_{10}O_5)_n$ samples with different molecular weights (molecular weight from 1500 to 400,000 Da, CAS#9004-54-0, Sigma-Aldrich) were used to determine the molecular weight cut-off (MWCO). Sodium chloride (NaCl, CAS# 7647-14-5, Merck) was used to prepare the draw solutions. Humic acid (CAS#68131-04-4, Sigma-Aldrich) was selected as model organic foulant to evaluate the membrane anti-fouling properties in the PRO fouling tests. Calcium chloride ($CaCl_2$, CAS#10043-52-4, Sigma-Aldrich) was used to adjust the background electrolyte composition of humic acid solutions. The deionized (DI) water was supplied by a Milli-Q system.

2.2. Membrane fabrication

The PEI hollow fiber membrane substrate in the current study was fabricated by the dry-jet wet spinning technique. The dope solution was prepared by dissolving the pre-dried PEI polymer and the LiCl additive in the NMP solvent with stirring at 60 °C. The resultant homogenous solution was then transferred into a stainless tank, and degassed under a vacuum at room temperature before spinning. In the spinning process, the dope was extruded through a spinneret at a controlled rate by a gear pump and went through an air gap into a coagulation bath. The resultant PEI hollow fibers were then collected and stored in a water bath for at least 3 days to remove residual NMP solvent. The spinning conditions are listed in Table 1.

Subsequently, the polyamide (PA) selective layer was synthesized on the inner surface of the as-spun hollow fiber PEI substrate by the interfacial polymerization of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) as monomers [27,31–33] to produce the TFC PEI hollow fiber membrane.

Finally, the as-prepared TFC PEI hollow fiber membrane was entirely immersed in a mixed solution (IPA/water, wt. 1:1) of APTMS (2 wt.%) at 60 °C for 120 min to generate the APTMS-grafted TFC PEI hollow fiber membrane. The resultant membrane was stored in a water bath for at least 3 days to remove unreacted APTMS.

2.3. Membrane characterization

The pure water permeability (PWP) of the membrane substrate was examined by a cross flow filtration set-up at a constant pressure of 1.0 bar. The molecular weight cut-off (MWCO) (defined as the molecular weight at 90% rejection) was measured on a Polymer Laboratories-GPC 50 Plus system. The overall porosity (ε) was determined through the gravimetric method. The dynamic contact angle was tested with a tensiometer (DCAT11 Dataphysics). And the mechanical strength was measured by a Zwick 0.5 kN universal testing machine. The detailed methods to determine the pure water permeability (PWP), molecular weight cut-off (MWCO), overall porosity (ε), dynamic contact angle and mechanical strength of hollow fibers are available from our previous publication [32]. The contact angle of the selective layer was measured by the sessile drop method coupled with digital image analysis (Contact Angle System OCA, DataPhysics Instruments GmbH). A field emission scanning electronic microscope (FESEM, JEOL JSM–7600F) equipped with an energy dispersive X-ray (EDX) spectrometer was used for morphological observation. ATR-FTIR spectra were collected by an IR Presitige-21 (Shimadzu) spectrometer over a scanning range of 650–4000 cm^{-1} with a resolution of 4.0 cm^{-1}.

2.4. Determination of water permeability, salt permeability and structural parameter

Prior to all the tests, 5 pieces of the TFC hollow fiber membranes were sealed in a Teflon module with an effective length of 22 cm.

Table 1
Spinning conditions for the fabrication of PEI hollow fiber substrate.

Dope composition (PEI/LiCl/NMP) (wt.%)	14/4/82
Dope flow rate (g/min)	3.26
Bore fluid (NMP/H_2O) (vol.%)	80/20
Bore fluid flow rate (ml/min)	2.5
Air gap (cm)	5
Take-up speed	Free fall
External coagulant	Tap water
Spinning temperature (°C)	23
Spinneret dimension, OD/ID (mm)	1.65/0.72

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