



Polyamide-imide hollow fiber membranes crosslinked with amine-appended inorganic networks for application in solvent-resistant nanofiltration under low operating pressure

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ABSTRACT

The development of polyamide-imide (PAI) hollow fiber membranes for solvent-resistant nanofiltration (SRNF) in polar aprotic solvents such as dimethylformamide (DMF) under low operating pressure of 2 bar is reported in current study. Highly porous PAI substrates were fabricated and crosslinked with (3-aminopropyl)trimethoxysilane (APTMS). The resultant membranes were solvent-stable and showed higher hydrophilicity and better mechanical property. A 30-min conditioning with either isopropanol or deionized water after the crosslinking reaction was found to affect the morphology of the membranes and thus their nanofiltration performance. Membranes conditioned with isopropanol consistently showed higher solvent fluxes coupled with lower rejections of Rose Bengal (RB) ranging 75–87%. On the other hand, membranes conditioned with deionized water had lower fluxes and high RB rejections of 96–99%. The best-performing membrane achieved a permeability of 6.4 L/(m² h bar) in IPA and 0.9 L/(m² h bar) in DMF with RB rejections of over 97% and 98%, respectively, under 2 bar operating pressure, showing their potential to be used in SRNF processes effectively.

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1. Introduction

The development of membranes for solvent-resistant nanofiltration (SRNF) processes have expanded their application potential in various industries such as petrochemical, food, fine chemical and pharmaceutical industries. By separating molecules ranging in 200–1000 Da through applying a pressure gradient across a membrane, SRNF can offer many advantages over conventional industrial separation processes, such as lower energy consumption and recycling of valuable solvents and reagents [1]. The key challenges faced in developing SRNF membranes lie in ensuring their excellent stability in organic solvents and achieving acceptable solvent permeabilities and target solute rejections over long-term operation. The majority of SRNF membranes that have been developed in the lab or commercialized are made from polymeric materials due to their lower cost, excellent processability and ease of scale-up. Significant progress has been made over the past

decade to improve the stability of polymeric membranes especially in aggressive solvents like dimethylformamide (DMF) and N-methyl pyrrolidone (NMP), for which integrally skinned asymmetric (ISA) and thin film composite (TFC) membranes have been developed [2–6].

TFC membranes usually comprise of polydimethylsiloxane (PDMS) [7,8] or polyamide [5,9,10] on a porous support while the polymers that have been used to fabricate integrally skinned asymmetric SRNF membranes include polyimide (PI) [2,3,11–13], polysulfone [13–15], polyphenylsulfone (PPSU) [16–18], poly(ether ether ketone) (PEEK) [19–22], polyaniline [4,23,24] and polybenzimidazole [25,26]. The crosslinking of polymer chains to form stable three-dimensional network structures has been shown to improve the chemical and mechanical stability of membranes. In particular, crosslinked polyimide membranes have found their application in SRNF in addition to gas separation and pervaporation [27]. For example, Lenzing P84[®] polyimide membranes showed good chemical stability in NMP, DMF, tetrahydrofuran and dichloromethane after being crosslinked by aliphatic diamines [2]. Recently, Siddique et al. [28] reported the advantages of using 3-aminopropyl trimethoxysilane (APTMS) as the crosslinking agent. Through the hydrolysis and condensation of methoxysilane

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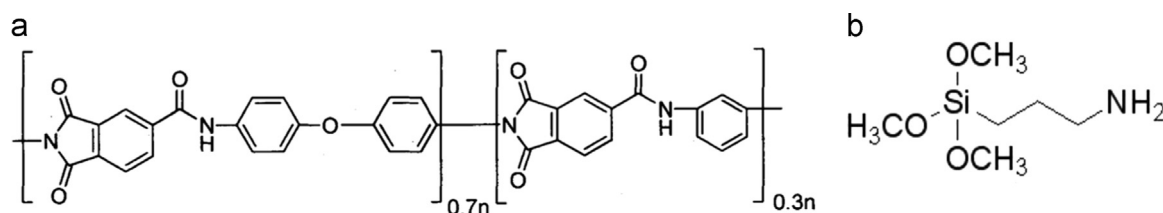


Fig. 1. Chemical structure of (a) PAI and (b) APTMS.

in APTMS, a rigid inorganic Si–O–Si network was obtained throughout the polyimide membrane, thus improving the mechanical properties of the membrane in addition to its chemical stability. Dutczak et al. [29] successfully crosslinked commercial polyamide-imide (PAI) support membranes using di-isocyanates. The crosslinked membranes were resistant to NMP and showed good mechanical properties.

Currently, commercial SRNF membranes are limited to a few flat sheet and spiral-wound modules [30]. Hollow fiber SRNF membranes are not known to be commercially available although they have the potential to make the process more efficient and attractive by operating at lower pressures and providing a higher membrane area to module volume ratio which enables the construction of more compact and simpler modules that are easy to scale-up [31]. The few hollow fiber membranes that have been applied in SRNF so far were evaluated at around 5 bar [18,24]. Literature has reported nanofiltration hollow fibers for water softening applications that are capable of operating at pressures as low as 2 bar, which would help to reduce energy consumption, increase productivity and lower costs [32–34]. Low pressure operation was possible due to the fabrication of a highly porous substrate that could reduce mass transfer resistance significantly, thus allowing the resultant composite membrane to achieve high flux and rejection. A similar strategy will be attempted in this study to develop hollow fibers that can be applied in SRNF under low pressure.

This study aims to fabricate and crosslink polyamide-imide (PAI) hollow fiber membranes to make them suitable for SRNF applications. PAI is chosen due to its excellent processability, mechanical property and good chemical and thermal stability [35]. PAI hollow fibers can be fabricated easily by non-solvent induced phase separation technique and have shown good performance in forward osmosis process after modification on a porous ultra-filtration substrate [36,37]. After fabrication, the PAI membranes will be crosslinked with APTMS through a ring-opening reaction between the imide groups of PAI and amine groups of APTMS which was previously confirmed by Zhang et al. [38]. To the best of our knowledge, this is the first study to develop PAI hollow fiber membranes for application in polar aprotic solvents under low operating pressure of 2 bar. The morphology, gel content, swelling, contact angle and mechanical strength of the modified membranes will be characterized and their performance in two common solvents, isopropanol (IPA) and DMF, will be evaluated.

2. Experimental

2.1. Materials

Polyamide-imide (PAI) Torlon[®] 4000T-MV, supplied by Solvay Advanced Polymers, was used to fabricate hollow fiber substrates. N-Methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck) and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) were used as the solvent and additive for preparing the dope solution respectively. Dextran with molecular weights from 6 kDa to 500 kDa (CAS#9004-54-0, Sigma) were used to

characterize the molecular weight cut-off (MWCO) of the hollow fiber substrates. The substrates were crosslinked with (3-aminopropyl)trimethoxysilane (APTMS, 97%, CAS#13822-56-5, Sigma). Raffinose (594.52 Da, CAS#17629-30-0, Merck), polyethylene glycol (PEG, 1 kDa, CAS#25322-68-3, Merck, and 2 kDa, Sigma) were used to measure the pore size distribution of the crosslinked membranes. For nanofiltration tests, iso-propanol (IPA, ≥ 99.8%, CAS#67-63-0, Merck) and N,N-dimethylformamide (DMF, CAS# 68-12-2, Merck) were used as the solvents and Rose Bengal (1017.64 Da, 95%, CAS#632-69-9, Sigma) was employed as the model solute. Milli-Q deionized water (18 M Ω cm) was used in all aqueous solutions. All the reagents were used as received. The chemical structures of PAI and APTMS are given in Fig. 1.

2.2. Fabrication of PAI hollow fiber substrates

Torlon[®] 4000T-MV was dried in a vacuum oven at 50 °C for at least 12 h to remove moisture before preparing the dope solutions. The polymer and LiCl were dissolved in NMP in a jacket flask and mechanically stirred for 3–4 days at 60 °C until a homogenous dope solution was obtained. Then, the solution was cooled to room temperature and degassed under vacuum overnight before spinning. A dry-jet wet spinning technique was used to fabricate the hollow fiber substrates. The dope and bore fluid were extruded through a spinneret at controlled flow rates and went through an air gap before entering the coagulation bath. The hollow fibers were collected by a roller and stored in tap water for 2 days to remove residual solvent. Subsequently, they were stored in deionized water for further use. Three batches of substrates, designated #1, #2 and #3, were fabricated under different spinning conditions as summarized in Table 1.

2.3. Post-treatment of PAI hollow fiber substrates

The hollow fibers were immersed in a 2% (wt/vol) APTMS solution in a 1:1 volume mixture of IPA and deionized (DI) water at 60–80 °C for 1–5 h. The membranes were then subjected to conditioning treatment for 30 min in either IPA or DI water to remove the excess crosslinker and subsequently dried overnight in ambient air.

Table 1
Spinning conditions.

Parameters	#1	#2	#3
Dope composition (PAI/LiCl/NMP) (wt%)	15/3/82	15/3/82	14/3/83
Dope flow rate (g/min)	6.26	6.26	6.32
Bore fluid (NMP/H ₂ O) (vol%)	25/75	25/75	25/75
Bore fluid flow rate (ml/min)	6	8	7
Air gap (cm)	5	5	10
Take up speed (m/min)	7	7	7
External coagulant	Tap water	Tap water	Tap water
Spinning temperature (°C)	23	23	23
Spinneret diameter (mm)	1.5	1.5	1.5
ID of bore fluid needle (mm)	0.7	0.7	0.7

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