Journal of Membrane Science 451 (2014) 148–156

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Simplified synthesis route for interfacially polymerized polyamide membranes

Sanne Hermans, Hanne Mariën, Elke Dom, Roy Bernstein, Ivo F.J. Vankelecom*

Centre for Surface Chemistry and Catalysis, Department of Molecular and Microbial Systems, KU Leuven, Kasteelpark Arenberg 23, PO Box 2461, 3001 Leuven, Belgium

ARTICLE INFO

Article history:
Received 6 June 2013
Received in revised form
5 September 2013
Accepted 3 October 2013
Available online 9 October 2013

Keywords:
Thin film composite
Interfacial polymerization
Aromatic polyamide
Membrane synthesis
Nanofiltration

ABSTRACT

A simplified method for the synthesis of thin film composite (TFC) membranes via interfacial polymerization was studied. Traditionally, the porous support layer is synthesized by phase inversion and subsequently impregnated with an aqueous amine solution before contacting it with an organic acyl chloride solution. In this simplified method, the phase inversion step and the impregnation with the amine monomer are carried out simultaneously by adding the amine to the coagulation bath before immersing the cast polymer film in it. This way, a two step process was successfully simplified into one step, combining both phase inversion and monomer impregnation of the support. Variation of synthesis parameters showed that a good membrane performance was achieved by adding 2 wt% *m*-phenylenediamine (as a monomer), triethylamine and sodium dodecyl sulfate (as a base/acylation catalyst and surfactant, respectively) to the coagulation bath. These synthesis conditions accord with the ones used in the traditional method. However, the polysulfone concentration, used for the synthesis of the support layer, could be lowered in the simplified method, without compromising in membrane performance. This method could lead to a more efficient, time and material saving synthesis of TFC membranes, which is of potential interest from a commercial and environmental point of view.

1. Introduction

Interfacial polymerization is an established technique for the synthesis of thin film composite (TFC) membranes. Particularly, TFC membranes with a polyamide (PA) top layer are highly abundant for reverse osmosis (RO) and nanofiltration (NF) in aqueous applications. The PA active layer is synthesized on a polymeric support layer in two steps: First, the support layer is impregnated with an aqueous amine solution, and subsequently put into contact with an immiscible organic solvent that contains a second monomer, typically a hexane-based acyl chloride solution. At the interface between the two phases, both monomers react and form a very thin polymer layer of a few tens to hundreds nanometer thick [1]. The thin and highly cross-linked active layer together with its high ability to form hydrogen bonds, leads to high salt removal as well as high water permeance, robustness and durability, hence, superior membranes for aqueous applications. The porous support layer is generally an ultrafiltration (UF) poly(ether)sulfone membrane and the PA top layer is polymerized using m-phenylenediamine (MPD) or piperazine as amines and trimesoylchloride (TMC) as acyl chloride [2,3]. Due to their vast usage, extensive research was conducted in order to optimize the conditions for the synthesis of PA membranes leading to membranes with an excellent performance in the desalination of brackish and sea water [4–9]. In addition, many researchers investigated the modification of the chemistry and morphology of the PA top layer to improve their performance and reduce their fouling propensity [10–15]. It was also demonstrated that several commercial membranes undergo surface modification during manufacturing [16,17]. However, the fundamental procedure for the synthesis of a TFC membrane is virtually consistent. Hence, the aim of this research is to present a simplified route for the synthesis of a PA TFC membrane, while maintaining its excellent properties.

The support membrane, which is impregnated with the amine solution, is prepared using the phase inversion technique, in which a polymer solution is solidified by immersion in a coagulation bath consisting of a non-solvent, usually water [1]. It is therefore quite surprising that in open literature the phase inversion of the support and the impregnation with amine monomers in an aqueous solution are carried out separately. In this study, both steps are combined by using an aqueous amine solution as the coagulation bath for the polysulfone (PSf) support. It is suggested that by simplifying the two step process into one step (henceforth called the “SIM method”), the synthesis of TFC membranes will become faster and easier, which is of potential interest from a

---

* Corresponding author. Tel.: +32 16321594.
E-mail address: ivo.vankelecom@biw.kuleuven.be (I.F.J. Vankelecom).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.10.005

commercial point of view. In addition, it is assumed that a better quality of the formed PA layer might get realized (less pinhole defects), since each pore in the support already contains the diamine at its origin. The impregnation of a preformed support, as in the traditional method, might cause less efficient pore wetting, hence less reagent presence. To the best of our knowledge, this approach has not been reported before in the peer-reviewed literature. Only one rather old patent describes the process of quenching a PSf solution in an aqueous MPD solution to gel the PSf, form the porous support and impregnate the support with MPD [18]. The essential procedure described in this patent thus seems similar to the here reported SIM method. However, the patent remains vague about exact formulations used to synthesize the membranes (*e.g.* in the examples dimethylformamide (DMF) is also added to the coagulation bath). Therefore, a systematic study of this method, with clear comparison with state-of-the-art approaches, was performed in this paper.

Membrane characteristics of TFCs synthesized via the SIM method were compared to those of membranes synthesized via the traditional method. Then, the SIM method was thoroughly studied to clarify the effect of various parameters such as PSf and monomer concentration, presence of additives and immersion time in the coagulation bath, on its performance. The performance of the prepared membranes was analyzed using high throughput techniques [19–21]. In addition, the properties of the synthesized membranes were thoroughly characterized by SEM, TEM, ATR-FTIR, AFM and XPS in order to link their performance to their fundamental properties.

2. Experimental

2.1. Materials

Polysulfone (PSf, Udel® P-1700) was purchased from Solvay. The non-woven polypropylene/polyethylene (PP/PE) fabric Novatexx 2471 was kindly provided by Freudenberg (Germany). Trimesoylchloride (TMC, 98%, Acros), *meta*-phenylenediamine (MPD, 99+%, Acros), triethylamine (TEA, 99.5+%, Sigma-Aldrich) and sodium dodecyl sulfate (SDS, 99%, Acros) were used for interfacial polymerization. *N*-methylpyrrolidone (NMP, 99%, Acros) and hexane (VWR, 97+%) were used as received. Magnesium sulfate ($MgSO_4$, anhydrous, 99%, Sigma-Aldrich) was applied as test solute. All experiments were carried out with Milli-Q water.

2.2. Membrane synthesis

2.2.1. PSf support

PSf UF membranes were synthesized via phase inversion. A homogeneous solution of PSf (dried overnight at 110 °C) in NMP was cast on a PP/PE non-woven, which was first impregnated with NMP, at constant speed (77 mm/s) using an automatic casting device (Braive Instruments, Belgium) at 200 μm wet thickness.

To synthesize a membrane via the traditional process, the polymer film was immersed in distilled water for 10 min. Hereafter, the membrane was rinsed for 5 min and stored in distilled water until further use.

To synthesize a membrane via the SIM method, the cast polymer film was immersed in an aqueous amine solution of 2 wt% MPD, 2 wt% TEA and 0.1 wt% SDS, unless specified otherwise. The coagulation time was 5 min when using the SIM method, unless specified otherwise.

2.2.2. Thin film composite

A thin PA layer was synthesized on top of the PSf support via interfacial polymerization. When applying the traditional process for membrane preparation, the PSf support was first immersed in an aqueous amine solution of 2 wt% MPD, 2 wt% TEA and 0.1 wt% SDS for 5 min. Hereafter, membrane synthesis based on the traditional process and the SIM method proceeded similarly. The excess aqueous solution was removed from the PSf membrane using a rubbery wiper. A solution of 0.1% (w/v) TMC in hexane was subsequently poured gently on the impregnated support layer. The hexane solution was drained off after 60 s of polymerization and the membrane was rinsed with hexane to remove unreacted TMC. After 1 min air drying, the membrane was put in a water bath to remove unreacted MPD. Finally, the synthesized TFC membrane was stored in distilled water.

2.3. Membrane characterization

2.3.1. Filtration experiments

The filtration experiments were done with a high throughput filtration module, which allowed six simultaneous dead-end filtrations under the exact same operating conditions [19–21]. The active area of each membrane inside the module was 5.31×10^{-4} m². The feed was stirred rigorously at 400 rpm to minimize concentration polarization. The membrane performance was tested with a 1 g/L $MgSO_4$ solution in Milli-Q water. Every membrane was tested three times.

Membrane permeance (L_p) was calculated using:

$$L_p = \frac{V}{At\Delta P} \quad (1)$$

where V is the permeate volume (L), A is the membrane area (m^2), t is the time (h) and ΔP is the applied pressure (bar).

The retention was calculated using:

$$R = \frac{\Lambda_f - \Lambda_p}{\Lambda_f} 100 \quad (2)$$

in which Λ_f and Λ_p are the feed and the permeate conductivity (Consort C3010, Belgium), respectively.

A "porosity factor" εr_p^2 was defined for the PSf support membranes based on the Hagen–Poiseuille pore flow model:

$$L_p = \frac{\varepsilon r_p^2}{8\mu\delta_m} \quad (3)$$

where L_p is the membrane permeance ($m^2\, m^{-1}\, Pa^{-1}\, s^{-1}$), ε is the membrane porosity, r_p is the pore radius (m), μ is the solution viscosity (0.001 Pa · s for water at room temperature), and δ_m is the membrane thickness (m), estimated from SEM cross-section images. Including both porosity and pore radius, this factor represents the overall effect of the pores on the permeance of the support membrane [22].

2.3.2. Electron microscopy

The cross-section morphology was analyzed with scanning electron microscopy (SEM), Philips XL 30 FEG SEM. Samples were broken in liquid nitrogen and coated with a thin (1.5–2 nm) gold layer using a Cressington HR208 high resolution sputter coater.

Transmission electron microscopy (TEM) was applied for top layer visualization at higher resolution. Unstained membrane samples were embedded in an araldite resin (Polyscience) and cut into ultrathin (70 nm) cross-sections with a Reichert Ultracut E microtome. Images were taken with a Zeiss EM900 TEM. Top layer thickness was calculated as the average of 20 equidistant spots along the entire cross-section.

2.3.3. Atomic force microscopy (AFM)

Membrane topographic images were acquired under water (TM Direct Drive holder) using a Dimension 3100 device (Bruker)