Journal of Membrane Science 476 (2015) 356–363

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Efficient synthesis of interfacially polymerized membranes for solvent resistant nanofiltration

Sanne Hermans [a], Elke Dom [a], Hanne Mariën [a], Guy Koeckelberghs [b], Ivo F.J. Vankelecom [a,*]

[a] Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, PO Box 2461, 3001 Leuven, Belgium
[b] Polymer Chemistry and Materials, KU Leuven, Celestijnenlaan 200F, PO Box 2404, 3001 Leuven, Belgium

ARTICLE INFO

Article history:
Received 25 August 2014
Received in revised form
17 November 2014
Accepted 23 November 2014
Available online 9 December 2014

Keywords:
Thin film composite
Interfacial polymerization
Solvent resistant nanofiltration
Membrane synthesis
Polyimide crosslinking

ABSTRACT

Thin film composite (TFC) membranes are used worldwide in aqueous applications. They mostly consist of a polyamide top-layer put on a polysulfone support via interfacial polymerization. Due to their thin and dense selective layer, these membranes are also interesting for filtrations in organic solutions. Polysulfone should then be replaced by a more solvent resistant material. The synthesis of solvent resistant nanofiltration TFC membranes via a newly developed method is reported: phase inversion, crosslinking and impregnation of a polyimide support are combined by adding amines to the aqueous coagulation bath. Next, a thin polyamide top-layer is formed on the support via interfacial polymerization. Several amines are tested as crosslinker for the support and as monomer for top-layer formation. The use of an amine mixture is also explored. Membrane stability, time in the coagulation bath, effect of solvent activation and mass and solvent intensity of the process are investigated. This novel synthesis method minimizes the use of (hazardous) materials, thus requires less reagents and creates less waste. Moreover, time and effort are saved during the synthesis process, which is of great interest for membrane producers and from an environmental point of view.

1. Introduction

Thin film composite (TFC) membranes synthesized via interfacial polymerization are abundantly used in aqueous applications, e.g. desalination. These membranes consist of a very thin (50–500 nm), yet dense top-layer, allowing high water permeances, while small solutes (like salts) are effectively retained [1]. Because of this ultrathin and crosslinked selective layer, such TFC membranes could be particularly interesting to improve the performance of current solvent resistant nanofiltration (SRNF) membranes. In SRNF, separations down to the molecular level can be realized in solvent streams by simply applying an external pressure over a membrane. It is an emerging technique in the food, pharmaceutical and (petro)chemical industry [2–4]. Today, commercially available SRNF membranes are mostly integrally skinned asymmetric membranes, having rather low solvent permeances, due to their intrinsically thicker selective layer (hence more resistance to mass transfer through the membrane) [5].

To prepare TFC membranes for aqueous applications, a porous polysulfone (PSf) support layer is typically impregnated with an aqueous diamine solution and subsequently put in a hexane-based acyl chloride solution. At the interface of both immiscible solvents, the monomers react, forming a thin, dense polyamide (PA) top-layer on the support [6]. Previously, we reported a method to combine phase inversion of the PSf support and its impregnation with amine monomers by using an aqueous amine solution as the coagulation bath [7]. For applications in many industrially relevant organic solvents (e.g. dimethylformamide, DMF), the typically used PSf support must be replaced by a more solvent resistant material, since PSf is known to swell extensively (or even dissolve) in many of these solvents. A well-known solvent resistant material for membrane applications is crosslinked polyimide (PI) [8,9]. Recently, this material was used as a support for the synthesis of SRNF TFC membranes and showed promising results [10,11]. However, the synthesis process of these membranes was cumbersome, time-consuming and required the use of a conditioning agent (polyethylene glycol) and large amounts of solvent (isopropanol, IPA) at different stages. Firstly, the PI dope solution was turned into a solid support membrane via phase inversion in a coagulation bath containing pure water. The formed support was kept in an IPA solvent exchange bath to remove residual water and preparation solvents. Subsequently, it was crosslinked by immersion in a solution of hexanediamine (HDA) in IPA for 16 h and washed with IPA for 3 h to remove residual HDA. IPA is used as the solvent for crosslinking because the PI support will swell in this medium, making the polymer chains thus more available for crosslinking by the diamine. After the crosslinking procedure, the support still had to be

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

http://dx.doi.org/10.1016/j.memsci.2014.11.046
0376-7388/

conditioned (in polyethylene glycol/IPA) overnight, before it could be dried and finally impregnated with the first monomer for the top-layer formation.

Vanherck et al. developed a simplified procedure for the crosslinking of PI membranes [12]. Herein, phase inversion and crosslinking are combined, by adding the diamine crosslinker directly to the water coagulation bath in which the phase inversion takes place, instead of crosslinking the membrane in a separate step by immersion in a diamine/organic solvent mixture. The crosslinking reaction thus occurs simultaneously with the membrane formation in the simplified procedure, avoiding the use of organic solvent and increasing efficiency, since the diamine no longer has to diffuse into the already solid membrane matrix for reaction to take place. The membranes prepared by Vanherck et al. were integrally skinned asymmetric membranes (thus without an extra top-layer) and directly applicable in SRNF. The thickness of their selective layer however limits the possibility to achieve high solvent permeances. In principle, the use of a thin selective layer, as in TFC membranes, would be more efficient as higher permeances through the selective layer can then be obtained.

In this work, a new synthesis process was developed to prepare SRNF TFC membranes with PA top-layers on crosslinked PI supports. As mentioned previously, in a TFC membrane synthesis via interfacial polymerization, the support is commonly impregnated with an aqueous diamine solution (in a separate step). In this newly developed method, diamines are added to the coagulation bath to act simultaneously as both a crosslinker for the PI support and a monomer for the top-layer formation. This way, three steps are now carried out simultaneously (further called the SIM process): phase inversion, crosslinking and monomer impregnation of the support. Moreover, the SIM process only requires the use of water as coagulation/reaction medium. In addition, the conditioning step is avoided, since drying of the support in between processing steps is no longer required.

A schematic overview of the traditional versus the SIM process for the synthesis of SRNF TFC membranes is presented in Scheme 1. This new method thus drastically shortens processing time, but also prevents the use of chemicals, i.e. polyethylene glycol and substantial quantities of IPA at different stages. Hence, it requires less reagents and creates less waste during the membrane synthesis. Moreover, the traditional problem of rewetting every single surface pore of the support with the first monomer solution (as a major cause of pinhole creation in the final TFC membrane) is avoided here since this monomer is intrinsically present already in each pore. Indeed, pores originate where non-solvent has nucleated and this non-solvent readily contains the reagent.

2. Experimental

2.1. Materials

Matrimid® 9725 PI was obtained from Huntsman (Switzerland). The non-woven polypropylene/polyethylene (PP/PE) fabric Novatexx 2471 was kindly provided by Freudenberg (Germany). Propanediamine (PDA, Chimica, 99%), butanediamine (BDA, Acros, 99%), hexanediamine (HDA, Acros, 99.5%), octanediamine (ODA, Fluka, 98%), tris(2-aminoethyl)amine (polyamine, SigmaAldrich, 98%+) and *meta*-phenylenediamine (MPD, Acros, 99+%) were applied as amines. Their chemical structures are shown in Fig. 1. Trimesoyl chloride (TMC, Acros, 98%), N,N-dimethylformamide (DMF, SigmaAldrich, 99+%), dimethyl sulfoxide (Acros, 99.5%), N-methyl-2-pyrrolidone (NMP, Acros, 99%), tetrahydrofuran (THF, Chemlab, 99.9%), methanol (MeOH, VWR, 99.5+%), ethanol (EtOH, VWR, 99.8+%) and hexane (VWR, 97+%) were used as received. Rose Bengal (RB, Fluka) was applied as test solute. All experiments were carried out with Milli-Q water.

2.2. Membrane synthesis

2.2.1. PI support

Support membranes were synthesized via phase inversion. A homogeneous solution of 14 wt% Matrimid PI (dried overnight at 110 °C) in NMP/THF (3/1) was cast on a polypropylene/polyethylene non-woven (Novatexx 2471, Freudenberg), which was first impregnated with NMP, at constant speed (77 mm/s) using an

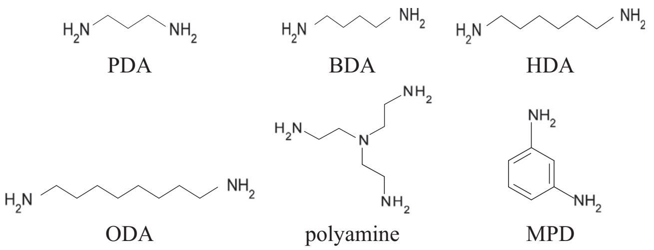
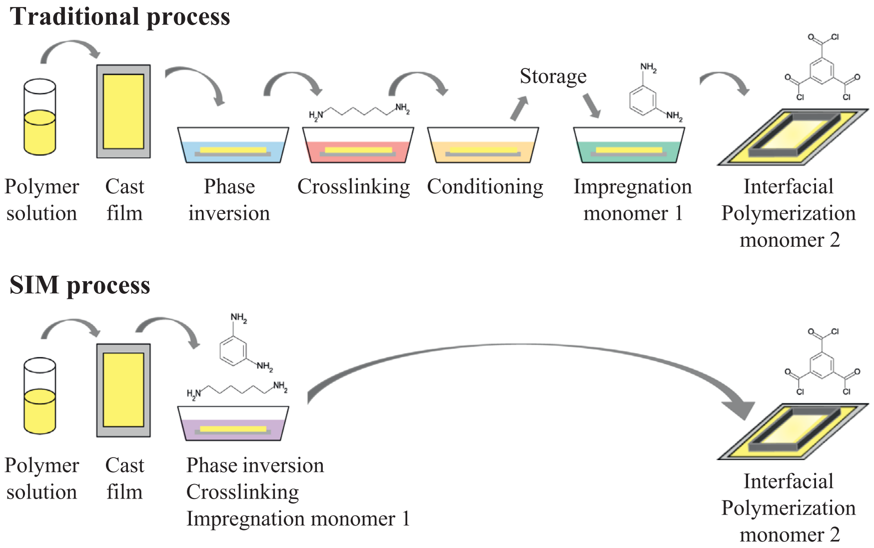


Fig. 1. Chemical structures of the amines used in the coagulation bath.



Scheme 1. Comparison of traditional and SIM process for synthesis of SRNF TFC membranes.