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Optimisation of a lab-scale method for preparation of composite membranes with a filled dense top-layer

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Abstract

The lab-scale optimisation is discussed of the synthesis of composite membranes prepared via dipcoating. Following the generally good performance of organomineral top-layers and with the recently reported strong performance of zeolite filled PDMS-membranes in solvent resistant nanofiltration (SRNF) in particular, composite membranes with such selective layers were selected as challenging case study.

Two different lab-scale coating procedures were compared first, so as to select one with which the top-layer thickness could be minimised by decreasing the concentration of the dipcoating solution and adjusting the coating angle. A polyimide (PI) support-layer with low surface roughness, as characterised by AFM, thus allowed synthesis of a defect-free top-layer with a thickness of 4 μm. With such thin top-layers and under the SRNF-conditions of high fluxes, the mass transfer resistance of the PI support was found to become rate limiting. A strategy was then followed to avoid pore collapse in the top region of the support, which mainly occurred during the thermal cross-linking of the PDMS-layer after the dipcoating. After developing an appropriate support treatment, applied before the actual dipcoating, fluxes could still be increased by more than one order of magnitude, proving the rate determining role of the support.

Keywords: Zeolite-filled PDMS; Composite membrane; Support; Solvent-resistant nanofiltration

1. Introduction

PDMS-based membranes are among the most popular in membrane technology, since they already proved to have a very good utility in pervaporation [1], gas separation [2], vapour permeation [3] and dialysis [4]. Despite the fact that PDMS-based membranes have been applied frequently in solvent-resistant nanofiltration (SRNF), stability problems arise in apolar solvents due to extensive swelling, leading to drastic loss of selectivity [5,6]. Polymer modifications by addition of zeolites proved to be very effective to improve stability without lowering the intrinsic permeability (with fluxes extrapolated by normalisation to a top-layer thickness of a few micrometers) [7,8]. However, the reported zeolite-filled PDMS membranes still showed low effective permeances, due to the thick top-layer (>20 μm) of these membranes.

When introducing new materials as promising selective layers for membrane separations, this is the point where open literature traditionally stops. Only if the material is really promising for industrial applications, further development of the composite membrane is initiated, but never made public. In such an often time and material consuming optimisation, the reduction of the top-layer thickness is mostly one of the main goals. This paper aims at shedding light on some of the aspects determining the actual performance of a composite membrane. At a lab-scale and in absence of sophisticated clean room conditions, a preparation method will be reported for zeolite-filled composite membranes with thin top-layers and hence high effective permeances when applied in SRNF. It can be anticipated that because of the addition of micron-sized fillers, the lower-limit for the top-layer thickness will be significantly higher than for unfilled PDMS-layers, where thicknesses below 1 μm can be obtained in industrial manufacturing.

This type of composite membrane can only operate well as long as the mass transfer resistance of the support is lower than the one of the top-layer [9]. This can be realised by increasing the surface porosity of the support, but only for as far as no

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intrusion of the top-layer material in the support takes place during dipcoating [10]. Compromises will have to be found, since such risks increase when applying more dilute coating solutions, which is essential to create thin top-layers. Moreover, a high surface porosity of the support increases the risk for defects [11], due to a higher surface roughness.

Considering the importance of support porosity and roughness, two types of support materials were selected for this study, namely a polyimide (PI) with a rather dense skin and a polyacrylonitrile (PAN) with a more open structure. For the latter support type, the chances on top-layer intrusion are lowered by filling the pores with water. The top-layer thickness will be minimised via polymer solution concentration and coating angle. The output parameters in this study are the thickness and uniformity of the PDMS top-layer and the performance of the final composite membranes in SRNF of two test liquids.

In order to minimise the resistance in the support-layer, it is thus crucial to keep the pore structure intact during the thermal curing of the PDMS top-layer. To prevent pore collapse, the water in the pores was exchanged with solvents having a lower surface tension [12]. To overcome the limited exchangeability between the water and the low surface tension hydrocarbons, solvents with intermediate polarity were used in between [13]. Combined with these solvent-exchange procedures, non-volatile additives were added as impregnating substances to fill up the pores before dipcoating, thus helping to avoid intrusion and keeping the pores available after the PDMS-curing. Examples of such additives in patent literature are glycerol [14], silicones or mineral oil [15]. The impregnated compound is then removed only during the first actual use of the membrane. The influence of these procedures was first evaluated on the permeance of the uncoated PI supports.

2. Experimental

2.1. Materials

The PDMS (RTV-615 A and B) and the adhesion promoter (SS 4155) were obtained from General Electric (USA). Component A contains a prepolymer with vinyl groups. Component B has hydrosilyl groups and acts as cross-linker. USY (CBV-780, PQ-corporation) was selected as zeolite material [8]. It was dried at 110 °C before use.

The polyacrylonitrile (PAN) support was provided by VITO (Mol, Belgium). It was synthesised via a phase inversion process using a 15 wt.% PAN (Faserwerke Lingen, 112,000 g/mol) solution in N-methylpyrrolidone (NMP). The pure water permeance is around 550 l/m^2 h bar. Before use, the PAN support was immersed in deionised water and the surface was wiped with a tissue to remove excess of water.

The PI support was prepared in the lab from a 15 wt.% PI solution (Matrimid 5218, Huntsman, Switzerland), containing 2 wt.% distilled water, 62.25 wt.% NMP and 20.75 wt.% tetrahydrofuran (THF) as solvents. This optimised support combined a good permeance for 2-propanol (3 l/m^2 h bar, untreated) with an acceptable mechanical stability and limited top-layer intrusion. When specified, the support was post-treated by solvent-exchange in 2-propanol (ChemLab), followed by hexane (Acros) or a [toluene (Vel)/2-methyl-4-pentanone (Acros)] mixture. Glycerol (Acros) and mineral oil (ÖlP3, Pfeiffer) were used as impregnating substances. Before the coating process, the PI support was air-dried at room temperature.

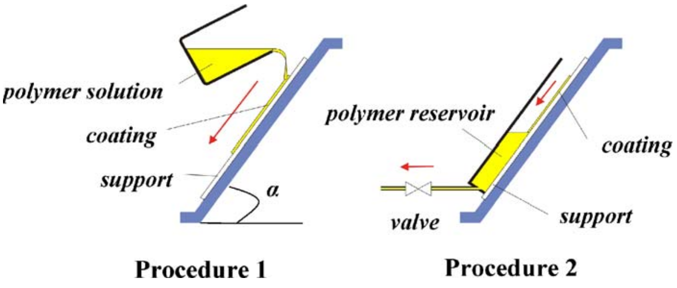

Fig. 1. The two lab-scale coating procedures applied in this work.

2.2. Membrane synthesis

2.2.1. Polymer solution preparation

The zeolites were dispersed in hexane via a treatment of 1 h in an ultrasonic bath to break crystal aggregates. The cross-linker was added to the zeolite dispersion and this mixture was stirred for 2 h at 40 °C. Finally, the prepolymer was added and the mixture was stirred for 1 h at 60 °C. The filler content in the membrane was kept constant at 30 wt.%.

2.2.2. Coating procedure

In procedure 1, the support was mounted on a stainless steel plate (Fig. 1). The plate is placed on a platform, which can be tilted to adjust the coating angle α. The polymer solution is poured at the top end of the support allowing a flow of the polymer solution over the support-layer.

In procedure 2, the support was mounted on one of the walls of a reservoir filled with the polymer solution. The reservoir is placed on the same platform as in procedure 1. The polymer solution is slowly removed from the reservoir by opening a valve at the bottom of the reservoir.

In both cases, the procedure was repeated three times to obtain a full coverage of the support and to minimize defects. Between each coating step, a period of 1 min was waited to allow evaporation of the solvent from the newly deposited layer. No intermediate thermal curing was applied. Unlike procedure 2, procedure 1 allows to turn the support between each coating step. This decreases the chances on preferential streaming patterns of the polymer solution over the support. After three coating steps, the PDMS was cured at 110 °C for 10 min.

2.3. Membrane characterisation

2.3.1. SEM-characterisation

Membrane cross-sections were obtained after breaking the membranes under liquid nitrogen. SEM-samples were coated with an Au-layer to reduce sample charging under the elec-