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Novel polytetrafluoroethylene tubular membranes for membrane distillation

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ABSTRACT

This paper deals with the preparation of novel polytetrafluoroethylene (PTFE) membranes from an aqueous dispersion of fluorinated polymer and a pore forming agent (PFA) sintered onto the outer surface of a porous tubular support. Different membranes were obtained by varying the ratio between PTFE and PFA in the starting dispersion as well as the number of dispersion layers sintered on the support. Membranes were characterized through scanning electron microscopy and gas–liquid displacement porosimetry. Distillation tests of the membrane were carried out on a laboratory scale unit fed with a NaCl solution. The characteristics and performance of the membranes were compared with those of commercial porous PTFE tubulets.

Keywords: Polytetrafluoroethylene; Hydrophobic membrane; Membrane distillation

1. Introduction

Because of its excellent chemical resistance and thermal stability, polytetrafluoroethylene (PTFE) represents one of the most attractive polymers for the preparation of porous membranes for filtration of very aggressive streams even under severe temperature conditions. In addition, the high hydrophobic character of these polymeric membranes suggests potential application in a process namely membrane distillation [1–4], which is today a subject of renewed and continuous interest as an alternative and advantageous means of reverse osmosis treatment for concentrated and, preferably, warm solutions. The majority of commercial PTFE porous membranes are produced by a very complicated process starting from a PTFE powder mixed with a lubricant liquid. The resulting paste is then extruded in the form of a flat sheet or tube to be properly stretched and sintered in order to generate a porous structure formed by nodes and tiny interconnected fibrils with pore size generally ranging from 0.1 up to 2–3 μm, depending on the preparation conditions [5]. Flat sheet expanded membranes are very thin and consequently are usually bonded to a polyethylene or polypropylene support, usually a woven or a nonwoven fabric, to obtain a final product with improved handling and mechanical properties but, unfortunately, also presenting lower heat and chemical resistance. Finally PTFE membranes are very expensive.

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This paper reports the preliminary results of a study aimed at preparing PTFE porous membranes through an alternative and simpler route consisting of the sintering of a thin layer of an aqueous polymer dispersion doped with a proper water soluble salt as a pore forming agent (PFA) onto the surface of a chemically stable and thermally resistant tubular support. Different membranes were prepared by varying some preparative parameters such as the PTFE/PFA ratio in the starting dispersion and the number of sintering cycles. Membranes were characterized through scanning electron microscopy investigation and gas–liquid displacement porosimetry and tested in a laboratory scale membrane distillation plant. Their properties and performance (water vapour flux and salt retention) were compared with those of commercially available porous PTFE tubular membranes.

2. Experimental

The PTFE aqueous dispersion (Aldrich 665800, 60% PTFE), diluted with deionized water and doped with the PFA, was cast as thin film on the outer surface of a tubular support (glass fibre braid). The PFA ($BaCl_2$) was chosen on the basis of its high solubility in water ($S = 400$ g/L) and melting point ($T = 962$°C) considerably higher than the sintering temperature of PTFE (400°C). In addition, $BaCl_2$ did not produce any negative effect on the stability of the dispersion.

The method used for preparing porous PTFE membranes involved the following steps:

(a) dissolving the PFA in an aqueous PTFE dispersion (Aldrich 665800, 60% PTFE) properly diluted with deionized water;
(b) casting the dispersion as thin film on the outer surface of a tubular support (glass fibre braid, length ca. 25 cm, outer diameter $\theta = 6$ mm, thickness $t = 0.5$ mm);
(c) drying the cast film with a jet of hot air ($t = 65$°C);
(d) sintering the dried film at 400°C for 10 min;
(e) cooling the sintered film in air at room temperature; and
(f) immersing the film in a water bath and leaching it for ca. 30 min.

The drying step (c) of the cast film leads to the formation of PFA salt crystals that, because of their high melting point, withstand the high sintering temperature (d) and dissolve during the successive water immersion and leaching steps (e–f) to form the pores.

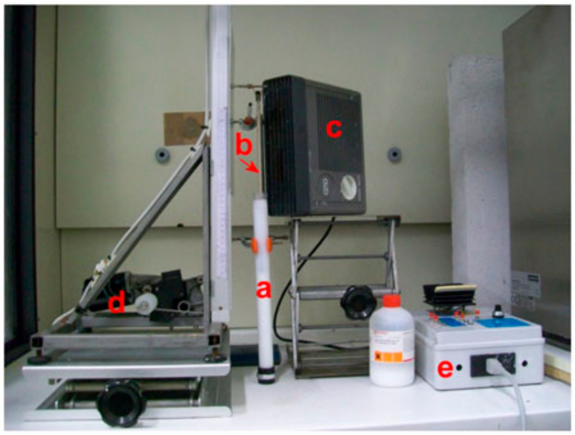

Fig. 1. Device used for the preparation of PTFE supported membranes: (a) PTFE aqueous dispersion; (b) braid coated with the PTFE dried film (in course of extraction from the dispersion); (c) fan for generating hot air jet; (d) electric motor and (e) extraction speed controller.

Fig. 1 shows an image of the simple device [5] used to obtain a homogeneous polymer coating on the outer surface of the support.

The immersion time of the braid in the PTFE dispersion was $t = 30$ s. The extraction speed from PTFE dispersion was $v = 0.8$ cm/s. Before immersion in the PTFE dispersion, a stainless steel bar was inserted into the braid lumen in order to impart to it a proper stiffness and to avoid penetration of the dispersion in the braid lumen. This bar was removed before the water immersion step (f) in order to facilitate PFA dissolution from the sintered film and inserted again before successive casting and sintering cycles. A variety of membranes was prepared by varying the PTFE/PFA ratio in the starting dispersion and the number of casting and sintering cycles.

The surface of the deposited layer was observed by a scanning electron microscope (SEM, LEO, STEREOSCAN 440). The pore size distribution was evaluated by a COULTER II air–liquid displacement porometer (GLDP) by using Fluorinert^{TM} (3M, MN, USA) as a wetting liquid and an air pressure to displace the liquid from the membrane pores. Details of this porosimetric technique are reported elsewhere [6]. Membranes (surface 0.03 m^2) were tested in a laboratory scale distillation unit with a hot aqueous NaCl solutions ($T = 80$°C, $C_{NaCl} = 30$ g/L). Fig. 2 shows the laboratory scale unit for membrane distillation tests. The membrane (a) is directly housed in the feed reservoir (b) containing the aqueous NaCl solutions heated and stirred by (h). The sweeping air, provided by the air pump (c), flows in the membrane lumen with a velocity of ca. 1 m/s. The vapour permeated is condensed by the two cooling

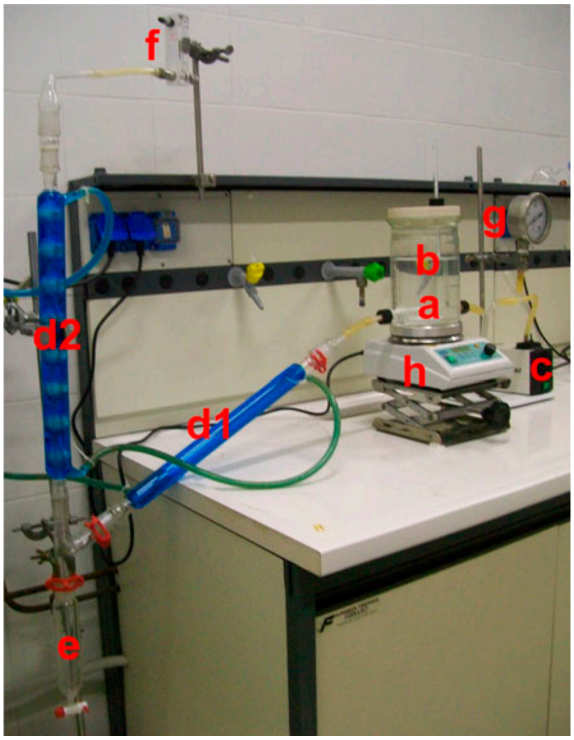

Fig. 2. Laboratory scale unit used for membrane distillation tests.

devices (d1, d2) arranged in series. The vapour flow rate is measured by evaluating the volume of condensate with a graduated cylinder (e) located below (d1) and (d2) at a given time. The sweeping air flow rate and the pressure are measured through the flow metre (f) and the manometer (g), respectively.

In order to connect the PTFE membrane to the glass housing (Fig. 3), the membrane ends are sealed to a small plastic tube with an epoxy resin (Fig. 4). An O-ring is then installed on the plastic tube's outer surface and squeezed by tightening the cup (j) onto the threaded glass tube of the reservoir (b). Commercial PTFE porous tubular membranes Poreflon TB-0403 (Sumitomo Electric, Japan) with outer diameter $\theta = 3$ mm and thickness $t = 0.5$ mm were tested on the same unit. A different type of connection to the glass housing was realized since the epoxy resin did not adhere to the outer surface of the membrane. The Poreflon membrane ends were first inserted into the lumen of two small PTFE cylinders and then squeezed on the cylinder walls by a metallic ferrule to provide a hydraulic seal (Fig. 4).

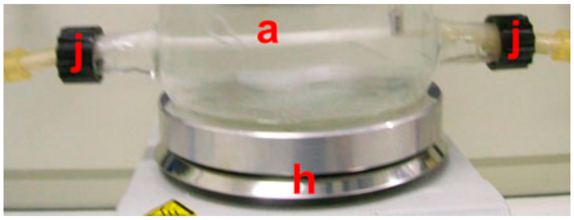

Fig. 3. Membrane connection (j) to the membrane distillation feed reservoir (a).

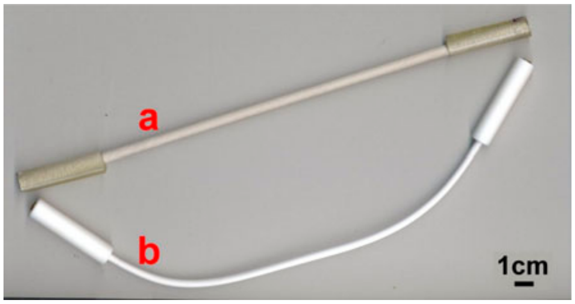

Fig. 4. End seal realized to connect PTFE supported membrane (a) and Poreflon membrane (b) membrane to the membrane distillation feed reservoir.

3. Results and discussion

Fig. 5 reports a picture of the braid (a), PTFE membrane (b) and commercial Poreflon membrane (c). Note the change of colour as well as of surface roughness between (a) and (b) due to the PTFE coating. The surface of the (white) Poreflon membrane appears very smooth and this fact, along with the poor adhesion properties of the fluorinated polymer, did not allow the sealing of the membrane ends through a simple potting process.

Attempts to treat the membrane end surface with commercial fluorocarbon etchants (e.g. Tetra-Etch®, W.L. Gore & Associates Ltd, UK) to make it bondable and pottable were unsuccessful since the reactive browns film formed on the surface by reaction between the fluorinated polymer and the etching agent presented a very low compatibility with the unreacted PTFE of the sublayer and, consequently, detached during potting process.

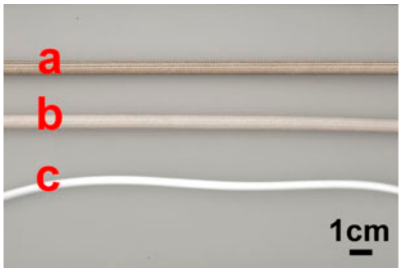

Fig. 5. Images of: braid (a), PTFE supported membrane (b), and Poreflon membrane (c).

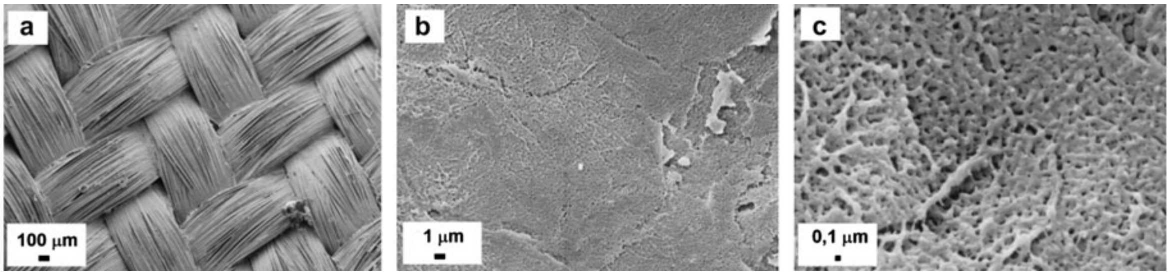

Fig. 6. SEM micrographs of the surface of the braid (a) and PT04 supported membrane (b) and (c). (Starting dispersion concentration: 15% PTFE–15% $BaCl_2$. Number of casting and sintering cycles: 4.)

Detailed information on the surface structure of the braid and different types of PTFE membranes can be obtained from the SEM micrographs shown in Figs. 6–8. More casting and sintering cycles were needed to cover the braid surface with a suitable PTFE film, especially starting from less concentrated PTFE dispersions.

Fig. 6 shows the SEM micrograph of the braid and the PTFE porous layer (PT04) deposited on the braid surface by eight casting & sintering cycles from 15% PTFE to 15% PFA water dispersion. As it can be seen the fibrous surface of the braid (Fig. 6(a)) completely disappears in Fig. 6(b) and (c) being covered by a PTFE layer characterized by the presence of a very large number of pores with a fairly narrow size distribution.

$BaCl_2$ added to the PTFE dispersion plays a role of paramount importance in the formation of these pores as shown in Fig. 7 where the SEM micrograph of the

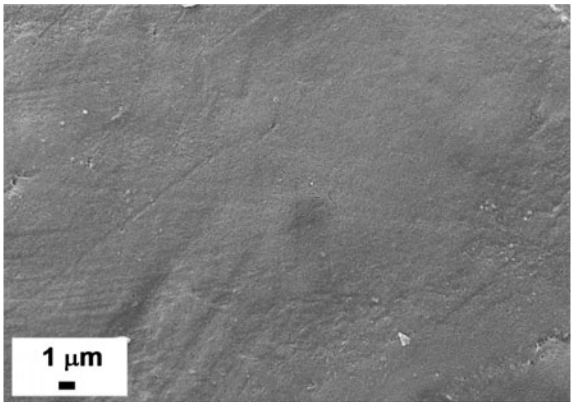

Fig. 7. SEM micrograph of the surface of PTFE supported membrane prepared from 15% PTFE dispersion (number of casting and sintering cycles: 4).

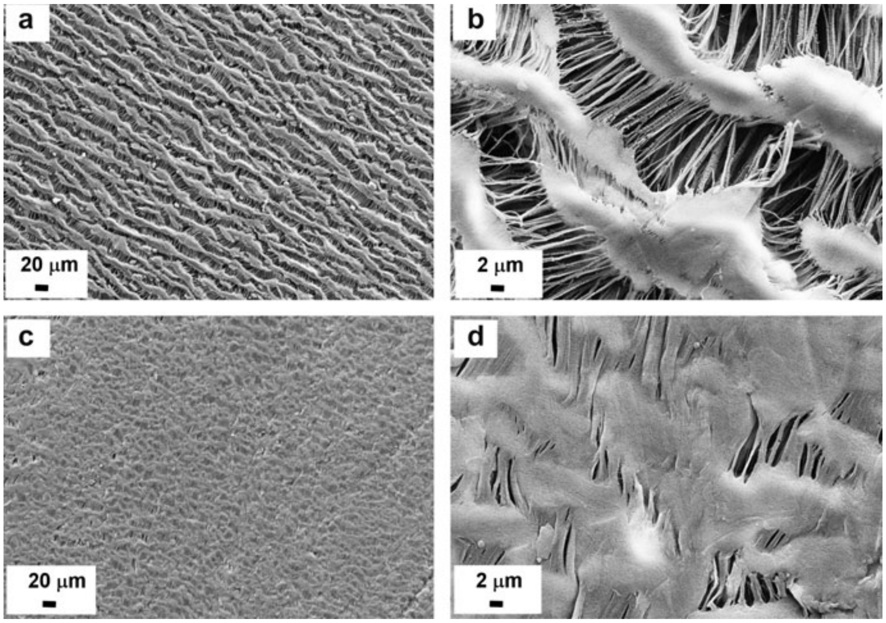

Fig. 8. SEM micrographs of the surface of the Poreflon membrane: inner surface (a) and (b); outer surface (c) and (d).

surface of a membrane obtained from a simple dispersion of PTFE (15 wt%) in water (without $BaCl_2$) is presented. Fig. 8 shows SEM micrographs of the two surfaces (inner and outer) of the Poreflon membrane. In Fig. 8(a) and (b) a typical highly porous structure of a PTFE-expanded membrane with the usual nodes connected by fibrils can be clearly observed, while in Fig. 8(c) and (d) the surface appears more dense and smooth.

Unfortunately, no information on the evolution of the structure from the inner to the outer surface of the membrane can be supplied because of the difficulties encountered to obtain a suitable cross-section by the usual cold (liquid nitrogen) fracturing technique. For the same reason, no information on the cross-section structure of the PTFE layer deposited on the braid as well as on its thickness was acquired. Anyway, by SEM observation of the braid lumen a fibrous structure similar to that reported in Fig. 6(a) was observed as well as no peaks ascribed to the fluorinated polymer appeared in the infrared (FTIR-ATR) spectra of said lumen. By weighing it was found that the amount of PTFE coated on the braid was in the range 0.01–0.025 g (PTFE)/cm (braid), depending on the composition of the starting dispersion as well as on the number and sintering cycles. The above-reported values are considerably lower with respect to 0.06 g (PTFE)/cm (membrane) for the Poreflon membrane (which is entirely made of PTFE). Keeping in mind the cost of the fluorinated polymer, it is apparent that the economic advantage of preparing asymmetric membranes start from a very cheap but chemically resistant and thermally stable support such as the fibre glass braid.

Table 1 summarizes the results of membrane distillation tests. A substantial improvement of the distillate flux of PTFE supported membrane, without any significant loss of the salt retention, was achieved by reducing the number of the casting and sintering cycles as well as the PTFE/PFA ratio in the starting dispersion. Further inspection of Table 1 reveals that the membrane distillation performance of PT18 and PT20 samples are very close to that of commercial one.

Table 2 lists the results of porosimetric mesurements. A very good agreement between the data reported in Table 2 and the values of distillate flux shown in Table 1 can be observed. Inspection of Fig. 9 reveals very narrow pore size distribution curves for all PTFE membranes and these findings agree quite well with the results of SEM investigation of the membrane surfaces shown in Figs. 6 and 8.

Table 1
Distillation performance of PTFE membranes

Membrane	Dispersion concentration (% wt)		Number of casting and sintering cycles	Distillate flux (L/h m^2)	NaCl retention (%)
	PTFE	PFA			
PT01	15	5	8	0.44	99.87
PT04	15	15	8	1.11	99.98
PT05	15	15	4	1.70	99.85
PT18	10	15	8	2.13	99.80
PT20	10	15	4	2.93	99.36
Poreflon TB-0403				2.57	99.99

Table 2
Porosimetric results obtained by GLDP measurements

Membrane	Hydraulic permeability (m/s Pa 10^{-6})	Average pore radius (μm)	Pore density (pores/cm^2 10^{12})	Porosity (%)
PT01	2.08	0.088	1.32	13.6
PT04	5.03	0.109	1.18	31.1
PT05	4.11	0.149	2.32	22.9
PT18	9.07	0.217	1.98	48.6
PT20	9.69	0.340	3.50	54.4
Poreflon TB-0403	7.37	0.084	8.29	45.3

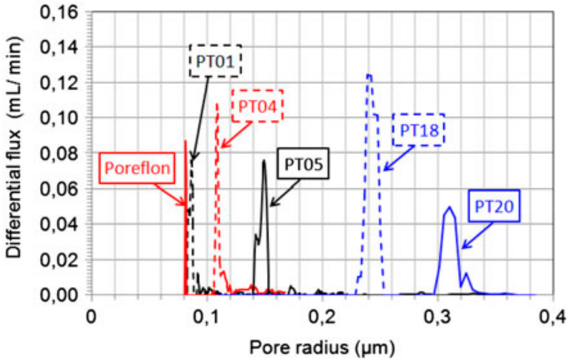

Fig. 9. Pore size distribution of PTFE supported and Poreflon membranes.

4. Conclusions

A simple method for making porous PTFE membranes has been proposed by varying preparative parameters such as the number of casting and sintering cycles and the PTFE/PFA ratio in the starting dispersion. Membranes with different porosities and membrane distillation performances were obtained. The vapour flux and salt retention of some of the prepared membranes were found to be very close to those of commercial tubular membranes. Important advantages of the developed membranes with respect to the commercial ones are the lower cost and the feasibility of sealing membrane ends through a simpler potting operation.

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