Dual-layered electrospun nanofibrous membranes for membrane distillation
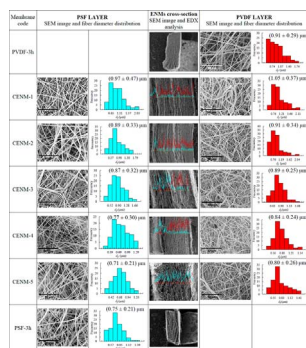
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GRAPHICAL ABSTRACT

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ABSTRACT

Dual-layered electrospun nanofibrous membranes (DL-ENMs) were prepared using the hydrophobic polymer polyvinylidene fluoride (PVDF) and the hydrophilic one polysulfone (PSF). The thickness of each layer was varied by changing the electrospinning time of each polymer solution maintaining the total electrospinning time at 3 h. The characteristics of the DL-ENMs and those of each layer were studied by means of different techniques and the results were compared to the single layer PVDF and PSF ENMs (i.e. SL-ENMs). The prepared DL-ENMs were tested in desalination by direct contact membrane distillation (DCMD) using different sodium chloride feed aqueous solutions. The DCMD permeate flux of the DL-ENMs was found to be higher than that of the PVDF SL-ENM and it increased with the decrease of the PVDF layer due not only to the reduction of the total thickness and to the increase of both the inter-fiber space and the void volume fraction, but also to the reduction of the path between the liquid/vapour interfaces formed at both side of the DL-ENMs. Compared to the proposed SL-ENMs in DCMD, it is better to use DL-ENMs adequately designed with hydrophobic and hydrophilic polymers than SL-ENM with only a hydrophobic polymer.

1. Introduction

Nanofibrous materials exhibit several important characteristics such as a very high surface area to volume ratio that can be as high as 100 times that of microfibrous materials, tunable and very high void volume fraction or "porosity" that can reach > 90%, inter-fiber space or "pore size" that can range from ten nanometers to several micrometers, flexibility in surface functionalities, interconnected open structure, good mechanical performance and possibility to construct a wide variety of fiber sizes and shapes (e.g. beaded, ribbon, porous and core-shell nanofibers). Therefore, nanofibrous materials have received extensive research interest for many potential applications in diverse

fields as drug delivery carriers, optical and chemical sensors, stimuli-responsive materials, bioreactors, tissue engineering scaffolds, electronic and semi-conductive materials, photovoltaic cells, battery applications, reinforced nano-composites, affinity membranes for different separation processes, etc. [1–11]

Polymer nanofibers have been fabricated by means of different physical, chemical, thermal and electrostatic techniques including template synthesis [12], liquid-liquid phase separation [13], self-assembly [14], vapour-phase polymerization [15] and electrospinning [11]. Among all these techniques, electrospinning is the most considered for the preparation of submicrometer-sized polymeric fibers because of its simplicity, cost and versatility permitting to organize nanofibers of various types (e.g. porous, hollow and core/sheath) into three-dimensional network. A lot of attention has been devoted to this technology using both natural and synthetic polymers and copolymers to produce fibers with different diameters from few micrometers down to tens of nanometers by adjusting electrospinning process parameters [16].

In membrane science and nanotechnology, electrospun nanofibrous membranes (ENMs) have been applied in different membrane separation processes such as microfiltration (MF), ultrafiltration (UF), engineered osmosis (EO) and membrane distillation (MD) [17–26]. For this last process ENMs offer interesting and attractive characteristics such as the high void volume fraction that provides large space for evaporation improving the water production rate, high hydrophobicity and less susceptibility to wetting by the feed water solutions if the inter-fiber space is adequately designed (i.e. high liquid entry pressure, *LEP*), high surface roughness and low thermal conductivity reducing therefore the heat loss by conduction (i.e. in MD the heat transfer by conduction through the fibers of the ENMs following Fourier's law is heat lost as no water vapour is associated to this heat) [27,28].

Both unsupported (i.e. non-woven mats) [29–32] and supported (i.e. backing material) [33–35] ENMs have been considered in different MD configurations. In fact, adequate supports should not enhance the mass transfer resistance but must provide the membrane with the necessary mechanical properties preventing its rupture when assembled in modules [10,21,27]. Essalhi and Khayet [36] observed an improvement of the mechanical properties of poly(vinylidene fluoride) (PVDF) SL-ENMs with the increase of the thickness (i.e. increase electrospinning time) but the MD permeate flux was reduced because the permeate flux is inversely proportional to the membrane thickness. Various surface or bulk modifications of ENMs including post-heat treatment have been studied in order to improve the physico-chemical and mechanical characteristics of the ENMs required in MD [26,36,34,35,37–48]. It is worth quoting that most of the prepared unsupported ENMs for MD are single hydrophobic layer obtained from a single hydrophobic polymer such as PVDF or the *co*polymer polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) with or without nanoadditives or mixed polymers such as polydimethylsiloxane (PDMS) and poly (methyl methacrylate) (PMMA) or PDMS and PVDF [25,29–32,36–46]. A supported triple layered hydrophobic/hydrophilic composite membrane has also been proposed for air gap membrane distillation (AGMD) applications [35]. This has been prepared using a PVDF electrospun nanofiber layer as the top layer (i.e., the active layer facing the feed), a PVDF cast middle microporous layer and a commercial backing support (polyethylene terephtalate, PET). It was claimed that the permeate flux of this triple layered membrane was 1.5 times higher (15.2 kg/m^2·h) than that of the dual layer membrane (i.e. membrane without the nanofiber selective layer).

Three research studies have been published so far on unsupported double-layered hydrophobic/hydrophilic ENMs for desalination by AGMD and direct contact membrane distillation (DCMD) [34,47,48]. Liao et al. [34] proposed a double-layered membrane with a thin superhydrophobic layer comprising PVDF and silica nanoparticles (i.e. 72 μm thick, 154° water contact angle) electrospun on a porous PVDF nanofibrous support. This membrane exhibited a stable permeate flux

Table 1
Surface tension (σ), electrical conductivity (χ) and viscosity (μ) of the PVDF and PSF dope solutions used in the preparation of the ENMs.

Polymer solution	σ (mN/m)	χ (μS/cm)	μ (Pa·s)
PVDF	32.2 ± 0.8	9.56 ± 0.02	3.02 ± 0.09
PSF	38.9 ± 0.5	2.51 ± 0.02	2.14 ± 0.07

Table 2
Electrospinning time of each layer and the membrane code used for the ENMs prepared in this study.

Membrane	Electrospinning time (h)	
	Bottom layer (PVDF)	Top layer (PSF)
PVDF-3 h	3	–
CENM-1	2.5	0.5
CENM-2	2	1
CENM-3	1.5	1.5
CENM-4	1	2
CENM-5	0.5	2.5
PSF-3 h	–	3

of 24.6 ± 1.2 kg/m^2·h when using a feed NaCl aqueous solution of 3.5 wt% during 25 h DCMD operation. Woo et al. [47] studied the effects of different hydrophilic nanofibrous supports on the desalination AGMD performance. The top layer, which faced the feed side was made of hydrophobic nanofibers (i.e. PVDF-HFP) while the bottom layer was made of hydrophilic nanofibers (i.e. polyacrylonitrile, PAN; polyvinyl alcohol, PVA or nylon-6, N6). The PVDF-HFP and support layer thickness ratio was maintained at 50/50. When using 3.5 wt% NaCl feed aqueous solution, it was observed permeate fluxes of the single and double-layered ENMs of 11–15.5 kg/m^2·h, which were greater than those of commercial PVDF membrane (i.e. about 5 kg/m^2·h under the same operating conditions). It was claimed that the hydrophilic ENM layer enhanced the permeate flux depending on its wettability and characteristics. The double-layered membrane prepared with N6 as ENM support exhibited the highest permeate flux (15.5 kg/m^2·h) with 99.5% salt rejection factor. Tijing et al. [48] prepared the same type of ENMs membrane (PVDF-HFP/PAN) with two different thickness ratio (50/50 and 25/75) being the total thickness 80 μm. The thickness of the membrane layers was controlled by manipulating the electrospinning time between 1.5 and 6 h. The two membranes exhibited the same membrane characteristics (i.e. void volume fraction, 90%; contact angle, 150/100°, surface pore size 0.6–2.5/6–16 μm; average fiber diameter 0.21/1.7 μm) except a slight difference of the liquid entry pressure (*LEP*), 85 and 94 kPa for the 50/50 and 25/75 PVDF-HFP/PAN membranes, respectively. These membranes were used in desalination by DCMD and a higher permeate flux was obtained (i.e. about 30 kg/m^2·h) with a salt rejection factor > 98.5%. This result was attributed to the thicker PAN layer, which decreased the mass transfer resistance. It was claimed that a thinner top ENM hydrophobic layer with high void volume fraction would lead to better DCMD permeate flux.

In fact, porous composite hydrophobic/hydrophilic flat sheet and hollow fiber membranes have been proposed for DCMD because of their high performance compared to single layer hydrophobic ones [27,28,49–56]. The hydrophobic thin layer is the responsible of the mass transfer and separation whereas the optimized thicker hydrophilic layer having bigger pores not only acts as support by increasing the mechanical properties of the membrane, but also reduces its heat transfer by conduction and improves the mass transfer [50–52]. For this type of membranes, the permeate liquid penetrates inside the bigger pores of the hydrophilic layer reducing therefore the distance between the liquid/vapour interfaces formed at each side of the hydrophobic thin layer. In addition, although the hydrophobic layer exhibited smaller pore size (i.e. an order of magnitude smaller than that of the