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Novel technique for fabrication of electrospun membranes with high hydrophobicity retention

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ABSTRACT

In a bid to mitigate the problem of pore wetting in membrane distillation, a superhydrophobic membrane was prepared by *in situ* deposition of teflon oligomer microparticles on poly (vinylidenefluoride-*co*-hexafluoropropylene) nanofibers during electrospinning. This new approach relies on dusting in the chamber where the threads of polymer solution are spun in the zone of fiber transition between liquid to solid. In addition to distributing the particles across the electrospun mat, the novel technique allows bonding of the particles to the solidified fibers. The prepared membrane was characterized and tested in direct contact membrane distillation (DCMD). The results show that the membrane, which was about 30 μm thick, was superhydrophobic and displayed a water contact angle of 155 ± 1°. The membrane also supported a contact angle of 153 ± 1° for a 3 mM SDS solution having lower surface tension (49 mN/m) than water (72 mN/m). The membrane had nominal and maximum pore diameters of 0.57 μm and 1.93 μm respectively, and was about 91% porous. The membrane also supported a liquid entry pressure of about 22 psi. Furthermore, the membrane gave average permeate fluxes of 7 kg m^{-2} h^{-1}, 10 kg m^{-2} h^{-1} when tested in DCMD at 60 °C and 70 °C feed temperatures respectively, with a salt rejection of 99.97%. Finally, the membrane supported a water contact angle of 140 ± 1° after it had been used in DCMD test, while the mean pore diameter, maximum pore diameter and porosity decreased to 0.32 μm, 0.83 μm and 86.5% respectively after test.

1. Introduction

With the ever-increasing scarcity and concomitant increase in demand of fresh water, membrane distillation (MD) has gained enormous popularity in recent times as an attractive technique for producing fresh water from seawater. Compared to other membrane separation processes, MD offers the advantages of low energy cost, high rejection of non-volatile solutes (theoretically 100%), less demanding membrane mechanical property requirements, and less fouling [1,2]. However, despite these advantages, low permeate flux and membrane wetting are major drawbacks limiting the commercial implementation of MD for desalination [3]. These drawbacks are clearly a function of the membrane itself. Thus, creating superhydrophobic surfaces, characterized by contact angles greater than 150°, can help mitigate the problem of membrane pore wetting during MD while controlling membrane thickness as well as membrane pore structure can help improve permeate flux [2,4]. Commercial microfiltration membranes made from polymers such as polytetrafluoroethylene (PTFE), poly(vinylidene-fluoride) (PVDF), polyethylene (PE) and polypropylene (PP) have been widely used in MD research because of their chemical resistance and inherent hydrophobicity [2,5–9]. These membranes are commonly prepared by such processes as sintering, stretching, and phase inversion. However, these methods result in membranes with low porosity and low surface hydrophobicity [2]. Membranes made from PTFE, which is the most hydrophobic of the listed polymers because of its low surface energy (19.1 mN/m), has a contact angle of only about 122° [6,10].

Electrospinning is rapidly emerging as a simple and reliable technique for the preparation of MD membranes because it offers a convenient way to control the morphology and properties of the resulting nanofibers [11–14]. The first attempt to use electrospun membranes as MD membranes for producing portable water from saline water was made by Subramanian's group [11,15]. Electrospun membranes have also been used in liquid filtration applications such as microfiltration and ultrafiltration, and more recently in nanofiltration [15–17]. They contain nonwoven, randomly oriented nanofibers and have unique features such as: interconnected pores, very large specific surface, high porosity, fine pore structure, micro-scaled pore size, and large aspect

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ratio, which enable them to have many biomedical and industrial applications [18]. Properties such as porosity, thickness, and fiber size of electrospun membranes can be tuned by controlling processing parameters as well as by post-fabrication heat treatment [17,19,20] making them even more attractive for MD. Electrospun membranes have porosities that are 10–20% greater than that of conventional membranes made by phase inversion [15]. They also tend to have higher surface hydrophobicity than membranes produced from the same materials *via* other methods [17,21]. This is because the cylindrical nanofibers obtained from electrospinning feature a first level re-entrant structure that leads to higher hydrophobicity [21]. However, electrospinning by itself may not be sufficient to produce superhydrophobic membranes. Hence, it is common to modify electrospun membranes by either additive blending or by post-fabrication treatments to achieve superhydrophobicity.

As mention previously, superhydrophobic surfaces are necessary to prevent pore wetting. It is well established that such surfaces can be constructed by creating re-entrant microtextures that induce roughness on membrane surfaces and/or coating membrane surfaces with low surface energy materials. The re-entrant structures minimize the contact area of a water droplet on a membrane surface by allowing pockets of air to exist between the surface and the droplet [22,23]. Several reports in the literature have investigated the modification of membrane surfaces to achieve superhydrophobicity. For example, Dong et al. [2] prepared superhydrophobic membrane by electrospinning a suspension of PTFE micropower in PVDF solution unto a microporous PTFE substrate. They achieved a static contact angle of about 152° for their membrane [2]. Prince et al. reported a contact angle of 154° after they fabricated electrospun membranes consisting PVDF blended with clay nanocomposites which were then tested in direct contact membrane distillation (DCMD) [24]. In another work, Liao et al. [25] fabricated robust superhydrophobic dual-layer membranes with contact angles exceeding 150° *via* electrospinning and tested them in DCMD. Their membrane consisted of an ultrathin three-dimensional superhydrophobic skin on a porous PVDF substrate. The superhydrophobic skin was achieved by modifying hydrophilic silica with α,ω-triethoxysilane-terminated perfluoropolyether ($(EtO)_3Si$-PFPE$Si(OEt)_3$) and Tetraethoxysilane (TEOS) and blending it with PVDF. Attia et al. [26] fabricated superhydrophobic composite membranes from electrospun PVDF and functionalized alumina. The superhydrophobic composite membranes displayed higher flux and rejection of heavy metals compared to pristine PVDF electrospun membranes when both were tested in air gap membrane distillation. In our most recent work [27], we reported a simple way to fabricate a superhydrophobic membrane. We coated the surface of an electrospun polyvinylidenefluoride-*co*-hexafluoropropylene (PVDF-HFP) membrane with microparticles of tetrafluoroethylene oligomer (OTFE). The contact angle increased from 124° for pure PVDF-HFP to 156° for the PVDF-HFP/OTFE membrane. In the present work, we take a step further from our most recent work and describe a novel technique to fabricate a membrane with both surface and bulk superhydrophobicity, and is capable of retaining high hydrophobicity after being used in MD.

2. Experimental

2.1. Materials

PVDF-HFP (Kynar Powerflex® LBG, Mw = 450,000 g mol^{-1}), tetrafluoroethylene oligomer (OTFE) powder (Cefral Lube V supplied from Central Glass Co. Ltd., molecular weight: 700–4000 g mol^{-1}, average particle size: 0.5–2.5 μm), acetone (Aldrich, CHROMASOLV®, for HPLC, ≥ 99.8%), and *N*, *N*-dimethylacetamide (Aldrich, CHROMASOLV® plus, for HPLC, ≥ 99.9%). All chemicals were used as received.

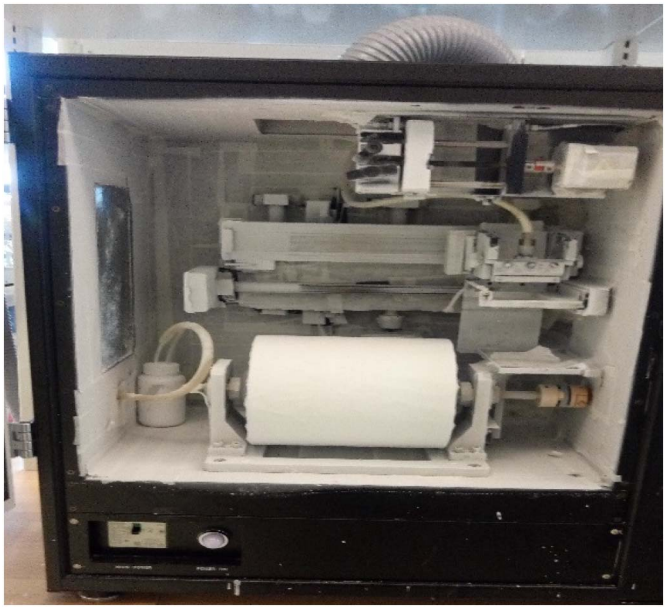

Fig. 1. Set up of electrospinning chamber.

2.2. Method of fabricating the superhydrophobic membrane

PVDF-HFP solution was prepared by dissolving 10 wt% of the polymer powder in a binary mixture of acetone and *N*, *N*-dimethylacetamide with a weight ratio of 7:3 at room temperature using a magnetic stirrer. The solution was then loaded into a 10-mL plastic syringe connected *via* a teflon pipe to a gauge-18 stainless steel needle (internal diameter = 0.838 mm). The loaded syringe was clamped into a Nanon-01A electrospinning set up (MECC Japan) containing a rotating aluminum drum collector. A plastic bottle containing OTFE micro-powder equipped with inlet and outlet connections was placed in the electrospinning chamber. While a potential difference of 25 kV was applied between the needle and the collector which was placed about 15 cm vertically below the needle, a feed rate of 1 mL h^{-1} was utilized under a relative humidity of 55% at room temperature. At the same time, OTFE dust was generated every 10 min using compressed air connected to the OTFE bottle inlet. The air pressure forces OTFE particles out of the bottle, creating an atmosphere of OTFE microparticles in the electrospinning chamber. The particle size range of OTFE as received form the supplier is between 0.5 and 2.5 μm. The air pressure chosen for dust generation was such that particle sizes at the lower end of the range exit the bottle and fill the electrospinning chamber. These particles then interact with the charged fiber jets and settle on the electrospun mat. The settling time was about 5 min. After spinning, the membrane collected on the aluminum foil was dried in a conventional oven at 50 °C for 24 h. The membrane was slightly hot pressed to infuse the surface particles in the polymer matrix. The produced superhydrophobic membrane is designated as PVDF-HFP/OTFE.

3. Characterization

3.1. Membrane thickness

The PVDF-HFP/OTFE membrane thickness was measured using a Mituoyo micrometer. Several measurements were taken and averaged.

3.2. Membrane morphology

A Quanta FEG 250 Scanning Electron Microscope (SEM) by FEI (Hillsboro, OR, USA), operating at 2–30 KeV, was used to examine the morphology of the PVDF-HFP/OTFE membrane. Prior to SEM imaging,