

ELECTROSPUN MEMBRANE: A REVIEW

NANOFIBER-COATED

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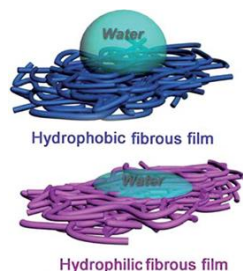
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Graphical abstract



Abstract

The nanofibre development offers various useful applications in many ways including energy and environmental application. Polymeric nanofibre fabricated by electrospinning has been seen as innovative membrane materials for water remediation owing to the high surface area, interconnected porous structure, and light weight. This paper reviews the exciting functionality of nanofibre involving the development of smart heterogeneous approaches in membrane material. These heterogeneous materials allow the water molecules to spontaneously penetrate from one side to another, while blocking penetration in reverse direction due to hydrophilic-hydrophobic differences. Composite membrane containing different features arrangements of nanofibres have been utilised for their ability for water applications especially in membrane distillation.

Keywords: Nanofiber, Coating, Hydrophobic, Hydrophilic

Abstrak

Pembangunan nanofiber menawarkan pelbagai aplikasi berguna, dalam pelbagai cara termasuk aplikasi tenaga dan alam sekitar. Nanofiber polimer diperbuat oleh penspinan elektrik yang dilihat sebagai bahan membran inovatif untuk pemulihan air kerana mempunyai permukaan yang tinggi, struktur berliang yang saling berkait dan ringan. Dalam kertas ini, kita mengkaji semula fungsi yang menarik nanofiber melibatkan pendekatan pembangunan heterogen pintar dalam bahan membran. Bahan-bahan ini mempunyai penembusan air secara spontan dari satu kawasan kepada yang lain, disamping menyekat arah penembusan berbalik yang disebabkan oleh perbezaan hidrofilik-hidrofobik memberi satu makna yang besar. Pelbagai susunan struktur membran komposit yang mengandungi ciri-ciri nanofiber yang berbeza telah menunjukkan kebolehupayaannya untuk aplikasi air terutamanya dalam aplikasi membran penyulingan.

Kata kunci: Fibernano, penyalutan, hidrofobik, hidrofilik

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1.0 INTRODUCTION

Nanotechnology has become a developing field that is concerned with materials and systems where the configuration and components exhibit novel and significantly improved features (e.g., chemical, biological) due to its nanosized structure [1]. The introduction of nanofibre in membrane application brings a new class of materials useful for many applications. The term nanofibre generally refers to fibre with less than one micrometre in diameter [2]. The nanofibre features of high surface to volume ratio and porosity have attracted its application in membrane filtration for environmental remediation [3], [4]. Most of porous polymer membranes manufactured via conventional phase inversion method have their limitations, for instance, low flux and high fouling tendency owing to its asymmetric void structure of pores formation across the membrane thickness and corresponding pore size distribution [5].

Nanofibre as a support membrane is one of the alternatives that can outperform conventional membranes. Nanofibre has a high porosity value (around 80%), hence giving high permeability, via entirely interconnected fibre with open pore structures [6]. Controllable pore size distribution from micron to submicron for water filtration and high surface to volume ratio are the other significant features of nanofibre. This feature makes these electrospun membranes easy to integrate its special functionality of nanofibre into an excellent absorption process for contaminant removal [3].

The following section reviews the basic fabrication of electrospun nanofibres via electrospinning and the application of nanofibres as filtration and membrane distillation.

2.0 NANOFIBER FABRICATION BY ELECTROSPINNING

The polymeric nanofibre fabrication involves a number of processing techniques such as electrospinning [7]–[9], melt blowing [10]–[13], template synthesis [14]–[18], self-assembly [19]–[21], and nanolithography [22]–[27]. Among these techniques, electrospinning is an effective process that can produce nanofibre from a wide range of polymeric materials. A basic electrospinning involves an electric field, by inducing a high-voltage power supply between polymer solution and a collector (a grounded metal electrode or rotating drum), which is separated at suitable distance (Figure 1). By applying high voltage, electric force would overcome the surface tension of the polymer surface solution and creating the pendent drop at the spinneret tip into a 'Taylor cone', producing the ejection of a thin jet [28]. The charged jet endures a stable stretching at first and starts bending and whipping randomly that leads to further stretching, owing to the effect of solvent evaporation and charge repulsion. Thus, the solidified fibre on the collector can

be in submicron diameter and has a randomly structured non-woven morphology. The morphological electrospun nanofibre is basically governed by these following factors [29]:

1. Molecular weight and molecular weight distribution of polymer.
2. Viscosity, conductivity, and surface tension of polymer solution.
3. Concentration, rate of flow, and electric potential of solution.
4. Temperature and humidity of surroundings.
5. Diameter of needle and distance between capillary to collector.
6. Rotational speed of collector.

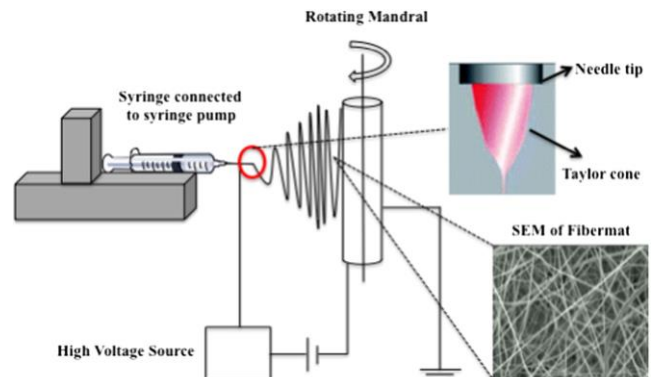


Figure 1 Schematic of a standard horizontal electrospinning setup including at least one syringe pump, a polymer solution, a high voltage supply, a source electrode, and a collector electrode [30]

3.0 NANOFIBER MEMBRANES FOR WATER FILTRATION

For water filtration, the fibrous scaffold structure of nanofibre has attracted much attention due to high filtration efficiency and low resistance provided. The versatility in nanofibre manufacturing process based on controllable pore size and pore size distribution gives an alternative to replace conventional membrane [31]. For instance, Gautman *et al.* demonstrated a solid-liquid clarification of a lignocellulosic hydrolysate and fermentation broth containing yeast cells using nanofibres [32]. Three commercial microfilters (polyethersulfone, polyvinylidene fluoride, and mixed cellulose ester) performed lower flux and higher irreversible fouling compared to the polyimide nanofibre membrane for both applications.

These results in water flux decline. Song *et al.*, 2011 studied the relationship between different membrane structures and their performance of a nanofibre composite (NC) and a homemade phase inversion (PI) membrane for forward osmosis application (Figure 2) [33]. In the study, the tortuous sponge-like structure dramatically inhibits salt diffusion in the porous support of PI membrane and results in low osmotic driving force, while the interconnected pore structure favours salt diffusion in the support layer of NC membrane

resulting in high osmotic driving forces. Thus, the diffusion resistance in FO has greatly reduced the ICP problem in PI membrane. Interconnected fibres break the bottleneck of internal concentration polarization (ICP) of forward osmosis (FO) membrane for high water production rate. FO is driven by osmotic pressure gradient across a semipermeable membrane. All of phase inversion membranes for FO application suffer ICP problem.

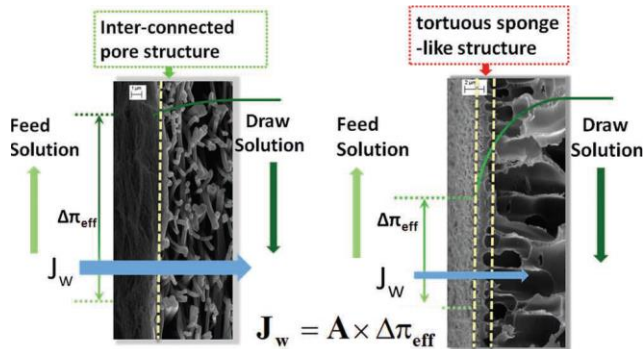


Figure 2 Comparison of the salt diffusion of concentration profile for NC and PI membrane [34]

In another application, the electrospun membrane for oil and water separation shows a vital indicator of their capability to treat oil waste water. The combination of super-hydrophobic and hydrophilic in nanofibrous scaffold structure gives new perspective for membrane application. Tai *et al.*, modified polyacrylonitrile (PAN) electrospun with SiO₂ and coated with silicone oil to produce membrane with ultrahydrophobic and superoleophilic features. The lab scale oil water separation test indicated the membrane had an excellent oil-water separation efficiency. Figure 3 shows the permeate flux of petroleum spirit, iso-octane, and hexane of 3032.4 ± 234.6, 1719.1 ± 36.2, and 2648.8 ± 89.7 L/m²h, respectively [35]. These values are comparable to or even higher than the other oil-water separation filtration membranes such as superhydrophobic polyvinylidene fluoride membrane (700–3500 L/m²h) [36], mineral-coated polypropylene microfiltration membrane (>2000 L/m²h) [37], and crosslinked poly(ethylene glycol) diacrylate-coated membrane (<100 L/m²h) [38].

Nevertheless, the higher density of water compared to most oils makes the position of superoleophobic upon superhydrophilic membrane system desirable. Ding *et al.*, effectively demonstrated the super wetting electrospun nanofibre membrane

that could separate water in oil as well oil in water in micron droplet size [39]. This brings to the conceptual of unidirectional water penetration electrospun composite simulated by Wu *et al.* [40]. A composite of hydrophobic polyurethane (PU) and hydrophilic crosslinked polyvinyl alcohol (c-PVA) fibrous layer was developed. By taking the benefits of the hydrophobic and hydrophilic differences, water can penetrate from hydrophobic side, but blocked on the hydrophilic side.

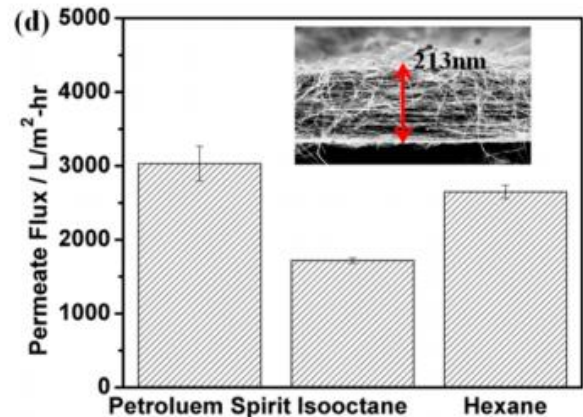


Figure 3 Permeate flux for different types of oils. The inset shows the cross-sectional view of the membrane thickness [35]

Based on Figure 4, water is dropped on the upward hydrophobic PU side and penetrated underneath the c-PVA layer within less than 3.5s. Wu *et al.*, hypothesized that water suffers two opposing forces, which are hydrostatic pressure (HP) and hydrophobic force (HF). HF tends to resist the water's downward penetration due to HP effect. As water goes deeper with the increasing HP (increasing water volume), the HF remains constant. But, once the penetration depth reaches the thickness of PU film, water will contact the lower hydrophilic c-PVA film. Then, capillary force (CF) provided by porous hydrophilic c-PVA film together with HP eases the water penetration and makes this process continuous. However, when water is dropped on the upward hydrophilic c-PVA side, the water spreads to a thin water film under capillarity. When the water reaches the interface of c-PVA and PU, HF provided by porous hydrophobic PU film resists water's further penetration and even not penetrated at all after 7 s of water dropping [40].

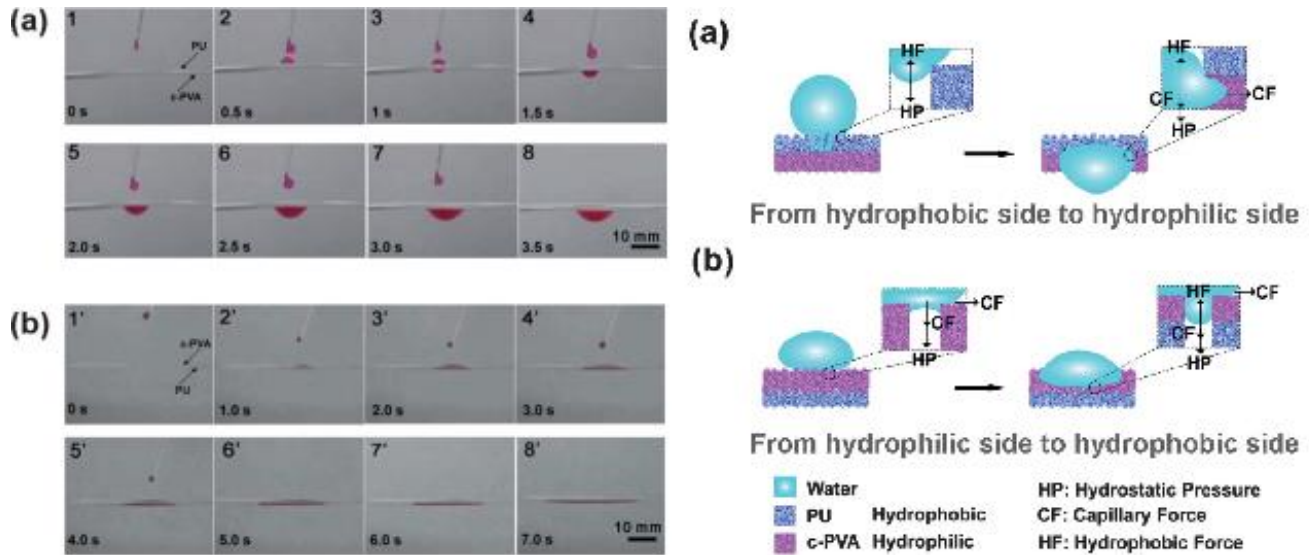


Figure 4 The snapshot of water penetration phenomenon from two side of heterogeneous composite film and mechanism of unidirectional water penetration on a heterogeneous wettable composite film [40]

4.0 NANOFIBER COATING FOR MEMBRANE DISTILLATION APPLICATION

Nanofibre as a membrane coater is one of the techniques in membrane surface modification. These modifications are according to the membrane functionality such as absorption [41]–[44], and photocatalytic [29], [45]–[48]. In fact, the nanofibre brings a different aspect for heterogenous material especially for membrane application. The highlight for heterogeneous conceptual idea/design is based on the distinct hydrophobic–hydrophilic differences that leads to rapid penetration upon the fibrous membrane. This heterogeneous material makes the water spontaneously penetrate through the nanofibre membrane, while blocking penetration in reverse direction due to hydrophilic-hydrophobic differences.

Many studies have concentrated on improving the membranes used in membrane distillation (MD) by increasing its hydrophobicity to avoid pore wetting. Pore wetting is defined as saturated fluid liquid in the membrane pores or vapour condensation phenomenon that leads to flux deterioration. Recently, Efome *et al.* [49] reported the modification of PVDF flat sheet nano-composite membranes by coating with electro-spun PVDF nano-fibres to increase the surface hydrophobicity (Figure 5). It successfully prevented liquid water from penetrating into the pores, hence increasing the liquid entry pressure (LEP_w) and resulting in more stable flux [3]. In addition, desalination of synthetic sodium chloride (NaCl) salt solution via nanofibre coated membranes by MD resulted in stable flux in the long-term testing than the membranes without coating.

Nanofibre application has been adapted by Prince *et al.* [50] by designing an innovative system to minimise pore wetting by proposing nanofibers-based

hydrophilic/hydrophobic membrane with a thin hydrophobic nanofibres layer on the top and a thin hydrophilic nanofibres layer on the bottom of the micro-porous membrane, which were fabricated by conventional phase inversion technique. The modification of hydrophilic/hydrophobic is functioned of surface modifying macromolecule (SMM) that brings into different hydrophobic-hydrophilic potential for preventing pore wetting phenomenon. Based on Figure 6, the highly hydrophobic PVDF nanofibre layer is repelling liquid and the highly hydrophilic PVDF/SMM nanofibre is absorbing the water molecule (condensed vapour) from the intermediate layer, which enhances the vapour flux across the membrane [49]. Both studies proposed that the structure with nanofibre-based hydrophobic/hydrophilic layers could be a promising solution for pore wetting issue in the MD processes.

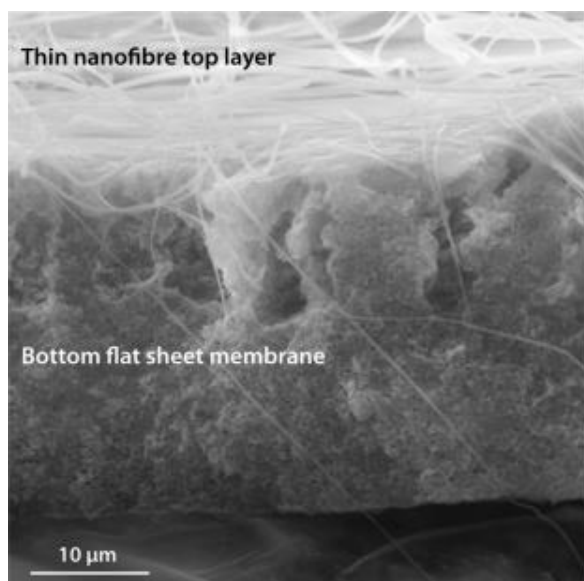


Figure 5 SEM image of the dual layer membrane [50]

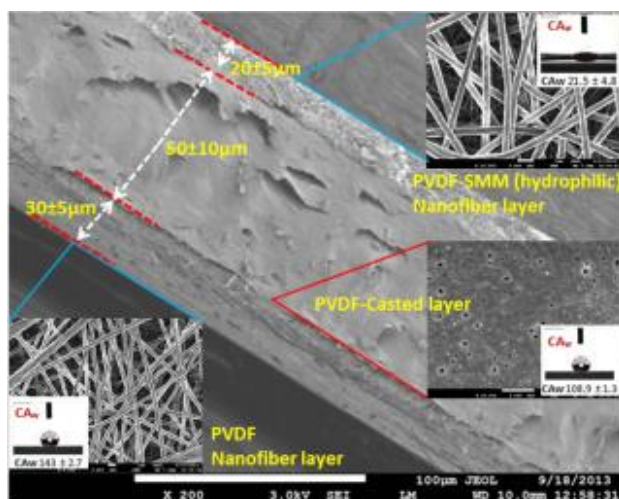


Figure 6 SEM image of the triple layer membrane [49]

5.0 CONCLUSION

Membrane in nanofiber form offers some unique benefits upon conventional membrane due to higher surface-to-volume ratio, controllable interconnected pore size, and easy surface modification. The practicality of nanofiber has been greatly improved with recent advance in membrane application, leading to sustainable and lower cost material consumption. In addition, the fabrication of nanofiber through electrospinning technology has been demonstrated to be a versatile technique in fabricating highly porous fibrous membrane. The innovation and scalable electrospinning process and flexible surface treatment make it particularly suitable for desirable membrane application. The surface modification of nanofiber surface leads to the production of heterogeneous materials by function of two intrinsic properties of hydrophilic and hydrophobic

differences. This review is to highlight the potential of nanofibers into unidirectional water penetration function. It is revealed that these heterogeneous features bring a significant impact especially in desalination for MD processes.

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