

# **Fabrication of Electrospun Nanofibrous Membranes for Membrane Distillation Application**

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## **Abstract**

Nanofibrous membranes of matrimide were successfully fabricated using electrospinning technique under optimized conditions. Nanofibrous membranes were found to be highly hydrophobic with high water contact angle of  $130^\circ$ . FESEM and pore size distribution analysis revealed the big pore size structure of electrospun membranes even greater than  $2\mu\text{m}$  and the pore size distribution is found to be narrow. Flat sheet matrimide membranes were fabricated via casting followed by phase separation. The morphology, Pore size distribution and water contact angle were compared with the electrospun membranes. Both membranes fabricated by electrospinning and phase separation techniques were subjected to membrane distillation (MD). Electrospun membranes showed high water vapour flux of  $56\text{ kg/m}^2\text{-h}$  and it is very high compared to the casted membrane as well as most of the fabricated and commercially available highly hydrophobic membranes.

Keywords: Electrospinning; Nanofibers; Membrane Distillation; Water Vapour Flux

## 1. Introduction

Our world is facing water and energy shortage. One-sixth of the world's population have no access to improved drinking water, and "All the signs suggest that it is getting worse and will continue to do so, unless corrective action is taken" [1]. Non-conventional water resources such as desalination will undoubtedly play an increasing role in meeting worldwide water needs, but it is limited by its high cost, which is largely dominated by energy costs [2]. This explains why the desalination technologies are mainly used in countries where the fossil-fuel is available. The separation of freshwater from saltwater can be achieved in many ways and these are discussed at length in standard texts on desalination [3].

As an alternatively new process, membrane distillation (MD) is being investigated as a low cost and energy saving by using low-grade energy waste heat source to the conventional thermal-based and membrane-based separation processes since the eighties [4-6]. MD is a thermally driven process in which water is the major component present in the feed solution to be treated. There is a thermally driven vapor transport through non-wetted porous hydrophobic membranes where the driving force is the partial vapor pressure difference across the two sides of membrane pores [6]. In MD process, the membrane acts only as a barrier between the two phases involving mass transfer and does not directly contribute to the process selectivity [8], the productivity, long term stability and energy efficiency of the process are highly dependent on the membrane properties [7-9]. Characteristics required for a good direct contact membrane distillation (DCMD) membrane to yield high water vapour flux, long term stability and high energy efficiency are high hydrophobicity, optimum pore size and pore size distribution, high bulk and

surface porosities, high degree of pores interconnectivity, low thermal conductivity and an optimum thickness [8,9].

Our research group developed polymeric nanofibrous membranes with exciting properties for MD desalination application. Electrospinning was employed as a technique for the fabrication of microporous nanofibrous membrane. Electrospinning is a cost effective method for the fabrication of nonwoven nanofibrous membranes having large surface to volume ratios and various fiber morphologies and geometries[10]. Researchers have been used electrospun nanofibers in various potential applications such as tissue engineering [11-13], photo voltaic cells [14,15], high performance air filters [16], membranes in separation processes [17, 18], sensors [19, 20], advanced composites [21,22] etc. Electrospun nanofibrous membranes have the properties such as large porosity and big pore size with narrow pore size distribution and large surface area. These properties are most desirable for MD process to produce high water vapour flux.

In this study, we have fabricated nanofibrous membranes of matrimide solution via electrospinning technique. The membranes were characterized and subjected to DCMD process for the sea water desalination. Influence of feed solution temperature as well as permeate temperature on water vapour flux was studied. Matrimide membranes were fabricated via casting followed by phase separation and their DCMD performance was compared with electrospun nanofibrous membranes.

## **2. Experimental**

Matrimide 5218 and N-methyl pyrrolidone (NMP) were purchased from Huntsmann Advanced Materials, USA and Sigma Aldrich respectively. Matrimide was dissolved in NMP to obtain 18 % (w/w) and was electrospun by using an electrospinning apparatus, ES 2000, Japan.

Matrimide solution was fed into a standard 5 ml glass syringe attached to 25G blunted stainless steel needle. A 30 kV DC voltage was applied to the syringe tip and the flow rate was adjusted to 15 $\mu$ L/min. Aluminium foil mounted on a rectangular metallic plate was fixed at a distance of 17 cm from the syringe tip and used as collector to collect polymeric nanofibers from the syringe. By increasing the voltage, the semi spherical form of polymeric solution at the tip of the syringe needle will deform into the form of a cone (Taylor Cone) and beyond a particular voltage a fast jet of polymeric solution will eject from the apex of the Taylor cone in the form of nanofibers to the grounded collector plate. The grounded collector plate was moved in zig-zag direction to collect nanofibers uniformly throughout the spinning process. Another batch of matrimide solution was prepared with the same concentration and electrospinning was carried out with the same spinning parameters on a polyester support mounted on a grounded collector plate to get composite matrimide nanofibrous membrane. After electrospinning the resultant matrimide nanofibrous membrane and polyester-matrimide composite membranes were peeled out from the aluminium foil and kept in a vacuum oven at 60°C for 12 h.

A part of above prepared matrimide solution was poured into a glass plate and using a 150  $\mu$ m knife, the solution was evenly spread throughout the surface of the glass plate and immediately dipped in a water bath for 1 h to get the flat sheet matrimide membrane via phase separation. The membrane was dried in a vacuum oven for 12 h. All the fabricated matrimide membranes were subjected to different characterization techniques as well as MD testing.

Membrane samples were sputter coated using Auto Fine Coater (JEOL JFC-1200) machine to coat a thin gold layer to make the film surface conductive. The surface morphology of polyimide nanofibers was studied under field emission scanning electron microscope (SEM; Quanta 200 FEG System: FEI Co., USA). The average fiber diameter distribution was analysed

from the SEM images using Image J analysis software. (Image J, National Institutes of Health, USA). Mean Flow pore size (MFP), First Bubble Point (FBP) and pore size distribution was measured using IB-FT Gm bH Porolux 1000 Porometer, Germany., by wet-up/dry-up method and the analysis was done using Automated Capillary Flow Porometer system software.

Hydrophobic nature of membranes fabricated via electrospinning and phase separation was measured using Attension, KSV instruments T 301, Finland. According to Young's equation [23],

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos \theta$$

where  $\gamma^{sv}$  is the solid surface free energy,  $\gamma^{sl}$  is the solid/liquid interfacial free energy,  $\gamma^{lv}$  is the liquid surface free energy and  $\theta$  is the contact angle.

All membranes were cut into 6 cm X 6cm pieces to fit into the MD module and subjected to MD testing at different optimized processing conditions using a lab scale MD set up. Seawater was preheated to desired temperatures and circulated through the membrane module, whereas the pure cold water was circulated through the other side of the membrane simultaneously in counter current direction. Salt concentrations of both permeate and feed solutions were determined by using conductivity meter (Oakton Eutech Instruments, Malaysia). The salt rejection ( $\beta$ ) and water vapour flux ( $J_v$ ) were determined by using the following equations.

$$\beta = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

$$J_v = M_w / At$$

Where  $C_p$  and  $C_f$  are the salt concentrations of bulk permeate and feed solutions respectively.  $M_w$  (kg) is the weight of collected permeates,  $A$  ( $m^2$ ) is the effective membrane area and  $t$  (h) represents the time interval. The influence of water vapour flux on feed solution temperature from a range of 40 °C to 80 °C was studied by keeping temperature of the permeate side at

20 °C. The influence of transmembrane flux was also studied form a range of 10 °C to 30 °C by keeping feed solution temperature constant at 60 °C.

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**Figure 1. Schematic of electrospinning set up**  
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**Table 1. Electrospinning Conditions for the fabrication of Nanofibrous membrane**  
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### **3. Results and Discussion**

Figure 1 shows the schematic diagram of an electrospinning set up. Polymeric nanofibrous membranes were obtained from matrimide solution. Table 1 shows the processing parameters and conditions used for electrospinning. Figure 2 shows the SEM images of nanofibrous matrimide membrane and membrane obtained via phase separation. Both the membranes show different morphologies. Nanofibers seem to be randomly distributed and highly porous with open structure whereas the membrane fabricated using phase separation shows smooth surface with many small pores. Figure 3 shows the fiber diameter distribution of nanofibers in the electrospun membrane and it reveals that the diameter distribution is narrow.

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**Figure 2. SEM Images of (a) Electrospun Nanofibrous Matrimide Membrane and (b) Composite Matrimide Membrane fabricated by Casting**  
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**Figure 3. Fiber Diameter Distribution of Electrospun Nanofibers**  
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More than 75% of fibers are having diameters in the range of 250-370 nm and the average fiber diameter was measured to be 290nm. MD process comes under micro filtration and membrane pore size plays a very important role in the mass transport across the membrane to get

considerable water vapour flux. Figure 4 shows the pore size distribution of the electrospun matrimide membrane. The mean flow pore size (MFP) of electrospun membrane was measured to be 2.15  $\mu\text{m}$  and the casted membrane was observed to be very small from the SEM image and was not detectable using the Porometer. The first bubble point (FBP) and smallest pore of electrospun membrane was measured to be 3.12  $\mu\text{m}$  and 1.71  $\mu\text{m}$  respectively.

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**Figure 4. Pore Size Distribution of Electrospun Matrimide Nanofibrous Membrane**

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**Figure 5. Water Contact Angle Measurements of Matrimide Membranes**

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**Table 2. Water Contact Angle Measurements of Matrimide Membranes**

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Figure 5 shows the images taken during water contact angle measurements of different matrimide membranes. The image of water droplet on electrospun membrane is more spherical than that of the composite membrane fabricated by phase separation. Table 2 shows the results of contact angle measurements. An average of five different measurements on a membrane was taken as the water contact angle of the membrane. It was observed that the water contact angle of electrospun membrane is considerably higher than that of the membranes fabricated via phase separation. Electrospun membranes show a water contact angle of  $130.0 \pm 2.2^\circ$  whereas the casted membranes show  $85 \pm 1.8^\circ$ , which is 35% less than that of electrospun membranes. It is possible to get high surface roughness during electrospinning process due to the nanofibrous morphology; moreover nanofibers are randomly overlaid throughout the membrane.

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### **Figure 6. Schematic Representation of Lab Scale DCMD Set Up**

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Figure 6 shows the schematic representation of lab scale set up of MD and Figure 7 represents the influence of feed temperature on water vapour flux at constant permeate temperature. Increase in the feed solution temperature results in the increase in the partial vapour pressure difference between the feed and permeate side of the membrane, which results in the increase in the trans-membrane flux across the membrane. It is clear that electrospun matrimide membranes yield high water flux reaching  $56 \text{ kg/m}^2\text{-h}$  at  $80 \text{ }^\circ\text{C}$  when compared to the composite matrimide membranes fabricated via phase separation and flux of the later was observed to be  $24 \text{ kg/m}^2\text{-h}$ . It is about 243 % increase in the water flux for electrospun nanofibrous membranes compared to the matrimide membranes fabricated via phase separation.

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### **Figure 7. Influence of Feed Inlet Temperature on Permeate Flux**

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### **Figure 8. Influence of Permeate Inlet Temperature on Permeate Flux**

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There is no significant deviation in the water vapour flux between non- supported electrospun matrimide membrane and the composite nanofibrous matrimide membrane obtained by the electrospinning on a polyester support. High water flux shown by electrospun membranes is attributed to their highly open pore structure with larger pore size, interconnectivity of pores and pore size distribution of membranes compared with the membranes obtained via phase separation. Theoretically, MD offers 100% salt rejection because of the fact that the hydrophobic

microporous membrane only allows passage of water vapours and non-condensable gases but it strictly prohibits the salts. In our study, all the fabricated membranes show high salt rejection of about 99.99%. While investigating the DCMD performance by changing permeate inlet temperature from 10 °C to 30 °C at constant feed solution temperature of 60 °C, a small decrease in water vapour flux was observed (Figure 8). This is because the vapour pressure formation at lower temperature is less than that at higher degrees of temperatures. Figure 8 shows the influence of permeate inlet temperature on the trans-membrane flux at constant feed solution temperature as well as constant feed and permeate flow rate for all types of fabricated membranes.

#### **4. Conclusions**

The main objective of this study was to fabricate the nanofibrous matrimide membranes by using electrospinning technique and testing their performance in DCMD process. The experimental results can be summarized as follows:

- (1) Nanofibrous matrimide membranes were successfully fabricated using electrospinning technique.
- (2) Fabricated membranes showed large pore size (2.1  $\mu\text{m}$ ), pore size distribution with high interconnectivity between pores which results in high water vapour flux with high salt rejection (99.99%).
- (3) Electrospinning process helped to fabricate membranes with maximum surface roughness and it results high water contact angle ( $130^\circ$ ) which prevent the pore wetting and hence increase the membrane life time.
- (4) DCMD performance of electrospun membranes were compared with the composite matrimide membranes fabricated via phase separation and found that the former membranes

showed magnificent results. In short electrospinning is a reliable and promising technique for the fabrication of membranes for MD process.

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