

# **Modifications of PVDF-co-HFP membranes for desalination by direct contact membrane distillation**

*By*

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## **CERTIFICATE OF AUTHORSHIP/ORIGINALITY**

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of candidate

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## **LIST OF ABBREVIATIONS**

MD: Membrane Distillation

LMH: Liter per Square Meter per Hour

FE-SEM: Field Emission Scanning Electron Microscopy

LEP: Liquid Entry Pressure

RO: Reverse Osmosis

FO: Forward Osmosis

DCMD: Direct Contact Membrane Distillation

AGMD: Air Gap Membrane Distillation

VMD: Vacuum Membrane Distillation

SGMD: Sweeping Gas Membrane Distillation

PVDF: Polyvinylidene Fluoride

NIPS: Non-solvent-induced Phase Separation

TIPS: Thermally Induced Phase Separation

VOC: Volatile Organic Compounds

PTFE: Polytetrafluoroethylene

PP: Polypropylene

PE: Polyethylene

CA: Contact Angle

PVDF-co-HFP or PH: poly (vinylidene fluoride-co-hexafluoropropylene)

PVDF-co-CTFE: poly (vinylidene difluoride-co-chlorotrifluoroethylene)

NTIPS: Nonsolvent-thermally-induced Phase Separation

CPL:  $\epsilon$ -caprolactam

PS: Polystyrene

PAN: Polyacrylonitrile

PET: Polyethylene terephthalate

DMAc: Dimethylacetamide

DMSO: Dimethyl sulfoxide

NMP: N-Methyl-2-pyrrolidone

THF: Tetrahydrofuran

RH: Relative Humidity

CBD: Chemical Bath Deposition

CVD: Chemical Vapor Deposition

PPFDA: poly (1H, 1H, 2H, 2H-perfluorodecyl acrylate)

LBL: Layer-by-layer

TFPTMOS: Alkoxides 3, 3, 3-trifluoropropyltrimethoxysilane

TMOS: Tetramethyl orthosilicate

i-pp: Polypropylene

SMM: Surface Modifying Macromolecules

PS $\mu$ M: Phase Separation Micromolding

PDA: Self-polymerized Polydopamine

NCC: Nanocrystalline Cellulose

PMMA: Poly (methyl methacrylate)

FPU: Fluorine End-capped Polyurethane

SLIPS: Slippery Liquid-infused Porous Surface

PCL: Poly (Caproectone)

PPFEMA: Polymerized Perfluoroalkyl Ethyl Methacrylate

DI: Deionized

PSD: Pore Size Distribution

# TABLE OF CONTENTS

ACKNOWLEDGEMENT .....	ii
LIST OF ABBREVIATIONS .....	iii
TABLE OF CONTENTS .....	vi
LIST OF FIGURES .....	ix
LIST OF TABLES .....	xi
ABSTRACT .....	xii
1. Introduction .....	2
1.2 Need of membrane designed for MD .....	3
1.3 Fabrication and modification of membrane for high LEP.....	4
1.4 Heat-press on electrospun membrane.....	5
1.5 Research objectives and scopes.....	5
1.6 Outline of thesis.....	6
2. Literature review .....	8
2.1 Membrane distillation.....	8
2.1.1 MD configurations .....	8
2.1.2 Development history of MD .....	11
2.1.3 Mechanism and modeling of MD .....	12
2.1.4 Critical conditions in MD setup.....	13
2.1.5 Hydrophobicity of membrane and wetting .....	16
2.1.6 Other phenomenon of MD affecting permeation performance .....	18
2.2 Membrane fabrication .....	18
2.2.1 Requirement of MD membrane .....	19
2.2.2 Current commercial membranes used in laboratory .....	20
2.2.3 Laboratory membrane fabrication via phase inversion.....	20
2.2.4 Membrane fabrication via electrospinning for MD .....	22
2.2.5 Membrane fabrication via other methods .....	22

2.3 Electrospinning.....	23
2.3.1 Development of electrospinning.....	24
2.3.2 Mechanism of electrospinning process.....	25
2.3.3 Preparation of polymer solution for electrospinning.....	26
2.3.4 Crucial parameters in electrospinning.....	27
2.4 Membrane modification for wetting resistance.....	31
2.4.1 Top-down approaches.....	32
2.4.2 Bottom-up techniques.....	35
2.4.3 Combination of top-down and bottom-up.....	36
2.5 Case study: pilot-scale MD plant in Plataforma Solar de Almeria (PSA), Spain (Guillen-Burrieza et al. 2014).....	39
2.5.1 Background.....	39
2.5.2 Membrane and membrane modules.....	40
2.5.3 Effect of fouling on characteristics of the fouled membranes.....	40
2.5.4 Discussion of cleaning strategies.....	41
3. Materials and methods.....	44
3.1 Materials.....	44
3.2 Membrane fabrication by electrospinning.....	44
3.3 Heat-press post-treatment.....	44
3.4 Characterization.....	47
3.5 Direct contact membrane distillation (DCMD) test.....	48
4. Effects of heat-press conditions.....	51
4.1 Effect of heat-press temperature on the membranes.....	51
4.1.1 Effect of heat-press temperature on MD permeation flux.....	55
4.2 Effect of heat-press pressure on the membranes.....	56
4.2.1 Effect of heat-press pressure on MD permeation flux.....	60
4.3 Effect of heat-press duration on the membranes.....	61



4.3.1 Effect of heat-press duration on MD permeation flux.....	65
5. Influence of thickness on electrospun membranes.....	67
5.1 Influence of thickness on membrane characteristics.....	67
5.2 Effects of heat-press on characteristics on membrane with various thickness.....	68
5.3 MD permeation performance with membrane having various thickness before and after heat-press .....	72
5.4 DCMD performance comparison with other studies using heat-pressed membranes.....	75
6. Conclusion and recommendations .....	78
6.1 Conclusions .....	78
6.2 Recommendations .....	79
6.2.1 Further study on heat-press conditions.....	79
6.2.2 Superhydrophobic modification with aerogel powder .....	80
6.2.3 Optimization of support layer and its adhesion to active layer with electrospinning .....	80
APPENDIX.....	82
REFERENCE.....	83

## LIST OF FIGURES

Figure 1-Current water treatment technology involving usage of membrane .....	2
Figure 2-Processes of various MD configurations: (a) DCMD and DCMD with liquid gap; (b) VMD; (c) SGMD and thermostatic SGMD; (d) AGMD (Khayet & Matsuura 2011). .....	9
Figure 3-Schematic diagram of MD mechanism .....	12
Figure 4-SEM images of supported layers: (a) scrim-backing; (b) non-woven. (Adnan et al. 2012).....	14
Figure 5-Variou states of wetting .....	16
Figure 6- Schematic of electrospinning process .....	24
Figure 7-Schematic diagram of taylor cone in electrospinning process .....	25
Figure 8-SEM images of PS fibers and beads electrospun with various solvents: (a) THF; (b) Chloroform; (c) CS <sub>2</sub> ; (d) NMP; (e) DMF (Eda et al. 2007). .....	29
Figure 9- SEM images of PTFE foils: (a) untreated; (b) treated with oxygen plasma for 60 s; (c) 120 s; (d) 10 mins (Li et al. 2007). .....	33
Figure 10.Illustration of assumed mechanism of heat-press on PVDF electrospun membrane.....	34
Figure 11-Membrane modules used in pilot AGMD plant at PSA.....	39
Figure 12-Impact of fouling on the major parameters of MD membranes .....	40
Figure 13-Comparison of CA, LEP, and BP with various cleaning strategies .....	41
Figure 14-Schematic diagram of DCMD process used in this study.....	49
Figure 15- SEM images of as-spun and heat-pressed PH membrane at magnifications of 10 K and 50 K: (a)as-spun neat membrane (Neat); membranes heat-pressed under (b) 140 °C (M0); (c) 150 °C (M1); and (d) 160 °C (M2). .....	51
Figure 16- Pore size distributions of as-spun and membrane samples heat-pressed under various temperatures. ....	52
Figure 17- Effects of temperature on thickness, porosity and contact angle .....	53
Figure 18-Flux comparisons of electrospun membranes heat-pressed at various temperatures .....	56
Figure 19-SEM images of heat-pressed PH membrane at magnifications of 10 K and 50 K: membranes heat-pressed under (a) 0.7 kPa (M1-A); (b) 2.2 kPa (M1-B); (c) 6.5 kPa (M1-C), and; (d) 9.8 kPa (M1-D).....	57

Figure 20- Pore size distributions of as-spun and membrane samples heat-pressed under various pressures. ....	58
Figure 21-Effects of pressure on thickness, porosity and contact angle .....	58
Figure 22- Flux comparisons of electrospun membranes heat-pressed at various pressures.....	61
Figure 23- SEM images of heat-pressed PH membrane at magnifications of 10 K and 50 K: membranes heat-pressed for (a) 1 h (M1-B-1); (b) 2 h (M1-B-2); (c) 4 h (M1-B-3); (d) 8 h (M1-B-4).....	62
Figure 24-Pore size distributions of as-spun and membrane samples heat-pressed for various durations. ....	63
Figure 25-Effects of heat-press pressure on thickness, porosity and contact angle.....	63
Figure 26- Flux comparisons of electrospun membranes heat-pressed at various durations.....	65
Figure 27-Comparison of CA and porosity of electrospun membrane with various thicknesses .....	68
Figure 28-Representative SEM cross section images of as-spun, PH3 (a: 400 K) and heat-pressed membrane, PH3' (b: 350 K; c: 1500 K).....	69
Figure 29-Effects of heat-press with optimal conditions on porosity and contact angles of membranes with various thicknesses.....	71
Figure 30-Comparison of DCMD permeation performance of selected membrane samples.....	74

## LIST OF TABLES

Table 1- Key parameters of membranes that affect MD permeation performance.....	19
Table 2-Key properties of the unused PTFE membranes .....	40
Table 3-Heat-press conditions and name conventions used in the present study. ....	46
Table 4- Characteristics of the membranes after heat-press at different temperatures .....	54
Table 5-Characteristics of the membranes after heat-press at different pressures.....	59
Table 6-Characteristics of the membranes after heat-press at different durations.....	64
Table 7-Comparison of membrane characteristics with various thicknesses.....	67
Table 8-Characteristics of the membranes with various thicknesses after heat-press .....	70
Table 9- Comparison of heat-pressed MD flat-sheet membranes for desalination with commercial PVDF membrane.....	75

## ABSTRACT

Membrane distillation (MD) has been considered as a promising next-generation technology for desalination because of its high efficiency regarding permeation performance and energy consumption. The foundation of MD mechanism is based on membrane contact rather than membrane permeation process. It means that only vapor molecular can pass through the membrane sheet rather than liquid water. In recent years, electrospun polymer fiber membranes are widely studied due to their high porosity, high hydrophobicity, controllable fiber distribution, and ease of fabrication and modification. However, because such membranes are susceptible to wetting in long-term operation, the robustness of these membranes are still not guaranteed, especially when the MD system is applied with relatively high feed temperature. Heat-press treatment is a simple and effective procedure to improve the morphology and thus characteristics of polymer membranes. More than 8 h stable MD performance with an average flux of 34 liters per square meter per hour (LMH) and 99.99% salt rejections may be achieved with heat-pressed membranes, while the membranes without the post-treatment can easily become wetted only in half an hour. In the current study, three controllable conditions during heat-press (which are temperature, pressure, and duration) were investigated, and their effects on the morphology and characteristics were carried out in separate stages, which would be addressed in detail in this report.

In stage 1, by applying heat-press on membrane with various temperatures, mechanical strength was proved to be improved greatly. Maximal stress of the electrospun membrane can be greatly increased from 11.7 to 103.9 MPa once samples were heat-pressed at 160 °C. However, the thickness of the membrane could be decreased significantly from 45 to 31 μm because of partially melting of the films, which could be observed through the relative FE-SEM images analysis. In stage 2, it was found out that increase in pressure from 0.7 to 9.8 kPa in heat-press process could result in the further reduction of surface pore size from 0.49 to 0.42 μm. Generally, heat-pressed membranes lost some hydrophobicity as the surface roughness decreased owing to premelting phenomenon, and the loss of hydrophobicity was confirmed by the reduction of contact angle. A decrease from 152° to 139° could be observed when membranes heat-pressed for 8 h. Nevertheless, the loss of hydrophobicity was offset by the increase in mechanical strengths. Impressive improvement of both tensile strength and LEP could be observed after heat-press. Therefore, based on the improvement of LEP and

mechanical, better resistance against wetting could be achieved in MD process. In stage 3, it was found that longer duration of heat-press could improve the membrane morphology and thus its characteristics as well. Membrane that had been heat-pressed for 8 h had smaller pore size and higher LEP than the ones heat-pressed for shorter duration. Furthermore, influence of membrane thickness was investigated, and optimum treatment conditions for the membrane were developed in the study. Then, the optimum conditions of heat-press were applied on the electrospun membranes with various thicknesses to verify whether the technique could be applied on thicker membranes and what was the degree of its effectiveness.