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

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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: Polyethene

CA: Contact Angle

PVDF-co-HFP or PH: poly (vinylidenefluorideco-hexafluoropropylene)

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

NTIPS: Nonsolvent-thermally-induced Phase Separation

CPL: ε-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

PSμM: 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 (Caprolectone)

PPFEMA: Polymerized Perfluoroalkyl Ethyl Methacrylate

DI: Deionized

PSD: Pore Size Distribution

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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 ^{o}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^{o} to 139^{o} 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.