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Tailoring and Characterizing Pore Size Distribution of Phase Inverted Porous Polymeric
Membranes: What, Why, and How?

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Civil Engineering

by

Minhao Xiao

2024

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2024

ABSTRACT OF THE DISSERTATION

Tailoring and Characterizing Pore Size Distribution of Phase Inverted Porous Polymeric Membranes: What, Why, and How?

by

Minhao Xiao

Doctor of Philosophy in Civil Engineering

University of California, Los Angeles, 2024

Professor Eric M.V. Hoek, Chair

In this thesis, the methodology of tailoring and characterizing pore size distribution (PSD) of phase inverted porous polymeric membranes is conducted with theoretical model simulations and experimental verification. The investigative journey begins with the revealing of the significance of pore size and pore size distribution for membrane performance with the CFD and other classical model analysis and culminates in the systematic fabrication matrix for membrane pore manipulation, which is strongly supported by precise characterizations and distinguished by the illustration of classical hydrodynamic models.

Chapter 2 initiates the effects of PSD mean, shape and scale on water permeance and solute rejection of membranes by using classical analytical models and computational fluid dynamics (CFD), which elaborates on the importance of precisely manipulating membrane pore

size and pore size distribution from a theoretical perspective, emphasizing the need to avoid excessively large or small pores.

Chapter 3 systematically examines the influence of polymeric membrane sample preparation techniques on their morphologies and structures as revealed by scanning electron microscopy (SEM) to develop a sample characterization method which not only serves as a guide for accurate SEM characterization of polymeric membranes, but also as a steppingstone towards standardizing protocols.

Chapter 4 involves fabrication of porous membranes and integrates the surface porosity characterization via SEM and the data derived from contact angle measurements (with dry-wet adjustment ratio applied in wet condition), establishing a novel method for quantifying surface porosity of porous membranes through contact angle measurements.

Chapter 5 investigates the water permeability and solute rejection of microfiltration (MF) and ultrafiltration (UF) membranes in pressure-driven filtration by integrating the surface porosity, mean pore size, pore size distribution, and skin layer thickness of dry membrane samples into three classic hydrodynamic pore-flow models (Hagen-Poiseuille (HP), Kozeny-Carman (KC), and Happel's cell (HC)). The dry-wet ratio, developed in Chapter 4, is conducted to correct and simulate the fully-wetted condition.

The culmination of these insights is found in Chapter 6, which presents a series of experimental methods for manipulating membrane pore size and pore size distribution. Here, the superiority of nano-bubble water as pore former is highlighted, characterized by enhanced water

permeance without trading off solute rejection, which indicates an innovative approach for the fabrication of polymeric porous membranes.

In summary, this thesis offers accurate and standardized methods for membrane characterizations from a novel and comprehensive perspective. Additionally, it elucidates the significance and provides techniques for precisely tailoring membrane pore size and pore size distribution through simulation models and experimental validation, which paves the way for advancement of mesoporous membrane design for a wide range of both academic and industrial applications.

The dissertation of Minhao Xiao is approved.

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University of California, Los Angeles

2024

DEDICATION

This dissertation is sincerely dedicated to my parents, Dongxuan Zhang, and Ling Xiao. Your unconditional love motivates me to finish this dissertation. There have been highs and lows on this journey, but you all have been encouraging and supporting me as always.

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PATENT

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Chapter 1 Introduction

1.1 Pore size distribution (PSD) of porous polymeric membranes

Porous polymeric membranes, operating via pressure-driven convective flux of water through continuous pores, play a pivotal role in numerous industries, including dairy, food and beverage, biopharmaceuticals, dye recovery, water degassing, drinking water and wastewater [1–5]. Porous membrane permeability and selectivity are both functions of membrane pore size and its distribution. Variability in pore size distribution (PSD) within ultrafiltration (UF) membrane batches can result in flux discrepancies of 30 to 45% [6]. Also, the majority of solvent flow occurs through the relatively smaller fraction of larger pores [7]. Thus, understanding and controlling PSD is crucial to achieve a desired permeability and size-selectivity. Moreover, analyzing particle size distribution (PSD) along with performance metrics like flux and rejection can provide insights into membrane transport and fouling mechanisms. Studies have employed PSD to explore transport behaviors, including geometric constraints, steric hindrance, and hydrodynamic effects [8–11]. Fouling is influenced by the uniformity of PSD; membranes with uniform pore sizes generally exhibit consistent performance, as each pore equally contributes to both filtration and fouling. In contrast, membranes with non-uniform pore sizes may experience uneven fouling, with larger pores staying more functional while smaller ones foul more rapidly [12–16].

1.2 State-of-the-art PSD characterizations

Direct pore size characterization techniques have significantly advanced over the past several decades, providing critical insights into pore properties. Techniques such as scanning

electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) offer detailed visualization of pore morphology, encompassing parameters such as mean pore size, size distribution, shape, and overall porosity. However, these methods are not without limitations. For instance, SEM, TEM, and AFM are constrained by a limited observation area, necessitate the analysis of fully dry samples in a vacuum, and require a conductive sputter coating, which can potentially alter the intrinsic properties of nanoscale pores [17-20].

In addition to these microscopy-based techniques, several other direct methods are employed to characterize pore properties. Liquid porosimetry, nitrogen adsorption, positron annihilation lifetime spectroscopy (PALS), Rutherford backscattering, and synchrotron small-angle X-ray scattering (SAXS) are among the notable methods. Each of these techniques provides unique advantages and insights. Liquid porosimetry measures pore volume and distribution by monitoring the intrusion and extrusion of a liquid. Nitrogen adsorption analyzes surface area and pore size distribution based on the physical adsorption of gas molecules at varying pressures. PALS offers atomic-scale resolution of free volume within the polymer matrix by detecting the lifetime of positrons. Rutherford backscattering provides depth profiling of elemental composition and structure, while SAXS enables the examination of pore structures at the nanometer scale using synchrotron radiation, which offers high resolution and contrast [21-24].

These advanced characterization techniques collectively contribute to a comprehensive understanding of pore properties in porous polymeric membranes. Despite the inherent

challenges associated with each method, ongoing developments and refinements continue to enhance their precision and applicability, thus advancing the field of membrane science and engineering.

1.3 Probability density function (PDF) analysis of PSD

The probability density function (PDF) is a critical tool for constructing PSDs based on either direct or indirect measurements [10]. In particular, the log-normal distribution has been predominantly used for its ability to capture the asymmetry of membranes [10,11,25–29], and showing consistency with experimental data based on solute and solvent transport [20,30]. However, the optimal selection of log-normal parameters continues to be a subject of debate, with prior research focusing on macroporous membranes with pore diameters greater than 50 nm [11,25]. Macroporous membranes filter out particles larger than a certain pore size threshold, so wide pores do not significantly harm the process as long as the largest size pore is below the threshold. Mesoporous membranes, on the other hand, require narrower and more uniform PSDs to achieve the more selective separation of sub-micron “colloidal” particles, macromolecules and molecules. In addition, the exploration of PSD’s broader characteristics, such as extreme skewness or alternative distribution forms like Pareto, gamma, Gumbel, and bimodal remains scarce, which underscores the need for an expanded examination of PSD models.

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Chapter 2 Exploring pore size distribution of porous polymeric membranes

In this chapter, we construct various hypothetical PSDs based on PSD data extracted from both commercial and hand-cast mesoporous polymeric membranes, and analyze the effects of PSD mean, shape and scale on membrane performance using both classical analytical models and computational fluid dynamics (CFD). We further validate performance predictions from our models with experimental data on water permeability and solute rejection. Then, we investigate how differing degrees of skewness affects membrane water flux and. Last, we compare different types of PSDs (log-normal, Pareto, gamma, Gumbel, and bimodal log-normal) in terms of their flux and rejection predictions to experimental data. By developing a more mechanistic understanding of the role of PSD on mesoporous membrane separation performance, this research paves the way for advancement of mesoporous membrane design for a wide range of industrial applications.

2.1 Model setup

The log-normal distribution represents a continuous probability distribution for a random variable whose logarithm follows a normal distribution. This distribution model has found applications across various scientific fields, often providing a more accurate fit than its counterparts such as the normal and Weibull distributions [1-3]. Its primary advantages include the capability to describe data ranges from zero to infinity and to effectively model data that are positively skewed and asymmetric [4].

For our analysis, we employed the SciPy library to derive the log-normal distribution [5]. The function for generating a log-normal distribution in SciPy requires three parameters: shape, location, and scale. The shape parameter is pivotal in defining the distribution's skewness and kurtosis, thereby influencing the tails and peak of the distribution. Meanwhile, the location and scale parameters are used to adjust the mean and standard deviation, respectively, facilitating the distribution's alignment and scaling. The probability density function for the log-normal distribution is mathematically articulated as follows:

$$f(y, s) = \frac{1}{s \cdot y \sqrt{2\pi}} \exp\left(\frac{-\log^2(y)}{2s^2}\right) \quad (2.1)$$

$$y = \frac{x - \mu}{\sigma} \quad (2.2)$$

where s is a shape parameter, x is an input variable that describes the range of pore sizes within a distribution, μ is a location parameter, and σ is a scale parameter.

We also evaluated various distribution models beyond the commonly used normal and log-normal distributions to express PSDs. These included the Pareto, gamma, Gumbel, and bimodal log-normal distributions, each offering unique perspectives due to their distinct characteristics. The Pareto distribution, a power-law probability distribution, is frequently utilized in both social and physical sciences to describe phenomena where a small proportion of causes lead to a large majority of outcomes, epitomized by the principle that 80% of outcomes result from 20% of causes [6,7]. This model is particularly relevant for membrane science, as it mirrors the rejection behavior of membranes where a few large pores dominate separation performance. The probability density function for the Pareto distribution is mathematically formulated as follows:

$$f(y, b) = \frac{b}{y^{b+1}} \quad (2.3)$$

$$y = \frac{x - \mu}{\sigma} \quad (2.4)$$

where b is a shape parameter for pareto distribution.

The gamma distribution stands out as a flexible and adaptive continuous probability distribution capable of modeling a diverse array of data types. Its utility is particularly noted in the accurate modeling of skewed data and the representation of complex multivariate relationships [8–11]. Given its adaptability in adjusting shape and managing skewness, the gamma distribution emerges as an excellent choice for depicting the PSD of mesoporous membranes. The PDF of the gamma distribution is mathematically represented as follows,

$$f(y, a) = \frac{y^{a-1} e^{-y}}{\Gamma(a)} \quad (2.5)$$

$$\Gamma(a) = \int_0^{\infty} e^{-t} t^{a-1} dt \quad (2.6)$$

$$y = \frac{x-\mu}{\sigma} \quad (2.7)$$

where a is a shape parameter for gamma distribution.

The Gumbel distribution, frequently employed in extreme value theory, excels in modeling the maximum values within a dataset. It is prevalently used in engineering and hydrology, especially for predicting events like floods and other extremes [12]. Characterized by its right-skewed heavier tail, the Gumbel distribution is apt for representing extreme values, making it particularly effective for modeling scenarios such as capturing large pores in membranes [13]. Notably, the Gumbel distribution differs from other distributions as it lacks a shape parameter, but it incorporates location and scale parameters.

$$f(y) = \exp(-(y + e^{-y})) \quad (2.8)$$

$$y = \frac{x-\mu}{\sigma} \quad (2.9)$$

The bimodal log-normal distribution is distinguished by its composition of two separate log-normal distributions, leading to a model with two distinct peaks. This contrasts with the

traditional single-peaked log-normal distribution. Its relevance spans across various fields including biology, medicine, and environmental science, where it offers valuable perspectives on phenomena that involve two distinct groups or processes [12-14]. An illustrative application of this distribution is in the study of blood glucose levels across different ethnic groups, where it helps identify distinct categories, indicating that diabetes may manifest as a separate condition rather than merely an outlier on a continuous scale [15]. Similar dual-peak patterns are also observed in the PSD of polymeric membranes [16,17].

For the analysis within this study, the SciPy library facilitated the construction of log-normal, Pareto, gamma, Gumbel, and bimodal distributions with different parameters. This comparison choice of different forms enables a nuanced representation of membrane PSD, capturing the inherent variability and complexity within the membrane structures that can affect membrane performance. The parameters used to form the distributions with different forms are given in Table 2.1.

Table 2.1. Distribution parameters for three different cases (log-normal, Pareto, gamma, and Gumbel)

Distribution		Distribution parameter		
form		Shape	Location	Scale
Log-normal		0.81	2.23	2.16
Pareto		1.76	0.003	2.69
Gamma		0.82	2.69	2.51
Gumbel		-	4.18	1.53

2.2 Membrane rejection calculation using mechanical sieving model

Membrane rejections by pores of different PSDs can be calculated by a mechanical sieving model, which conceptualizes the pores as uniform cylindrical capillaries all with identical pore radius [18]. According to this model, solutes are restricted from approaching closer than their own radius to the pore wall. This gives rise to:

$$\frac{A}{A_0} = \frac{(r_p - a_p)^2}{r_p^2} \quad (2.10)$$

where r_p is a pore radius, a_p is a solute radius, A is the pore area available for solute transport, and A_0 is the total pore area. Building upon this foundation, the mechanical sieving model extends the concept and posits that the ratio of A to A_0 is directly proportional to the ratio of solute concentration in the permeate relative to that in the feed, and hence,

$$X_s = 1 - \frac{A}{A_0} = \left[1 - 2 \left(1 - \frac{a_p}{r_p} \right)^2 + \left(1 - \frac{a_p}{r_p} \right)^4 \right]. \quad (2.11)$$

where X_s is a membrane rejection between 0 and 1. In our study, the solute radius fell in the range of 2-10 nm. This analytical framework is frequently employed to deduce the average pore size of a membrane based on solute retention experiments, provided the solute radius is known [19,20]. It is important to note that all aforementioned models operate under the assumption that there are no interactions among the solvent, solute, and membrane.

2.3 Solvent transport through porous arrays

Solvent (water) transport is calculated using two equations: the Navier-Stokes and the Hagen-Poiseuille equations, and these calculations are then compared to experimental data on water flux. The Hagen-Poiseuille equation can be derived equally from the Bernoulli equation and the Navier-Stokes equation. It specifically describes the flow of an incompressible, Newtonian fluid through a circular conduit under laminar flow conditions [21].

The Navier-Stokes equation (NSE) serves as the foundational mathematical model for momentum transport in computational fluid dynamics (CFD). This equation, which is derived from Newton's second law of motion, describes the behavior of fluid flow by accounting for various influencing factors such as pressure gradients, viscous forces, and external forces acting on the fluid [22]. The comprehensive nature of the (NSE) makes it indispensable for simulating fluid motion under a specific set of conditions [23]. Herein, the numerical NSE is used to analyze fluid in membrane pores using a numerical solver (COMSOL Multiphysics® v. 6.2., Stockholm, Sweden) equipped with robust meshing schemes for efficient convergence and solution [24]. The computational process involves discretizing the domain into a finite number of control volumes, applying appropriate boundary conditions, and iteratively solving the equations to obtain a prediction of the fluid flow characteristics. The scheme consists of a conforming finite element method with the velocity–pressure formulation for the NSE under several assumptions including steady-state, single-phase isothermal flow. The fluid is continuum, Newtonian, and incompressible [25,26]. The NSE is solved along with the continuity equation (conservation of mass).

$$\rho_0 \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu_0 \Delta \mathbf{u} \quad (2.12)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2.13)$$

where u is the fluid velocity, μ_0 is the fluid viscosity, p is the gauge pressure (not the absolute pressure), and ρ_0 is the density of the fluid.

The Navier-Stokes equations form a nonlinear system that requires a nonlinear solver. Given the assumption of a steady-state system in this study, a stationary nonlinear solver is employed. This solver iteratively approaches the final solution by solving a linearized version of the system at each step using a linear solver. A damped Newton method is chosen as a non-linear solver, starting with a low initial damping factor to avoid the potential negative impact of a full Newton step when the initial values are not near the final solution. The damping factor is dynamically adjusted by the nonlinear solver algorithm to ensure convergence to a solution.

Imaginary 2D pore geometries consisting of a 13x13 circular pore array are generated using the PoreSpy library [27], based on distributions derived from SEM images of commercial membranes. These unitless images are converted to meters using a pore density of $110 \text{ ea}/\mu\text{m}^2$ observed in the SEM images. The 2D geometries are then transformed into 3D structures using the extrude function in COMSOL. The pore length is standardized at 100 nm to simulate the typical thickness of membrane skin layers. The system is configured for dead-end filtration, with a feed compartment above and a permeate compartment below the pores. The height of both compartments is set to be 100 times the pore length, reflecting the significant disparity between the channel dimensions and the membrane thickness. Hydraulic pressure is maintained at 20 psi on the feed side, while an average pressure of 0 psi is applied at the permeate side as boundary conditions.

The Hagen-Poiseuille equation (HPE) elucidates the dynamics of viscous fluid flow through a conduit. It is instrumental in analyzing the influence of pressure, fluid viscosity, and conduit geometry on flow rates [28]. The HPE expression in standard fluid mechanics notation is:

$$Q = \frac{\pi r_p^4 \Delta P}{8 \mu L} \quad (2.14)$$

where Q is the volumetric flow rate, ΔP is the pressure difference between the pore inlet (feed) and outlet (permeate), L is the straight pore length (membrane thickness), μ is the dynamic viscosity, and r_p is the pore radius. It is important to note that multiplying tortuosity by pore length yields an effective pore length. However, in our CFD simulations, we employed straight pore geometries, thereby eliminating the need to consider tortuosity. Applied to membrane pore flow, this equation models the laminar flow of viscous fluids through cylindrical pores, enabling the calculation of volumetric flow rate and flux. This flow rate is directly proportional to the pressure drop over the pore length and the pore radius to the fourth power, while being inversely proportional to the fluid viscosity. For the equation's application in pore flow models aimed at estimating membrane water permeability, a set of simplifying assumptions is necessary: 1) The flow through membrane pores is assumed laminar, with the fluid exhibiting Newtonian behavior, indicating a constant viscosity for all shear rates. 2) Pores are considered as straight, uniform cylinders. 3) Fluid molecules obey the no-slip condition at pore walls, signifying no movement at the fluid-solid interface. 4) The flow is steady-state with constant fluid properties. 5) The fluid is treated as incompressible with a constant density. 6) Fully developed flow is assumed at the pore entrance and exit, streamlining the model for greater analytical feasibility [29–31].

2.4 Impacts of shape parameter on flux and rejection

In this section, the shape parameters for the commercial UF membranes PSD were altered to create distributions with lower and higher skewness. In all three cases, the PSDs have the same location (mean pore size) and scale (standard deviation) parameters. The case with a low shape parameter exhibits the narrowest and most uniform PSD (Fig. 2.1a) with most of the points located around the mean value and a short tail extending to the right side. Although the case with a high shape parameter has its peak shifted toward smaller pore sizes, it features the longest tail extending towards the large pore size end. The average predicted rejections for the low shape parameter, commercial, and high shape parameter cases were 94, 87, and 75%, respectively. The shorter tail of the low shape parameter case resulted in the majority of pores producing rejections between 75 and 100%, whereas the longer tail of the high shape parameter case allowed an even number of pores to produce rejections ranging from 0 to 100%. Consequently, the minimum rejection values are critical in determining the overall rejections. As illustrated in Fig. 2.1c, the area filled with green color (representing the low shape parameter case) displays the highest minimum rejection values for solutes with radii up to 10 nm. For the high shape parameter case, the area shaded in grey illustrates a consistent minimum rejection of 0%. These results align with previous observations that a small fraction of large pores governs the overall membrane rejection for porous membranes [7]. To maximize rejection, a lower shape factor is required to maintain the minimum rejection value above zero for the target solute sizes of interest.

Normalized water flow rates and pressure drops across pores obtained from CFD simulations are demonstrated in Figure 2.2a. For each case, 169 imaginary pores (13 X 13) were constructed based on the given PSDs in Fig. 2.2a, and the water flows through the geometries are

calculated in COMSOL. The pore number (from 1 to 169) is sorted by pore radius in descending order, so Number 1 has the largest pore radius and Number 169 has the smallest pore radius. The case with a high shape parameter produced higher water flux than the commercial membrane case, with its normalized flux frequently appearing above a value of 5 with the first 40 largest pores, whereas very few pores in the commercial membrane case achieved a normalized flux near to 5. Most pores in the low shape parameter case generated water flux below a normalized value of 2.

In Fig. 2.2b, average normalized fluxes from the HPE and NSE [21] differ because of the assumption of perfectly circular pores in the HPE. For the commercial case, the average normalized flux was 0.76 according to Navier-Stokes calculations and 0.21 according to Hagen-Poiseuille calculations. The linear slopes, representing normalized flux over shape parameter, were 1.13 for Navier-Stokes and 2.34 for Hagen-Poiseuille, indicating that the Hagen-Poiseuille case sees a rapid increase in water flux with an increasing shape parameter. This discrepancy highlights the difference caused by the assumption of perfectly circular pores. Circular pores, as considered in the Hagen-Poiseuille equation, may promote more streamlined flow paths for fluids, leading to lower resistance and higher overall flow rates compared to the more realistic, irregularly shaped pores modeled by Navier-Stokes [33,34]. Additionally, interactions at the pore entrances and exits are neglected in the Hagen-Poiseuille calculation, which tends to reduce mass transport resistance compared to the more detailed Navier-Stokes calculation, where these factors are taken into account.

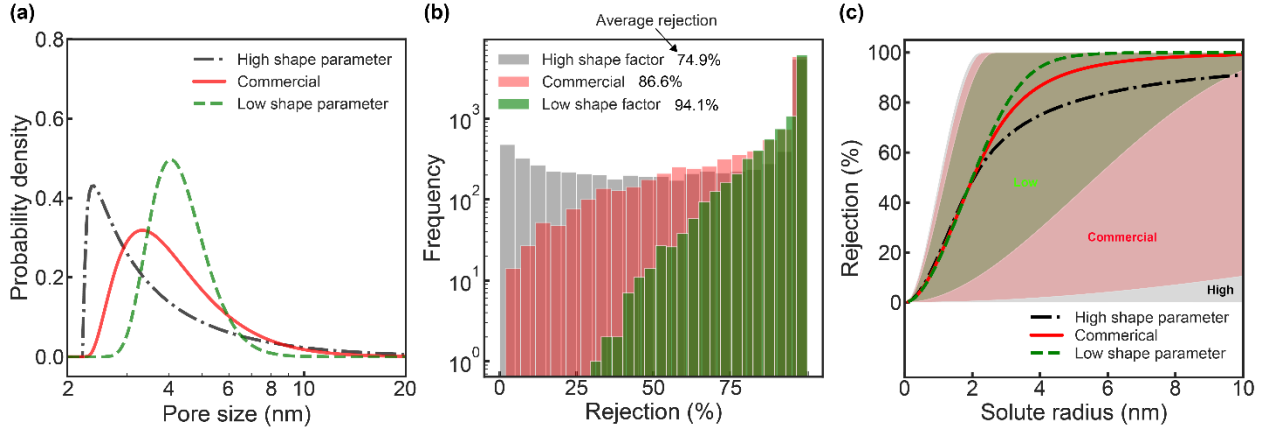


Figure 2.1. (a) Probability density function of log-normal distribution with three different shape parameters. The commercial shape parameter for log-normal distribution was extracted from the SEM images of two commercial membranes. High shape parameter is 2-times higher than the commercial shape parameter. Low shape parameter is half of the commercial shape parameter. The x-axis is in log scale. (b) Rejection histograms of the three cases and average rejection values for 4 nm solute radius. (c) Rejection changes with different solute sizes from 0.1 nm to 10 nm. The color fills indicate the minimum and maximum rejection ranges for a certain solute radius.

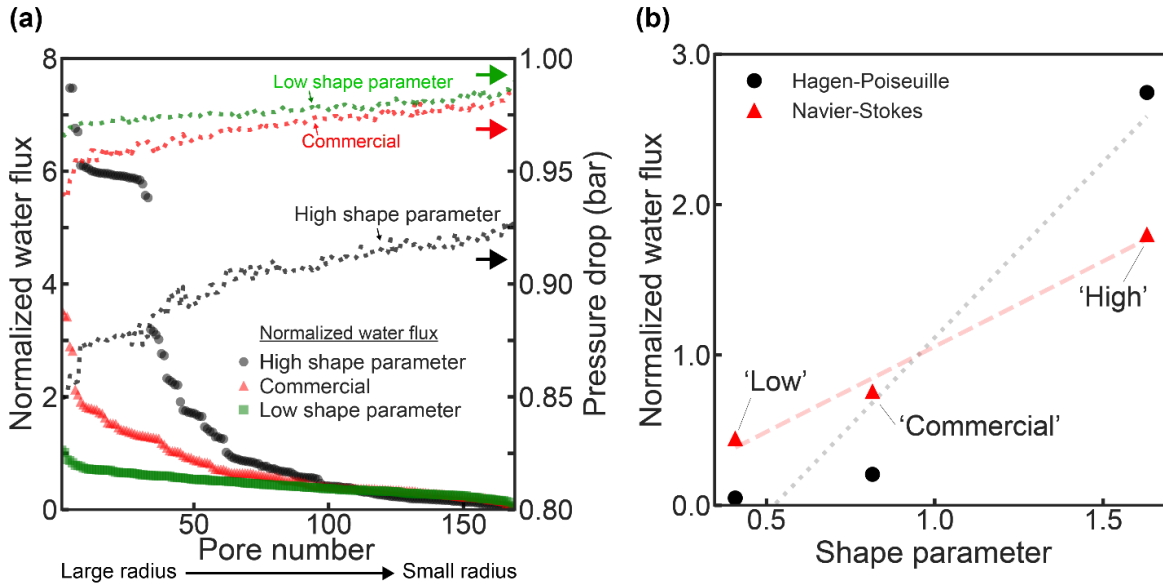


Figure 2.2. (a) Normalized flux values for three cases obtained by CFD with Navier-Stokes equation. The x-axis is the number of pores sorted by size in descending order. Each case has 169 values. The mean flux of 507 values was used to normalize the flux values. The markers correspond to the left y-axis (normalized water flux) and the dotted lines correspond to the right y-axis (pressure drop). (b) Average normalized flux calculations by Hagen-Poiseuille and Navier-Stokes equations with three different cases. Linear lines are obtained by linear regression of the three points.

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Chapter 3 Sample preparation matters: scanning electron microscopic characterization of polymeric membranes

3.1 Introduction

The structural and morphological characterization of polymeric membranes using Scanning Electron Microscopy (SEM) is a cornerstone in the field of membrane science and technology [1-5]. SEM analysis provides invaluable insights into the surface morphology and cross-sectional architecture of membranes, which are critical determinants of their performance in applications such as microfiltration (MF) [6-9], ultrafiltration (UF) [10-12], and reverse osmosis (RO) [13-15]. However, the reliability of SEM imaging is highly contingent upon the sample preparation techniques employed. Variations in sample preparation can lead to discrepancies in the interpretation of membrane structures, ultimately affecting the understanding and development of these vital materials.

The application of sputter coating, particularly the thickness of the platinum layer used, and the accelerating voltage during SEM imaging have been identified as significant factors influencing the quality of the surface morphology data obtained [16, 17]. While prior research has shed light on the general practices of sample preparation [18-21], a systematic study that correlates the nuances of these practices with the quality of SEM imaging is still lacking. This study seeks to bridge that gap by investigating the impact of coating thickness and accelerating voltage on the SEM imaging of MF, UF, and RO membranes, aiming to identify the optimal

conditions that preserve the integrity of the sample while providing the highest resolution possible, while avoiding technical artifacts.

Furthermore, the method of sample sectioning is another critical factor in SEM analysis, with techniques such as Direct-Freeze-Fracture (DFF) and Indirect-Freeze-Fracture (IFF) offering different advantages depending on the analytical focus. The need to consider the fabric layer within the membrane samples further complicates the choice of sectioning method. Additionally, the influence of the sample's hydration state on the cryogenic sectioning process and its subsequent impact on membrane structure has not been thoroughly explored. This chapter comprehensively assesses the effect of wet versus dry sample states in cryogenic sectioning, providing clarity on how these conditions affect the SEM imaging of polymeric membranes.

Through the systematic examination of key SEM sample preparation techniques, this research aims to establish a suite of refined protocols designed for broad adoption, which will ensure the precise and consistent characterization of membrane materials. The significance of this study extends beyond the immediate findings, with the potential to catalyze the standardization of SEM methodologies. Such advancements promise to enhance membrane science and technology by reducing subjective interpretation in the SEM analysis of microfiltration, ultrafiltration, and reverse osmosis membranes, thus fostering more accurate and objective research outcomes.

3.2 Materials and Methods

3.2.1 Materials

Dimethylformamide (DMF, ACS reagent grade) was purchased from Sigma Aldrich Co. (St. Louis, MO, USA). Polypropylene (PP, PC 15080) fabric was kindly provided by Hollingsworth-vose Inc. Milli-Q water was used in all experiments. All chemicals were used without any further purification. Ultrason PSF was generously supplied by BASF (Charlotte, North Carolina, USA). Hand-cast (16% PSF/DMF) UF membrane was prepared via phase-inversion in DI, referring to the approach in previous study [6]. Commercial MF (PVDF) and UF (PS20) membranes were sourced from Solecta, Inc., (Oceanside, California, USA). Commercial brackish, FilmTec BW30XFRLE, (BWRO) and sea water, FilmTec SW30XFR, (SWRO) reverse osmosis membranes were purchased from DWS Advantage (Bellevue, Washington, USA).

3.2.2 Sample cross-section preparation

Scissor/razor Sectioning: All samples (MF, UF, and RO) are conditioned in a desiccator for 24 hours. Samples sectioned by scissors are referred to as scissor-sectioning (SS). The use of a razor to section samples from the active layer side is denoted as razor-sectioning-active layer (RSA), and from the fabric layer side as razor-sectioning-fabric layer (RSF).

Cryo-Sectioning: To elucidate the effects of moisture on sample fracture behavior, we employ both wet (stored in deionized water) and dry (stored in a desiccator) conditions before cryo-sectioning. We compare three cryogenic approaches:

Direct-Freeze-Fracture (DFF): Membrane strips measuring 10 mm by 50 mm are immersed in liquid nitrogen for 5 minutes. Afterward, the frozen strips are subjected to a

controlled bending and snapping technique using two pairs of tweezers. One pair holds one end of the strip in place while the other pair performs the bending action (multiple times if needed), causing the strip to snap along the bend, reminiscent of breaking a brittle object. While the non-woven fabric remains intact due to its mechanical strength [15]. Subsequently, a razor is used to trim the fabric beneath the fractured polymers. The samples are then desiccated for 24 hours before being mounted on SEM stubs with carbon tape.

Indirect-Freeze-Fracture (IFF): Following the DFF protocol, the IFF method involves the additional step of removing the fractured polymer sections from the non-woven fabric. These are then de-watered and affixed to stubs for SEM imaging. The terminology 'Direct' and 'Indirect' Freeze-Fracture refers to whether the fabric layer is present ('Direct') or removed ('Indirect') during the fracturing process.

Cryo-Razor-Sectioning (CRS): In contrast to DFF and IFF, CRS involves sectioning the frozen samples directly with a razor while under cryogenic conditions.

3.2.3 Sputter coating

All samples undergo sputter coating with platinum to a designated thickness ranging from 1 to 5 nm using Luxor coater (Luxor Tech, Belgium) in preparation for SEM analysis.

3.2.4 SEM operation

SEM imaging is performed using a ThermoFisher Phenom Pharos G2 Desktop SEM FEG-SEM, sourced from Nanoscience Instruments (VA, USA). For all samples, scanning is performed at accelerating voltage of 5, 10, and 15 kV, respectively. Images are taken for each

membrane at magnifications up to 200,000 $\times$. For surface imaging, a 50%/50% combination of backscattered electron detector (BSD) and secondary electron detector (SED) is employed, while for cross-sectional imaging, only BSD is utilized.

3.2.5 Post-imaging Analysis

Surface SEM of the MF and UF membranes are processed via NIH Image J software to calculate the porosity and average pore diameters. The extracted gray scale image is converted into a black and white image where the white areas are solid polymer and the black areas are pores [6, 15]. Average pore diameter d_m (nm) and surface porosity ε (%) are then determined.

3.3 Results and Discussion

3.3.1 Sample preparation impacts on surface imaging

The thickness of the sputter coating was found to have a significant impact on the surface imaging quality of the membrane samples. A discernible color variation on the membrane surface, observable with the unaided eye, was noted as a result of a mere 2 nm difference in sputter coating thickness, shown in Fig. 3.1. Across all sample types—MF, UF and RO—a platinum coating of 1 nm was insufficient, yielding drifting images that were challenging to focus and thus obscuring membrane morphology. In contrast, coatings of 3 nm and 5 nm improved the sample conductivity, facilitating easier focusing. Notably, in MF and UF membranes, a coating thickness of 5 nm resulted in the appearance of a smoother membrane surface, reduced porosity, and a decrease in average pore size, shown in Fig. 3.2 and Table 3.1, when compared to the 3 nm coating (see Fig. 2.3(a-c) for MF, (d-f) for hand-cast UF, and (g-l)

for commercial UF.) Quantitative analysis, presented in Table 3.1, shows ~ 3% difference in mean pore diameter (d_m) and ~13.3% variation in porosity (ϵ) for MF membranes coated with 3 nm compared to those with 5 nm of platinum. These differences are magnified in UF membranes, where the Δd_m ranges from ~15.9% to ~20.0% and $\Delta \epsilon$ from ~22.5% to ~29.7% for 3 nm versus 5 nm coatings, suggesting an excessive coating may obscure the nano-surface-structures, potentially leading to misinterpretations of the membrane's intrinsic properties. This is particularly relevant for UF membranes, which have pore sizes on average five times smaller than MF membranes. (Fig. 3.2, Fig. 3.4 and Table 3.1). In post-imaging analysis via NIH Image J software, the original image dimensions are precisely converted to pixel units, ensuring accurate scale representation—one pixel equates to a length of 1.8 nm for 150,000X magnified images and 1.4 nm for 200,000X. This level of detail permits the resolution of 5.6-11.1 pixels per 10-20 nm pore diameter in MF images and 7.1-14.2 pixels in UF images, thus confirming the ability to discern the reported nanometric differences. These pixel counts across the pore diameters substantiate our capability to accurately measure and compare pore sizes and porosities across different sputter coating thicknesses. The correlation between the pixel size and the magnification is shown in Fig. 3.5 and Table 3.2. However, for the RO samples, there was no notable difference in imaging quality between the 3 nm and 5 nm coatings, in Fig. 3.3 (j-o).

Accelerating voltage is a critical parameter in the quality of SEM imaging, as demonstrated by our analysis of UF and RO membrane samples. At a lower voltage of 5 kV, the images of both UF and RO samples exhibit less sharpness compared to those taken at higher voltages, compromising the visualization of finer details (Fig. 3.6a for MF, Fig. 3.6d for UF, and Fig. 3.6g for RO). Increasing the accelerating voltage to 10 kV significantly enhances the

resolution, providing high-detail visualizations without inducing damage to the polymer structure, as evidenced in Fig. 3.6b for MF, Fig. 3.6e for UF, and Fig. 3.6h for RO. This voltage strikes a balance, offering sufficient energy to elicit a strong signal without the adverse effects associated with higher voltages. However, polymeric membranes can be extremely beam sensitive and can shrink, swell, or rupture when exposed to the electron beam [17]. At the highest tested voltage of 15 kV, although there is an increase in contrast and sharpness, there is also a noticeable presence of grey areas. These areas could potentially represent damaged or charged regions, suggesting that this elevated voltage may lead to some degree of sample degradation or charging, which can obscure true surface features [22-24].

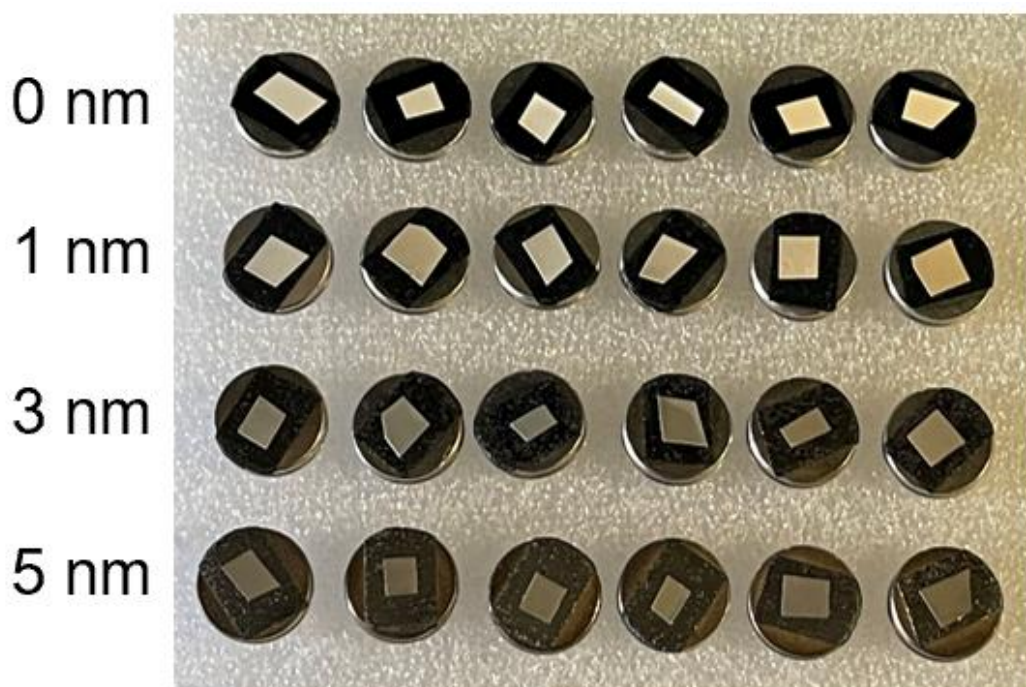


Figure 3.1. Samples coated with 1 to 5 nm platinum showing color variation on the membrane surface.

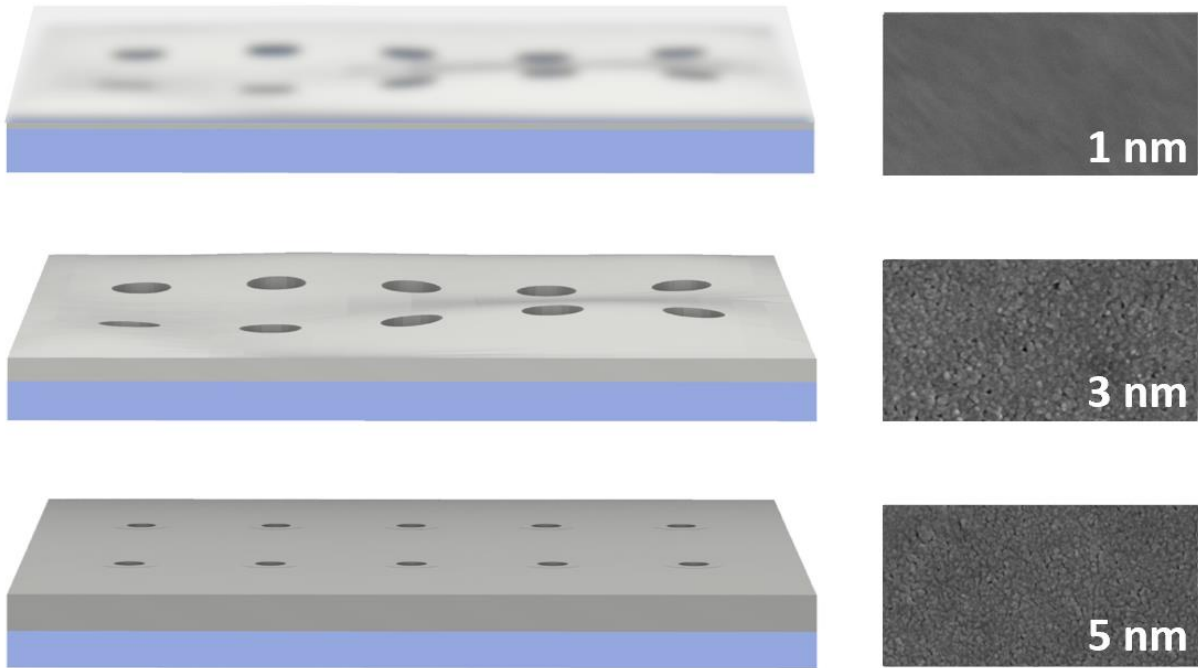


Figure 3.2. Schematic of how thickness of the sputter coating affects the surface imaging quality.

Table 3.1. Surface porosity and mean pore radius of the MF and UF samples with different platinum coating thickness.

Membrane	Mean pore radius (nm)		Surface porosity (%)	
Coating thickness	3nm	5nm	3nm	5nm
MF (Commercial PVDF)	49.7 ± 4.6	48.2 ± 5.2	13.46 ± 1.97	11.66 ± 2.53
UF (Hand-cast)	10.5 ± 1.7	8.4 ± 1.8	2.86 ± 0.26	2.01 ± 0.27
UF (Commercial PS20)	11.3 ± 1.5	9.5 ± 1.3	2.44 ± 0.51	1.89 ± 0.32

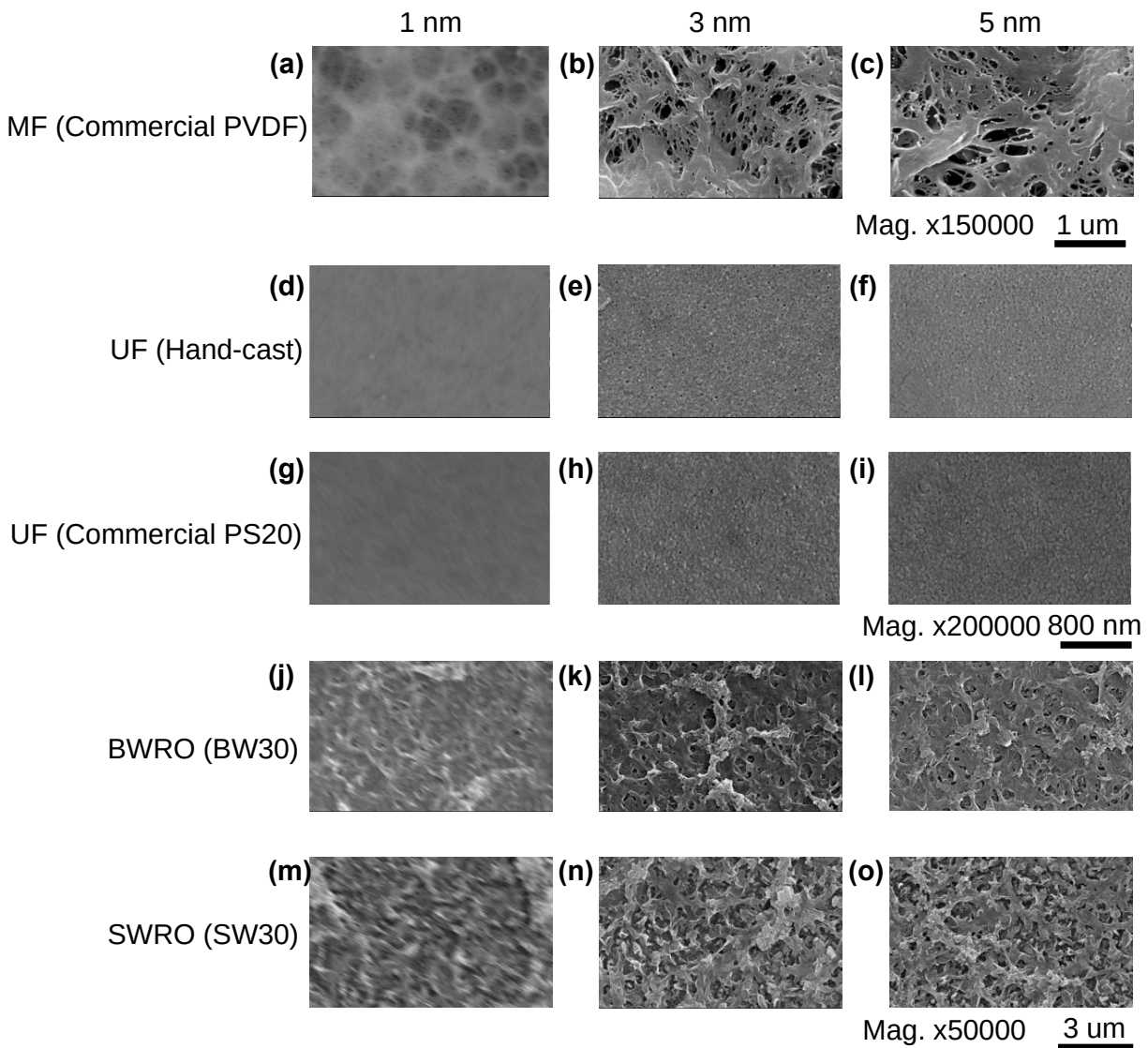


Figure 3.3. Impacts of sputter coating thickness on surface imaging. (a-c) Commercial MF membranes. (d-f) UF prepared of 16% PSF. (g-i) Commercial UF membranes. (j-l) Commercial BWRO membranes (m-o) Commercial SWRO membranes. All images are taken at 10 kV accelerating voltage with 50%/50% mix of BSD and SED.

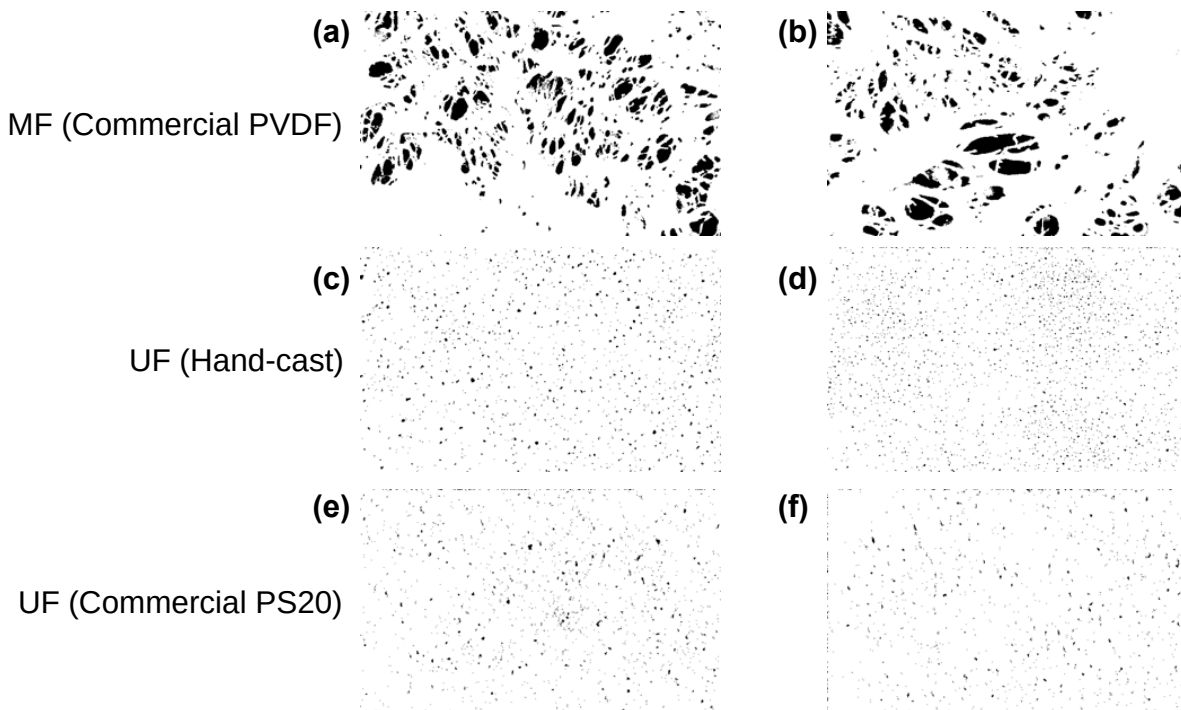


Figure 3.4. Surface SEM images of MF and UF membrane with post-imaging analysis.

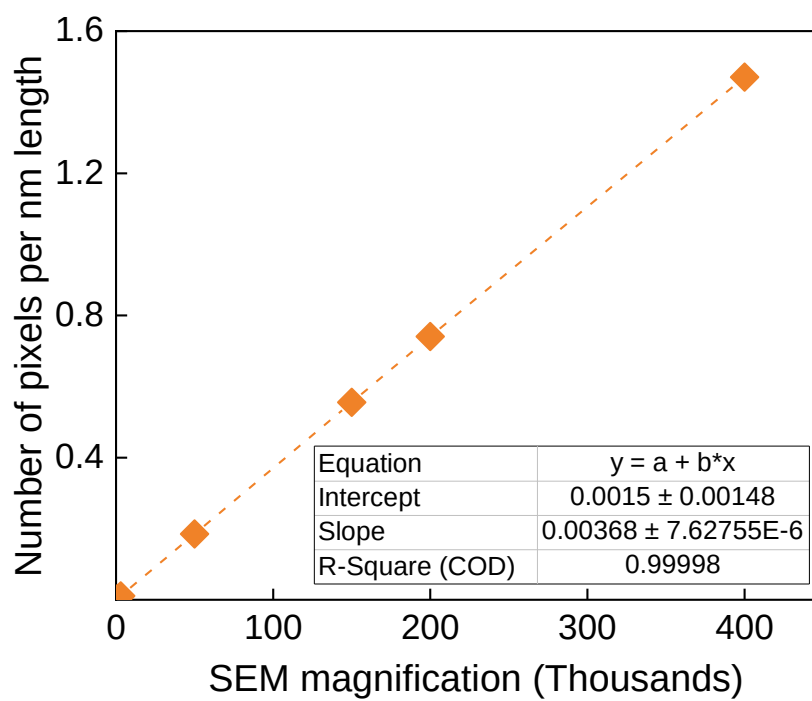


Figure 3.5. The correlation between the pixel size and the magnification.

Table 3.2. The correlation between the pixel size and the magnification.

SEM magnification (Thousands)	length per unit pixel (nm)
1	270
3	90
50	5.4
150	1.8
200	1.35
400	0.68

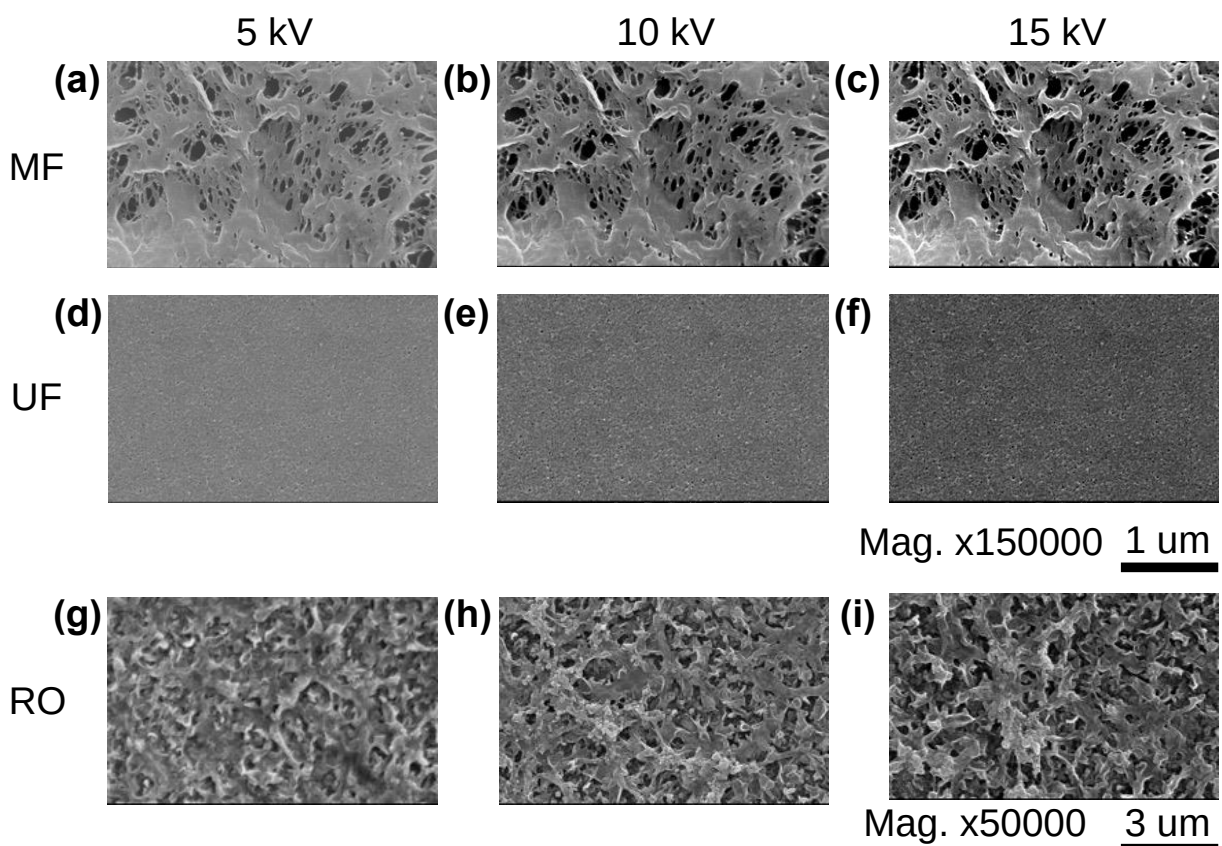


Figure 3.6. Impacts of accelerating voltage on surface imaging. (a-c) MF images under 5, 10 and 15 kV, respectively. (d-f) UF images under 5, 10 and 15 kV, respectively. (g-i) RO images under 5, 10 and 15 kV, respectively. All samples are coated with 3 nm platinum.

3.3.2 Sample preparation impacts on cross-section imaging

The structural integrity of polymeric membranes as observed in cross-sectional SEM imaging is highly contingent on the method of sample preparation. Razor-Sectioning-Active Layer (RSA), Razor-Sectioning-Fabric Layer (RSF), and Scissor-sectioning (SS) were found to inflict varying degrees of damage to all membrane types, compromising their structural integrity and rendering them suboptimal for sectioning polymeric samples (Fig. 3.7(d-f) for MF, Fig. 3.7(j-l) for UF, and Fig. 3.7(p-r) for RO).

Cryo-sectioning methods generally yielded higher quality cross-sections. Nevertheless, Cryo-Razor-Sectioning (CRS) exhibited some degree of structural disturbance due to shear forces applied during cutting, thus it is not the preferred method (Fig. 3.7c for MF, Fig. 3.7i for UF and Fig. 3.7o for RO). The more favorable techniques, Direct-Freeze-Fracture (DFF) and Indirect-Freeze-Fracture (IFF), maintained the membrane structures intact and are recommended for most applications. However, the DFF approach occasionally resulted in obscured cross-sections due to the non-woven fabric layer (Fig. 3.8). In cases where the fabric layer is not the focus of the study, the IFF method is advised as it avoids this issue and provides clear and undistorted structural details (Fig. 3.7a for MF, Fig. 3.7g for UF, and Fig. 3.7m for RO).

Fig. 3.9 demonstrates the minimal effect of initial sample hydration on the quality of cryogenic sectioned SEM images. Direct-Freeze-Fracture (DFF) and Indirect-Freeze-Fracture (IFF) methods were applied to both wet and dry samples of UF and RO membranes. The structural analysis did not reveal significant differences in membrane and pore morphology between the conditions. Notably, there was a slight increase in the measured thickness of hydrated samples. This may be attributed to water's influence on pore structure during the

freezing process, where the density of water, being greater than that of ice, could lead to structural alterations due to volumetric expansion. However, the dehydration step in cryo-sectioning likely allows the membrane to return to its pre-hydrated structure, aligning with the known viscoelastic properties of polymeric materials.

The observed sample thickness in SEM images can also be affected by the sample's alignment relative to the electron detector. A tilted sample can give the impression of reduced thickness, underscoring the necessity for careful positioning. Additionally, the inherent asymmetric structure of the membrane may further complicate accurate thickness measurements. It's essential to examine multiple locations across the sample to mitigate measurement discrepancies, as previous studies suggest a high standard deviation in SEM thickness measurements [25]. For consistent comparisons, identical preparation protocols and characterization conditions should be employed across different membrane samples to eliminate variability.

Additionally, our results indicate that while the sputter coating thickness does not alter the inherent structure or morphology of the membrane's cross-section, a 3 nm coating is superior in producing sharper images compared to a 1 nm coating, shown in Fig. 3.10.

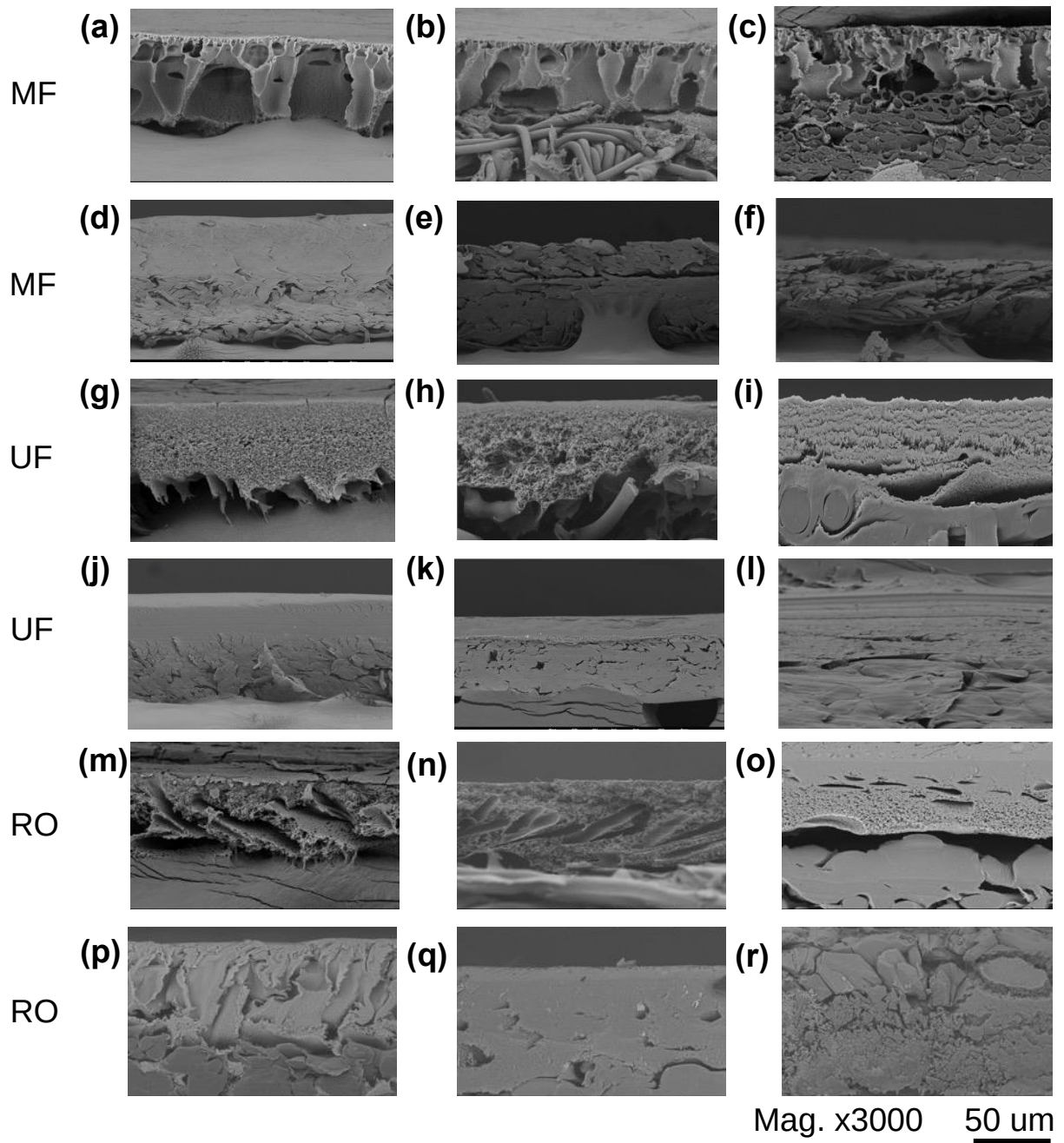


Figure 3.7. Membrane cross-sectional SEM images of different preparation approach. (a) Indirect-Freeze-Fracture (IFF) on MF. (b) Direct-Freeze-Fracture (DFF) on MF. (c) Cryo-Razor-Sectioning (CRS) on MF. (d) Razor-Sectioning-Active Layer (RSA) on MF. (e) Razor-Sectioning-Fabric Layer (RSF) on MF. (f) Scissor-sectioning (SS) on MF. (g) IFF on UF. (h) DFF on UF. (i) CRS on UF. (j) RSA on UF. (k) RSF on UF. (l) SS on UF. (m) IFF on RO. (n) DFF on RO. (o) CRS on RO. (p) RSA on RO. (q) RSF on RO. (r) SS on RO.

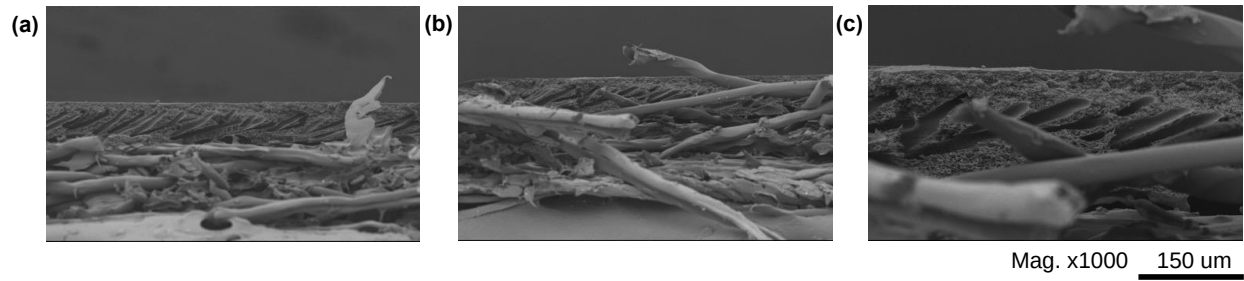


Figure 3.8. Non-woven fabrics blocking certain locations of the cross-section in DFF approach.

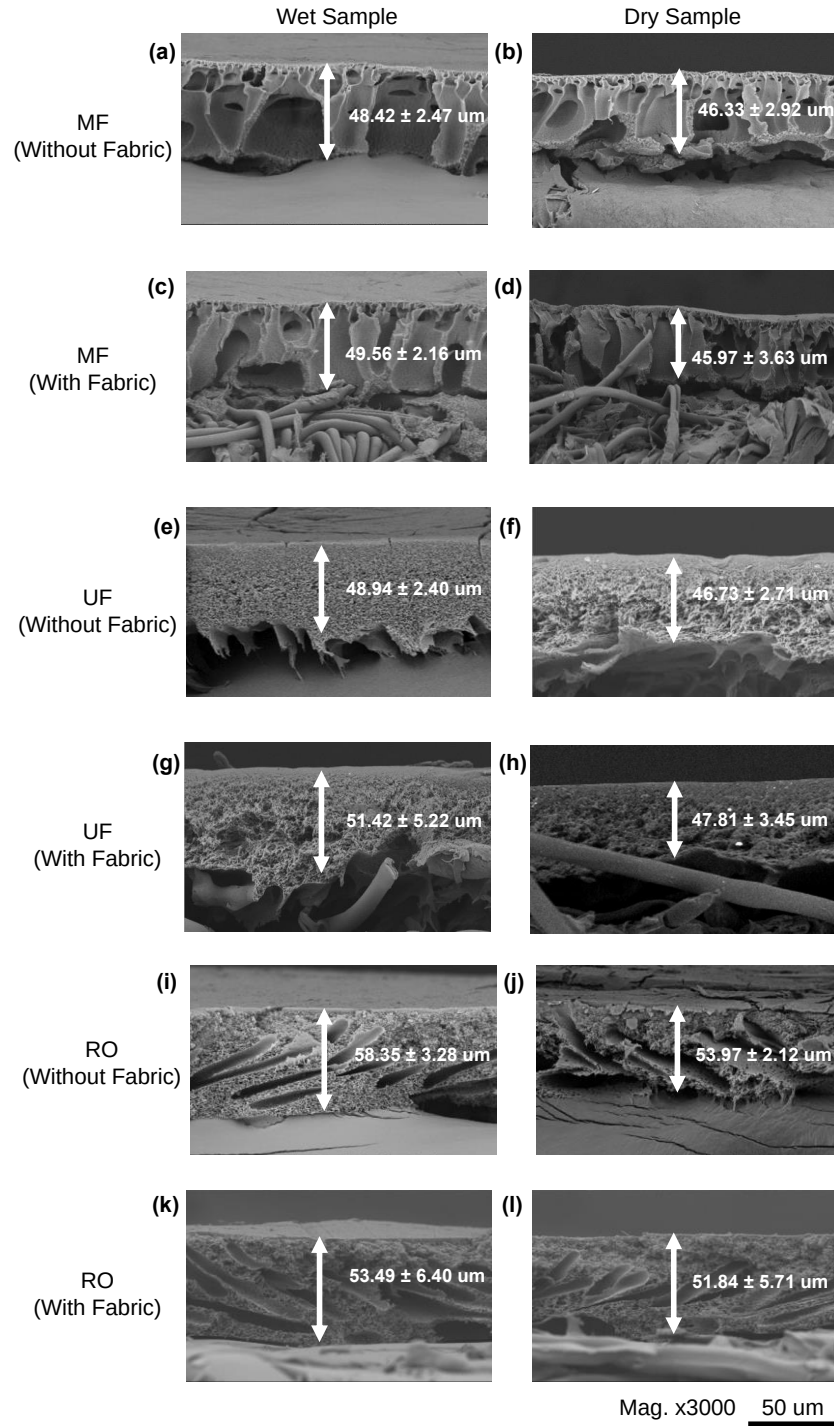


Figure 3.9. Impacts of initial sample hydration on the resultant cryogenic sectioned images. IFF on (a) wet and (b) dry MF sample. DFF on (c) wet and (d) dry MF sample. IFF on (e) wet and (f) dry UF sample. DFF on (g) wet and (h) dry UF sample. IFF on (i) wet and (j) dry UF sample. DFF on (k) wet and (l) dry UF sample.

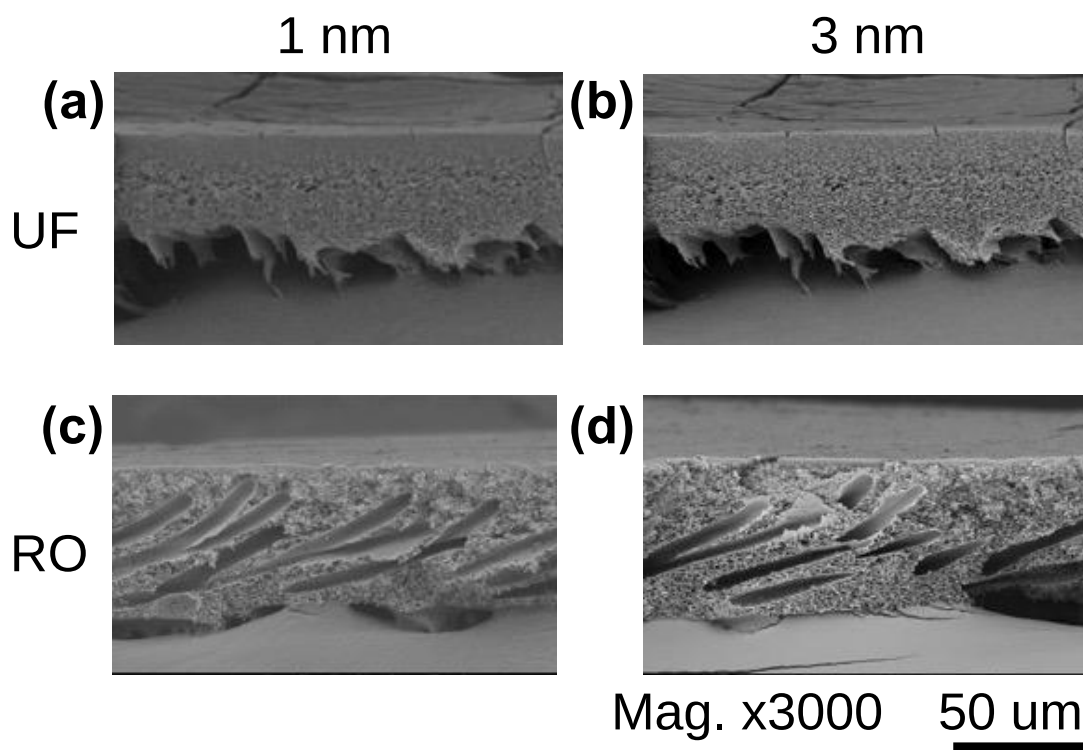


Figure 3.10. Cross-section SEM images of UF and RO membrane samples with different sputter coating thickness.

3.4 Conclusions

This chapter has highlighted the critical role of sample preparation and imaging parameters on SEM imaging of polymeric membranes. Our results demonstrate the thickness of sputter coating is a pivotal factor that greatly impacts the quality of membrane surface morphology imaging. Specifically, we have established that a coating thickness of 3 nm of platinum optimizes SEM imaging of microfiltration and ultrafiltration membranes by ensuring adequate conductivity without compromising surface detail or porosity analysis, while a 10 kV accelerating voltage provides high-resolution images without damaging the polymer structure. In

this chapter, we also delineate preferred cross-sectioning techniques: indirect-freeze-fracture for cases where the fabric layer is not of analytical concern and direct-freeze-fracture when fabric morphology is of interest. For consistent comparisons, identical preparation protocols and characterization conditions should be employed across different membrane samples to eliminate variability. These conclusions not only serve as a guide for accurate SEM characterization of polymeric membranes, but also as a steppingstone towards standardizing sample preparation protocols, thereby enhancing the precision and reliability of membrane research.

3.5 References

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Chapter 4 Characterizing Surface Porosity of Porous Membranes via Contact Angle Measurements

4.1 Introduction

Porous membranes are used in a wide range of applications such as membrane distillation, aeration and de-aeration where membranes are not internally saturated with water as well as drinking water filtration, membrane bio-reactors, protein separations, sterile filtration and other aqueous separations where membranes are internally saturated with water [1,2]. Membrane characteristics such as surface porosity, cross-sectional porosity, pore size and contact angle are widely used to understand membrane separation performance as well as fouling propensity and ease of cleaning [8-12]. For example, the cross-sectional porosity of a membrane can be estimated by its water uptake and this is critical for understanding transport properties in membrane distillation, aeration and de-aeration [13]. Membrane pore size can be determined by the bubble point method and molecular weight cut-off (MWCO) experiments [9,14]. However, determining surface porosity, particularly for asymmetric membranes is non-trivial.

While many studies have shown SEM images analyzed via ImageJ binary analysis can characterize dry membrane surface porosity, this is an expensive and complicated experimental technique [15-20]. Further, the SEM-ImageJ method can only be applied to analyze completely dry membrane samples, which means we can't really understand the surface porosity of the membrane when it is saturated with water and fully swollen [21-23]. Therefore, it is necessary to develop characterization methods that allow direct quantification of membrane surface porosity under both wet and dry conditions.

In chapter 3, we propose that contact angle measurements of membrane surfaces can be used to calculate the surface porosity. A variety of methods (Wilhelmy plate, capillary rise, sessile drop, and captive bubble) have already been employed to characterize interfacial tensions of various solid materials [24-30]. However, for porous membranes, the interface is not as easy to be defined because of the pores, which may either be filled with air (dry) or water (wet). We hypothesize that the contact angle of water (θ_w) on a wet membrane should be defined by the contact angles of the pure membrane material and water-filled pores ($\theta_w = 0^\circ$); whereas the contact angle of a dry membrane should be defined by the contact angles of the pure membrane material and air-filled pores ($\theta_w = 180^\circ$).

In this chapter, a series of porous membranes are fabricated with different polymer contents to tailor pure membrane material hydrophilicity and using different non-solvent compositions to tailor membrane porosity. Sessile drop (SD) and captive bubble (CB) contact angle measurements are used to determine water contact angles of dry and fully wetted samples, respectively. Solid, non-porous polymer films provide the pure polymer contact angles. We then calculate the surface porosity based on the measured contact angle data for various porous polymer films. The surface porosity of dry membrane samples is also captured by analysis of SEM images. Water uptake and membrane swelling measurements enable creation of a dry-to-wet conversion factor that allows one to calculate wet membrane porosity from dry membrane SD contact angle and SEM measurements. Finally, we assess the relative accuracy and correlation of the membrane surface porosity obtained by contact angle measurements and SEM images for both dry and wet situations.

4.2 Materials and Methods

4.2.1 Materials

Polyvinylidene fluoride (PVDF, 0.288 g/cm³, Kynar 761) and polyvinylidene fluoride-poly (methyl methacrylate) block co-polymer (PVDF-PMMA, Kynar DH100) were kindly provided by Arkema Inc. Dimethylacetamide (DMAC) and isopropyl alcohol (IPA) (ACS reagent grade) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). Polypropylene (PP, PC 15080) fabric was kindly provided by Hollingsworth-vose Inc. Milli-Q water was used in all experiments. All chemicals were used without any further purification.

4.2.2 Preparation of PVDF& PVDF-PMMA flat-sheet membranes

Flat-sheet membranes were prepared by the non-solvent induced phase separation (NIPS) method [4, 31-33]. Casting solutions of known concentration (typically, 16 wt% total polymer) was prepared by mixing the PVDF powder and DMAC at 80 °C with continuously stirring at 150 rpm using an All-Purpose Mixer (MXD Process, Jeffersonville, Indiana) until the solution became homogeneous. For the solution with additives, 1 wt% and 2 wt% of PVDF-PMMA co-polymer powder were mixed with 15 wt% and 14 wt% PVDF powder in DMAC, respectively, to form dope solutions with fixed total polymer concentration (16 wt%). The dope solutions were cooled to ambient temperature (23 °C) and stored in the desiccator overnight for degassing. Thin polymer films were cast at room temperature (23 °C) on the PP nonwoven sheets by a casting knife (Gardco co., Pompano Beach, Florida) set at blade height of 150-μm. The cast membrane was immediately immersed in coagulation bath until it was detached. The composition of the coagulation bath was varied in this study. The tested compositions of the coagulation bath

(20 °C) were water and IPA: water (vol: vol) ratios of 10:0, 9:1, 7:3, 5:5, and 4:6. The membranes were kept in the coagulation bath for 10 min and then washed by the Milli-Q water (water, 20 °C) five times for complete removal of residual solvents. Solidified membranes were stored in Milli-Q water at room temperature (23 °C) until used. Furthermore, membrane samples with relative higher polymer concentrations (including 25 wt% PVDF only, 23.4 wt% PVDF+1.6 wt% PMMA, and 21.9 wt% PVDF+3.1 wt% PMMA) were also prepared in the coagulation bath with pure Milli-Q water as the pure polymer layer for investigating the surface morphology and measurements of surface porosity. Other factors were the same as described for 16 wt% membranes.

4.2.3 Characterization

Membrane morphology: Membrane surface morphology was visualized by means of scanning electron microscope (SEM) (Zeiss Supra 40 VP, Carl Zeiss Microscopy, LLC, NY). Membrane samples were secured on SEM stubs using double-sided carbon tape and sputter-coated (Ion beam sputtering/etching system, South Bay Technology, San Clemente, CA) with platinum for 90 s at 15 mA prior to analysis. Scanning was performed at 10.0 kV. Images were taken for each membrane at magnifications of 60,000 $\times$.

Contact angle: Contact angle measurements were conducted using a contact angle goniometer (Model: 250, ramé-hart instrument co., Succasunna, NJ). The sessile drop (SD) method and captive bubble (CB) method were used to measure the contact angle of the membranes under completely dry and fully wetted conditions, respectively. Sessile drop method

was measured by deposition of a liquid droplet with a fixed volume onto the dry membrane surface by using a normal 'I'-shaped needle, while the captive bubble method was conducted by forming an air bubble onto the immersed fully-wetted membrane surface in the liquid by using a 'J'-hook needle. Milli-Q water was used as a liquid for both SD and CB methods. To guarantee a statistical integrity, three samples were used for each membrane and contact angle measurements were performed on at twelve positions on each sample. The maximum and minimum values were removed, and the result was obtained by averaging the remaining 10 values. *Sessile drop method:* Membrane samples were dried at 40 °C in the oven (Fisherbrand Isotemp, Fisher Scientific Co LLC) overnight. Membrane samples were secured on glass slides using double-sided tape. The contact angle was then measured as follows. A droplet of 3 μL of Milli-Q water was carefully deposited to membrane surface to avoid the effect of gravity. The images were captured by a digital camera allowing apparent static contact angles to be measured. *Captive bubble method:* Membrane samples were used as taken out from the preservation condition (Milli-Q water at room temperature) without any further preparation. Membrane samples were attached to glass slides using double-sided tape and immersed into an environmental chamber (Quartz Cell, raméhart instrument co., Succasunna, NJ) filled with Milli-Q water at room temperature. A 'J'-hook needle was used to dispense an air bubble (3 μL) from beneath the membrane sample. Other processes such as capturing and calculating were the same as described for the sessile drop method.

Thickness and total membrane porosity: The thickness of each membrane was measured with a thickness gauge (ID-C112XBS, Mitutoyo Corp, Kawasaki, Japan). The sample size was $2.5 \times 7.5 \text{ cm}^2$. The total porosity of the membrane is defined as the ratio of the pore volume to the total volume of the membrane (fabric support). The pore volume was determined by

measuring the dry and wet weight of membrane and fabric support. MilliQ-water was used as the wetting agent. Membrane samples were soaked in water at room temperature overnight prior to analysis. Based on previous introduction, the total porosity (ε_f) of the fully wetted fabric support was calculated using the Eq. 4.1. The total porosities ($\varepsilon_{tot(wet)}$) of the fully wetted polymer layer of the supported composite membranes were calculated by Eq. 4.2. The total porosities ($\varepsilon_{tot(dry)}$) of the dry polymer layer of the supported composite membranes were calculated by Eq. 4.3 with the known bulk density (ρ_p) of PVDF 761 (0.288 g/cm³), as follows [34,35],

$$\varepsilon_f = \frac{(m_{fw} - m_{fd})}{\rho_w A L_f} \quad (4.1)$$

$$\varepsilon_{tot(wet)} = \frac{(m_w - m_d) - \rho_w A L_f \varepsilon_f}{\rho_w A (L - L_f)} \quad (4.2)$$

$$(m_d - m_{fd}) = A(L - L_f)[(1 - \varepsilon_{tot(dry)})\rho_p + \varepsilon_{tot(dry)}\rho_{air}] \quad (4.3)$$

where m_{fw} is the weight of the wet fabric support (g), m_{fd} is the weight of the dry fabric support (g), ρ_w is the density of water (g/ml), A is the effective area (cm²), L_f is the total thickness (cm), ε_f is the total porosity of the fully wetted fabric support calculated by Eqn. (1), m_w and m_d are the weight of the wet composite membranes (g) and the weight of the dry composite membranes (g), respectively. And L is the total thickness of the composite membranes (cm), $\varepsilon_{tot(wet)}$ is the total porosity of the polymer layer in the fully wetted composite membrane calculated by Eq. 4.2. Since $\rho_{air} = 0$, Eq. 4.3 can be simplified to

$$\varepsilon_{tot(dry)} = 1 - \frac{(m_d - m_{fd})}{A(L - L_f)\rho_p} \quad (4.4)$$

where $\varepsilon_{tot(dry)}$ is the total porosity of the polymer layer in the dry composite membrane and ρ_p is the bulk density of PVDF polymer. In this study, $\varepsilon_{tot(wet)}$ and $\varepsilon_{tot(dry)}$ are used to calculate a "dry-to-wet conversion factor" ($\frac{\varepsilon_{tot(dry)}}{\varepsilon_{tot(wet)}}$) to obtain estimates of surface porosity of wet membranes from SEM porosity measurements of dry membranes. The conversion factor is

calculated based on the bulk porosities (Eq. 4.2-4.4) and is used to transform surface SEM porosities because it accounts for expansion of the existing structure of the membranes.

Surface porosity determination by SEM-ImageJ analysis: SEM images were analyzed by open-source ImageJ software (v1.8.0) to evaluate the surface porosity of membranes. For ImageJ analysis, the SEM images were converted to 8-bit mode to present. Brightness and contrast (B&C) adjustment was used to remove the noise in the background of the images. Automatic thresholding was then used to convert images to binary (black and white), in which the black areas represent the pores and white areas represent the membrane surface [36].

Surface porosity determination by contact angle-based calculation: Surface porosity was calculated by averaging the results of measurements at three different locations in the same membrane as the following equations:

$$\theta_{m(SD)} = \theta_p(1 - \varepsilon_{SD}) + \theta_{air}\varepsilon_{SD} \quad (4.5)$$

where $\theta_{m(SD)}$ is the contact angle of dry membrane samples measured by the sessile drop method, θ_p is the contact angle of high concentrated (25 wt%, 23.4 wt%+1.6 wt%, and 21.9 wt%+3.1 wt%) polymer layer which can be regarded as the “pure polymer” measured by the sessile drop method, θ_{air} is the contact angle of air, which is known as 180°, and ε_{SD} represents the surface porosity of the membranes. Eq. 4.5 can be then re-written as follow,

$$\varepsilon_{SD} = \frac{\theta_{m(SD)} - \theta_p}{180^\circ - \theta_p} \quad (4.6)$$

For captive bubble method, surface porosity of fully wetted membranes was calculated by Eq. 4.7

$$\theta_{m(CB)} = \theta'_p(1 - \varepsilon_{CB}) + \theta_{water}\varepsilon_{CB} \quad (4.7)$$

where $\theta_{m(CB)}$ is the contact angle of fully wetted membrane samples measured by the captive bubble method, θ'_p is the contact angle of the “pure polymer” measured by the captive bubble method, θ_{water} is the contact angle of water, which is known as 0° , and ε_{CB} represents the surface porosity of the membranes calculated by the captive bubble method. Eq. 4.7 can be then simplified to

$$\varepsilon_{CB} = 1 - \frac{\theta_{m(CB)}}{\theta'_p} \quad (4.8)$$

4.3 Results and discussion

4.3.1 Sessile Drop Contact Angle and Dry Membrane Surface Porosity

Sessile drop (SD) contact angle measurements and SEM images were independently used to characterize the surface porosity of dry membranes. Results from SEM and SD contact angle analyses are shown in Table 4.1. For the synthesized membrane samples, there are two major variables: (1) the polymer recipe and (2) the composition of non-solvent. With fixed polymer composition and concentration, contact angle increases with the increase of the IPA component, from $83.2 \pm 0.5^\circ$ to $92.2 \pm 0.9^\circ$ (16% PVDF), $82.3 \pm 0.5^\circ$ to $91.0 \pm 1.2^\circ$ (15% PVDF+1% PMMA), and $81.2 \pm 0.6^\circ$ to $90.7 \pm 0.5^\circ$ (14% PVDF+2% PMMA). In contrast, contact angle decreases with increasing PVDF-PMMA co-polymer content because the methacrylate groups in PMMA are quite hydrophilic, but the blended membrane contact angles increase with IPA content in the non-solvent: from 83.2° to 81.2° (DI only), 86.4° to 84.4° (10% IPA), 88.6° to 85.5° (30% IPA), 89.9° to 87.7° (50% IPA), and 92.2° to 90.7° (60% IPA).

Table 4.1. Surface porosity calculated by SEM-ImageJ and sessile drop contact angle data (according to Eq. 4.5 and 4.6)

Membrane samples	CA(SD) (°)	$\varepsilon_{SEM-dry}$ (%)	ε_{SD} (%)
25% PVDF DI*	80.3±0.5	0.8±0.2	0 (assumed)
16% PVDF DI	83.2±0.9	2.3±0.6	2.5±1.0
16% PVDF 10%IPA	86.4±0.7	5.4±0.7	5.1±0.9
16% PVDF 30%IPA	88.6±1.4	7.8±0.6	8.3±1.0
16% PVDF 50%IPA	89.9±1.5	10.2±0.6	9.7±0.9
16% PVDF 60%IPA	92.2±0.9	12.9±0.6	11.8±0.8
23.4% PVDF+1.6% PMMA DI*	77.1±0.4	1.1±0.1	0 (assumed)
15% PVDF+1% PMMA DI	82.3±0.5	4.4±0.4	4.3±0.9
15% PVDF+1% PMMA 10%IPA	85.1±0.5	8.4±0.6	7.8±0.8
15% PVDF+1% PMMA 30%IPA	86.8±1.1	8.8±0.7	9.4±1.0
15% PVDF+1% PMMA 50%IPA	88.7±1.4	12.3±0.6	11.3±0.9
15% PVDF+1% PMMA 60%IPA	91.0±1.2	14.1±0.6	13.5±1.0
21.9% PVDF+3.1% PMMA DI*	76.6±0.6	1.2±0.5	0 (assumed)
14% PVDF+2% PMMA DI	81.2±0.6	4.2±0.6	4.4±1.1
14% PVDF+2% PMMA 10%IPA	84.4±0.7	8.0±0.7	7.7±0.8
14% PVDF+2% PMMA 30%IPA	85.5±0.7	8.5±0.6	8.8±0.8
14% PVDF+2% PMMA 50%IPA	87.7±1.0	11.8±0.7	10.8±0.8
14% PVDF+2% PMMA 60%IPA	90.7±0.5	14.5±0.7	13.8±1.2

In Fig 4.1A, it is clear that decreasing polymer concentration, increasing PVDF-PMMA co-polymer content and increasing IPA content all increase porosity. In addition, membranes phase inverted with IPA in the non-solvent have a dramatically different surface pore morphology elongated and irregular versus nearly spherical without IPA. Binary black and white images help illustrate the changes in porosity and pore morphology. More importantly, the

surface porosity values calculated from the contact angle data is very close to those determined from SEM images (Table 4.1). The binary SEM-ImageJ images are shown in (Fig. 4.1B). The three high-concentration membranes [25% PVDF (a1), 23.4% PVDF+1.6% PMMA (a2), and 21.9% PVDF+3.1% PMMA (a3)] have very low porosity values (all $<1.2 \pm 0.5\%$), which supports our assumption that the high-concentration membranes can be treated as “pure polymer” surfaces ($\varepsilon = 0$).

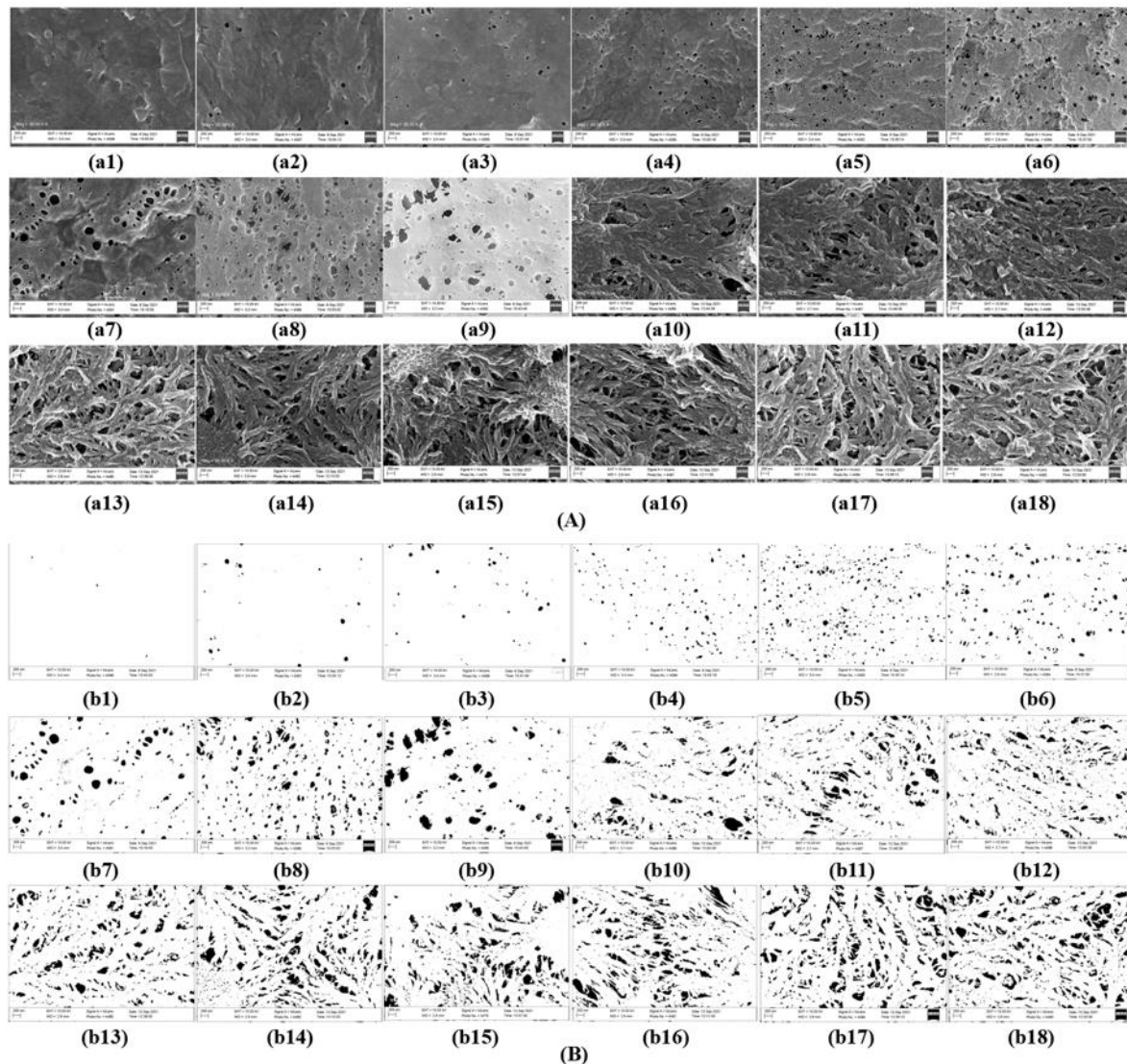


Figure 4.1. (A) grey scale SEM images of PVDF-PMMA flat-sheet membranes after phase inversion in different recipes: (a1) 25% PVDF in DI, (a2) 23.4%PVDF+1.6%PMMA in DI, (a3) 21.9%PVDF+3.1%PMMA in DI, (a4) 16% PVDF in DI, (a5) 15% PVDF+1%PMMA in DI, (a6) 14% PVDF+2%PMMA in DI, (a7) 16% PVDF in 10%IPA, (a8) 15% PVDF+1%PMMA in 10%IPA, (a9) 14% PVDF+2%PMMA in 10%IPA, (a10) 16% PVDF in 30%IPA, (a11) 15% PVDF+1%PMMA in 30%IPA, (a12) 14% PVDF+2%PMMA in 30%IPA, (a13) 16% PVDF in 50%IPA , (a14) 15% PVDF+1%PMMA in 50%IPA, (a15) 14% PVDF+2%PMMA in 50%IPA, (a16) 16% PVDF in 60%IPA, (a17) 15% PVDF+1%PMMA in 60%IPA, and (a18) 14% PVDF+2%PMMA in 60%IPA, (B) binary black and white images (b1-b18) in ImageJ corresponding to (A).

4.3.2 Captive Bubble Contact Angle and Wet Membrane Surface Porosity

Six representative membrane samples (25% PVDF in DI, 16% PVDF in DI, 21.9% PVDF+3.1% PMMA in DI, 14% PVDF+2% PMMA in DI, 14% PVDF+2% PMMA in 30% IPA, and 14% PVDF+2% PMMA in 60% IPA) were selected to investigate the relationship between captive bubble (CB) contact angle and wet membrane surface porosity (Table 4.2). The CB contact angles are greatly reduced (24° to 44°) relative to the SD contact angles for the same membranes. Also, the membrane porosity increases for fully wetted membranes because the membranes swell by about 7 to 12% (Fig. 4.2) [37,38]. Using the dry-to-wet conversion factors, dry membrane SEM-derived surface porosity data are not significantly different from wet membrane CB contact angle-derived surface porosity values. In addition, by comparing wet/swelling-corrected SD-derived surface porosity data and CB contact angle-derived surface porosity values, the practicability and accuracy of the dry-to-wet conversion factors were further verified (Fig. 4.3).

Table 4.2. Surface porosity calculated by SEM-ImageJ data with dry-to-wet conversion factors and captive bubble contact angle data (according to Eq. 4.7 and 4.8)

Membrane	CB (°)	ε_{CB} (%)	$\varepsilon_{tot(wet)}$ (%)	$\varepsilon_{tot(dry)}$ (%)	$\frac{\varepsilon_{tot(dry)}}{\varepsilon_{tot(wet)}}$	$\varepsilon_{SEM-dry}$ (%)	$\varepsilon_{SEM-wet}$ (%)
25% PVDF DI*	60.3±0.6	0 (assumed)	16.0	14.9	0.935	0.8±0.2	0.9±0.2
16% PVDF DI	58.7±0.8	2.7±0.8	32.9	30.6	0.926	2.3±0.6	2.5±0.7
21.9% PVDF+3.1% PMMA DI*	56.5±1.2	0 (assumed)	16.0	14.8	0.926	1.2±0.5	1.3±0.5
14% PVDF+2% PMMA DI	51.2±0.9	5.0±0.9	34.1	31.3	0.917	4.2±0.6	4.6±0.7
14% PVDF+2% PMMA 30%IPA	47.5±0.9	9.4±0.6	45.1	40.7	0.901	8.5±0.6	9.4±0.7
14% PVDF+2% PMMA 60%IPA	46.7±1.6	17.4±0.5	50.3	45.1	0.893	14.5±0.7	16.2±0.8

* Same data as in Table 3.1, shown here for ease of comparison.

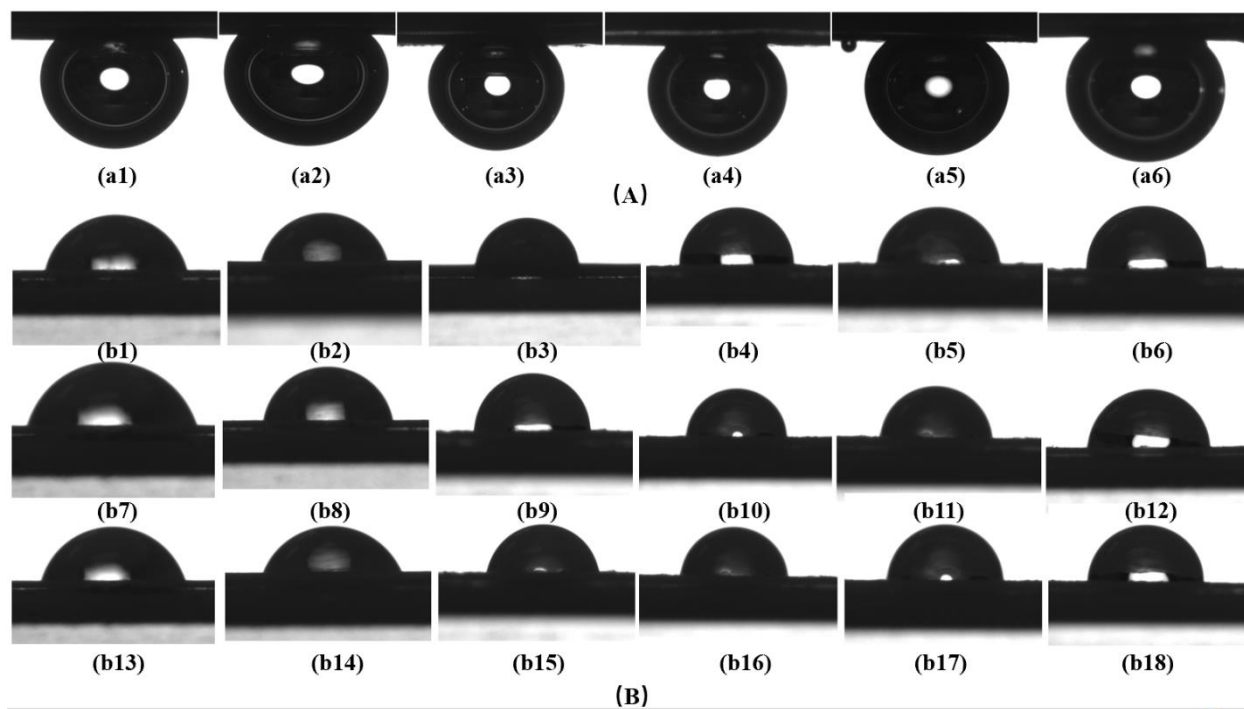


Figure 4.2. (A) Contact angle images captured by captive bubble method, from left to right: 25% PVDF DI, 16% PVDF DI, 21.9% PVDF+3.1% PMMA DI, 14% PVDF+2% PMMA DI, 14% PVDF+2% PMMA 30%IPA, and 14% PVDF+2% PMMA 60%IPA, (B) contact angle images captured by sessile drop method: 25% PVDF DI, 16% PVDF (DI 10%IPA, 30%IPA, 50%IPA, and 60%IPA), 23.4% PVDF+1.6% PMMA DI, 15% PVDF+1% PMMA (DI 10%IPA, 30%IPA, 50%IPA, and 60%IPA), 21.9% PVDF+3.1% PMMA DI, and 14% PVDF+2% PMMA (DI 10%IPA, 30%IPA, 50%IPA, and 60%IPA).

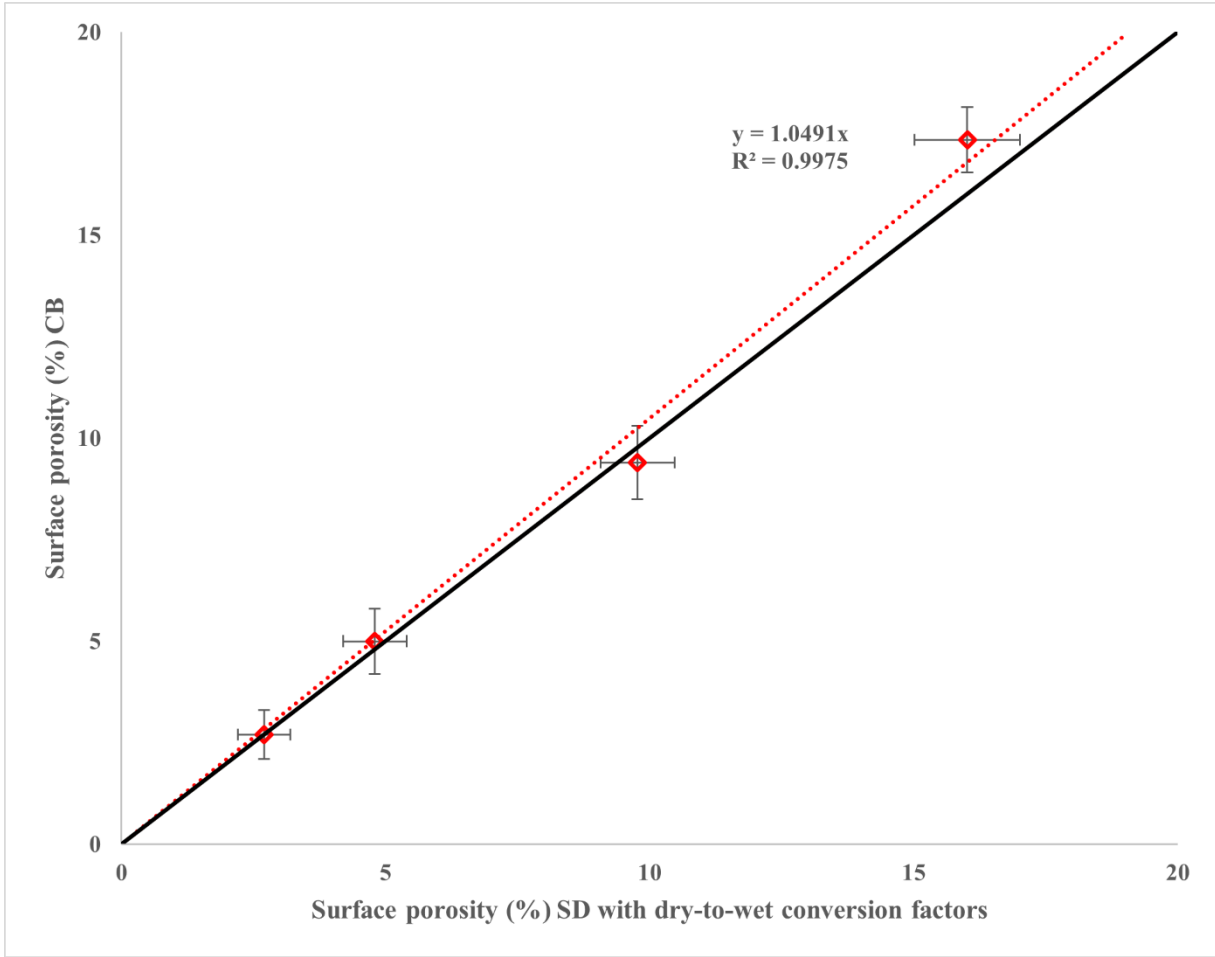


Figure 4.3. Comparison of the membrane surface porosity obtained by the sessile drop method modified by dry-to-wet conversion factors and the captive bubble method (16% PVDF in DI, 14% PVDF+2% PMMA in DI, 14% PVDF+2% PMMA in 30% IPA, and 14% PVDF+2% PMMA in 60% IPA).

4.3.3 Comparative Analysis of Wet and Dry Membrane Porosity

In Fig. 4.4, we also compare all wet and dry membrane surface porosity values obtained by contact angle measurements with dry membrane and wet/swelling-corrected SEM image porosity values. The solid black line in Fig. 4.4 is a line of symmetry. The black dotted line is a linear regression of wet membrane CB contact angle derived surface porosity ($y = 1.0212x, R^2 = 0.9996$) and the blue dotted line is a linear regression of dry membrane SD

contact angle derived surface porosity ($y = 0.9659x, R^2 = 0.9961$). And the red dotted line represents a linear regression of wet/swelling-adjusted SD contact angle derived surface porosity ($y = 1.0212x, R^2 = 0.9996$). Most of data are located very near the line of symmetry deviating on average by 2 to 3%. It can be seen that the dry surface porosity data is almost identical to the wet surface porosity data for high polymer concentration membranes (with surface porosity <6%), while for relatively looser membranes (with surface porosity >8%), the wet surface porosity values are 1 to 2% higher than dry surface porosity values. Overall, the contact angle and SEM image derived porosity values agree very well and it appears the difference is largely explained by membrane swelling for fully saturated membranes.

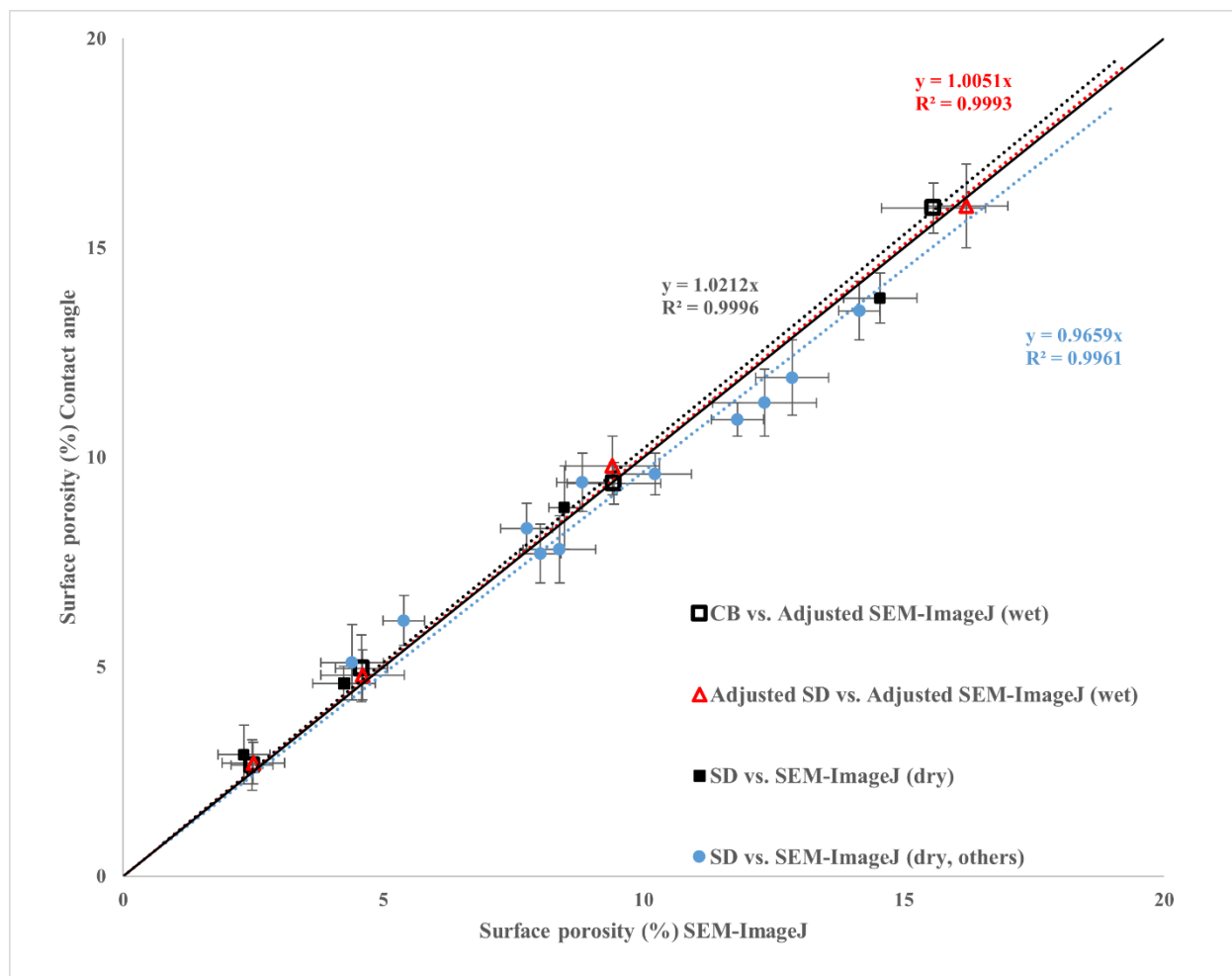


Figure 4.4. Comparison of the membrane surface porosity obtained by the SEM-ImageJ method and the contact angle methods (SD and CB), the hollow black square represents wet surface porosity (16% PVDF in DI, 14% PVDF+2% PMMA in DI, 14% PVDF+2% PMMA in 30% IPA, and 14% PVDF+2% PMMA in 60% IPA) and the solid black square represents dry surface porosity of the same membrane samples, the blue circle represents the dry surface porosity of other remaining membranes in the experimental database.

4.4 Conclusions

This chapter established a novel method for characterizing surface porosity of porous membranes via contact angle measurements. To investigate the method, a batch of porous membranes with different polymer compositions and non-solvent recipes were fabricated via

NIPS method. Contact angle was conducted by sessile drop method and captive bubble method in dry and wet conditions, respectively. Dry membrane surface porosity was visualized by SEM and further analyzed by ImageJ. The dry-to-wet conversion factors were obtained by the water uptake method to derive fully wetted surface porosity. Our results suggest that with fixed polymer composition and concentration, contact angle increases with the increase of IPA in the coagulation bath. In contrast, contact angle decreases with increasing PVDF-PMMA co-polymer content because of the hydrophilic methacrylate groups, but the blended membrane contact angles also increase with IPA content in the non-solvent. More importantly, both wet and dry contact angles correlate strongly with SEM derived porosity values (deviating on average by 2 to 3%), while for membranes with surface porosity >8%, the wet surface porosity values are 1 to 2% higher than dry surface porosity values, which also emphasizes the importance of membrane swelling in determining membrane porosity for aqueous filtration applications. However, this study may not be feasible for commercial membranes because the commercial membranes could have unknown/proprietary additives and treatments which would prevent anyone other than the manufacturer from preparing a pure polymer film.

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Chapter 5 Comparison of classical hydrodynamic pore-flow models of transport through porous membranes

5.1 Introduction

Porous polymeric filtration membranes are used in a wide range of applications including protein separation and concentration, sterile filtration, diffusion dialysis, drinking water filtration, membrane bio-reactors, and other aqueous separations [1-6]. In low-pressure membrane filtration applications, the target solute rejection and water permeability are the key performance indicators. Increasing water permeability holds considerable merit as it reduces the required applied pressure, energy consumption and operational cost [7,8]. Over the years, researchers have explored a wide array of method to increase the permeability of microfiltration (MF) and ultrafiltration (UF) membranes without decreasing their rejection [9,10]. However, the correlation between membrane morphology, membrane chemistry, and membrane separation performance remains difficult to predict.

While it is well known that the permeability of porous membranes is governed by membrane pore size, porosity and pore length, many other studies suggest other factors may contribute [11,12]. Furthermore, the characterization of membrane surface properties, namely pore size and surface porosity, predominantly adopts a top-view perspective, which overlooks the skin layer thickness and pore tortuosity, which are critical factors. Therefore, it is necessary to identify appropriate simulation models that integrate the analytical insights derived from membrane characterization to comprehensively understand and predict membrane permeability.

It is apparent that the principles of hydrodynamics are indispensable for understanding the mechanisms governing transport across membranes by elucidating concepts such as flow path, viscosity, porosity, and pressure drop [13,14]. Generally, there are three hydrodynamic permeability models for any porous media – Hagen-Poiseuille (HP), Kozeny-Carman (KC), and Happel’s cell (HC) pore-flow models. The HP model considers the flow model from a force balance on flow through a cylindrical conduit, while a tortuosity correlation is empirically introduced to apply the model to porous media – including membranes [15,16]. The KC model describes a porous medium as a bundle of straight, cylindrical capillaries with a proportionality constant that accounts for the fact that in reality a porous media presents a more tortuous path than a straight, cylindrical capillary [17,18]. In the HC model, the porous medium is taken to be a random assemblage of spherical particles that is assumed to consist of a number of “cells,” each of which contains a particle surrounded by a fluid envelope. The model produces a correction factor to the Stokes drag coefficient for a spherical particle to account for the impact of the particle assemblage fluid streamlines and frictional losses[19].

In this chapter, a series of porous polymeric membranes were fabricated using different polymer concentrations to tailor their water permeability and solute rejection in pressure-driven filtration. Surface porosity, mean pore size, pore size distribution, and skin layer thickness of dry membrane samples were captured by image analysis of surface SEM images. Water uptake and membrane swelling measurements enable a dry-to-wet conversion factor that allows one to calculate wet membrane pore morphology from dry membrane characteristics. We also investigate the accuracy and correlation of a classical sieving model by comparing model results and experimental solute rejection data. Finally, we assess the relative accuracy of hydrodynamic

pore-flow model predictions of water permeability and solute rejection with experimental filtration data.

5.2 Theory

5.2.1 The Darcy equation

In pressure-driven, porous membrane separations, water permeates via convection through interconnected pores across the membrane separating layer. The relationship between pressure and flow can be described via Darcy's equation as follows [20]:

$$\frac{Q_0}{A_m} = u_0 = \frac{k_D}{\mu} \frac{\Delta p}{\Delta x} \quad (5.1)$$

where u_0 is the superficial velocity, k_D is the Darcy permeability coefficient, μ is the solution viscosity, $\frac{dp}{dx}$ is the hydraulic pressure gradient and driving force for water transport, Q_0 is water flow rate, and A_m is the projected area of the membrane (or porous media). The actual “interstitial” velocity is based on the area open to the flowing fluid, which is the free volume or porosity, ε , giving:

$$\frac{Q_0}{\varepsilon A_m} = \frac{u_0}{\varepsilon} = u_i \quad (5.2)$$

In most membrane studies, the pressure-flux relationship is given as follows [21]:

$$\frac{Q_0}{A_m} = J_v = L_p \Delta P_m \quad (5.3)$$

where J_v is the volumetric flux through a membrane, ΔP_m is the available trans-membrane pressure drop, and $L_p [= k_D / (\mu \cdot \Delta x)]$ is the water permeance.

5.2.2 Hagen-Poiseuille pore-flow model (HP)

The HP equation was developed by Hagen and independently by Poiseuille from a force balance on flow through a single cylindrical conduit [15]. An alternate approach to deriving the HP equation begins with Fanning's equation for the pressure drop through a cylindrical conduit due to friction,

$$-\frac{dp}{dx} = 4f \frac{\rho u_i^2}{2d_H}, \quad (5.4)$$

where f is the friction factor ($= 16 \cdot \text{Re}^{-1}$ for laminar flow) and u_i is the average flow velocity through the cylindrical conduit. Substituting $16 \cdot \text{Re}^{-1}$ for f and applying the standard definition of Reynolds number ($= \rho u_i d_H / \mu$) into Eq. 5.4 yields (dropping the negative sign):

$$\frac{dp}{dx} = 4 \frac{16}{\text{Re}} \frac{\rho u_i^2}{2d_H} = 4 \frac{16\mu}{\rho u_i d_H} \frac{\rho u_i^2}{2d_H} = 32\mu \frac{u_i}{d_H^2}, \quad (5.5)$$

or

$$u_i = \frac{d_H^2}{32\mu} \frac{dp}{dx}. \quad (5.6)$$

Now, this is the flow through a single cylindrical conduit (or one membrane pore) of diameter d_H , which is the pore diameter. From Eq. 5.6, we can determine the superficial velocity through all of the pores, which provides

$$\frac{u_0}{\varepsilon} = \frac{r_p^2}{8\mu} \frac{dp}{dx}, \quad (5.7)$$

or in the form of a volumetric water flux

$$J_v = \frac{\varepsilon r_p^2}{8\mu} \frac{dp}{dx}. \quad (5.8)$$

Here we note that the definition of porosity, ε ($= N_p \pi r_p^2 / A_m$), is the number of pores (N_p), times the area of a single pore (πr_p^2) and divided by the total membrane area.

Finally, membrane pores are rarely perfectly parallel and straight, so it is common to apply a tortuosity factor to account for the longer permeation path length. A common expression for tortuosity of porous media is [22]

$$\tau^2 = 1 - \ln(\varepsilon^2), \quad (5.9)$$

which yields

$$J_v = \frac{\varepsilon r_p^2}{8\mu\tau} \frac{dp}{dx} \quad (5.10)$$

This is the most common form of the Hagen-Poiseuille equation for porous membranes. The tortuosity of a porous media versus porosity is provided in Fig. 5.1, and the key attributes of the Hagen-Poiseuille equation are illustrated in Fig. 5.2a [16].

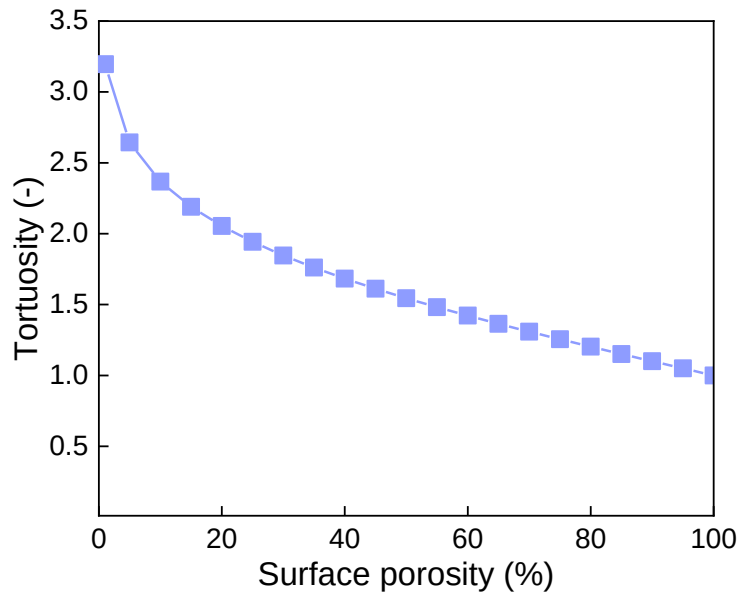


Figure 5.1. Plot of tortuosity vs. porosity using Eq. 5.9.

5.2.3 Kozeny-Carman pore-flow model (KC)

The Kozeny-Carman pore flow model assumes a porous media comprised of spherical particles is adequately described as a bundle of straight capillaries defined by some effective (average) hydrodynamic diameter and length [23,24]. It begins with the assumption that the permeability is dimensionally proportional to the cylindrical capillary diameter squared, ($k \sim d_e^2$), where d_e is the effective capillary diameter. First, we solve for d_e in terms of a hydraulic diameter, d_H , which is four times the hydraulic radius, r_H , which is the ratio of effective cross-sectional area open for flow, A_e , to the wetted perimeter, P_w , of the conduit,

$$(d_e =) d_H = 4r_H = 4 \frac{A_e}{P_w} \frac{L}{L} = 4 \frac{V_e}{A_w} = 4 \frac{\varepsilon V}{A_w}. \quad (5.11)$$

Here, V_e is the effective pore volume, A_w is the wetted surface area, L is the depth of porous media, V is the total volume and ε is the porosity of the porous media. The wetted surface area is the total number of media particles multiplied by the surface area of a single media particle,

$$A_w = N_p \pi d_m^2, \quad (5.12a)$$

where d_m is the media particle diameter, $\varepsilon (= 1 - \phi)$ is the porosity and ϕ is the solid volume fraction. The number of particles is the solid volume fraction divided by the volume of a single spherical particle. Inserting this into Eq. 5.12a gives

$$A_w = \frac{V(1 - \varepsilon)}{\frac{\pi d_m^3}{6}} \pi d_m^2 \quad (5.12b)$$

Therefore, the hydraulic diameter becomes

$$d_H = 4 \frac{\varepsilon V}{V(1 - \varepsilon) \pi d_m^2} \frac{\pi d_m^3}{6} = 4 \frac{\varepsilon V \pi d_m^2}{V(1 - \varepsilon) \pi d_m^2} \frac{d_m}{6} = 4 \frac{\varepsilon}{(1 - \varepsilon)} \frac{d_m}{6}. \quad (5.13)$$

The specific surface area of the media, S , is the total wetted surface area, A_w , divided by the media volume, $V(1 - \varepsilon)$, which works out to $6/d_m$ [25]. Substituting S into Eqn. 5.13 and solving for d_H^2 gives

$$d_H^2 = \frac{16}{S^2} \frac{\varepsilon^2}{(1 - \varepsilon)^2} \quad (5.14)$$

Kozeny dropped the 16 and added a fitting parameter, K_{KC} , the “Kozeny constant” to the denominator of Eq. 5.14 to be determined from filtration data. This then yields

$$k_{KC} = \frac{\varepsilon^2}{K_{KC} S^2 (1 - \varepsilon)^2}. \quad (5.15)$$

Substituting this into the Darcy equation produces

$$\frac{u_0}{\varepsilon} = \frac{\varepsilon^2}{K_{KC} S^2 (1 - \varepsilon)^2 \mu} \frac{dp}{dx}, \quad (5.16)$$

or

$$u_0 = \frac{d_m^2 \varepsilon^3}{36 K_{KC} (1 - \varepsilon)^2 \mu} \frac{dp}{dx} \quad (5.17)$$

Substituting back in d_H for d_m and converting into the pore radius form as in Eqn. 5.7 gives

$$J_v = \frac{k_{KC}}{\mu} \frac{\Delta P}{\Delta x} = \frac{\varepsilon r_p^2}{4 K_{KC} \mu} \frac{\Delta P}{\Delta x} \quad (5.18)$$

P.C. Carman [17] later proposed an empirical value of 5.0 for K_{KC} based on extensive experiments, which makes $k_{KC} = \varepsilon r_p^2 / 20$ (Fig. 5.2b). A tortuosity factor is not required when using the Kozeny-Carman permeability as shown below.

Now, from the definition of the hydraulic diameter of a porous media in Eq. 5.13, we can also define a Reynolds number

$$\text{Re} = \frac{\rho u_i d_H}{\mu} = \frac{\rho u_0}{\mu \varepsilon} \frac{2 \varepsilon d_m}{3(1 - \varepsilon)} = \frac{2}{3} \frac{\rho u_0 d_m}{(1 - \varepsilon) \mu}. \quad (5.19)$$

And, if we re-arrange and expand Eq. 4.15 as follows

$$\frac{dp}{dx} = 180 \frac{u_0 (1 - \varepsilon)^2 \mu}{\varepsilon d_m^2 \varepsilon^2} = 180 \frac{2}{3} \frac{2}{3} \frac{u_0}{\varepsilon} \left(\frac{3}{2} \frac{\rho u_0 (1 - \varepsilon) \mu}{\rho u_0 \varepsilon d_m} \right) \left(\frac{3 (1 - \varepsilon)}{2 \varepsilon d_m} \right) = 4 \frac{40 \rho u_0^2}{\text{Re} 2 d_H}, \quad (5.20)$$

and hence, we can extract the laminar flow friction factor for a porous media as

$$f = \frac{40}{\text{Re}} \quad (5.21)$$

This shows that the frictional losses through a porous media will be higher than through a straight cylindrical conduit ($f = 16/\text{Re}$) because of the more tortuous flow path.

5.2.4 Happel's Cell model (HC)

Happel considered a porous medium as an ordered assemblage of “cells” each comprising a particle surrounded by a fluid envelope. The fluid envelope is assumed to contain the same volumetric proportion of fluid to solid as exists in the entire assemblage. This determines the envelope radius of each cell as illustrated in Fig. 5.2c. Happel further assumed that each cell remains spherical and that the outside surface of the cell is frictionless; that is, the shear stress vanishes at the outer boundary of the cell. The flow is considered to be inertia free and to obey the Stokes equation with a moving coordinate system. Happel showed that the drag force per particle could be described by a modified form of the Stokes equation [26],

$$F = 3\pi\mu d_m U A_s, \quad (5.22)$$

where A_s is described by

$$A_s = \frac{3 + 2\phi^{5/3}}{3 - \frac{9}{2}\phi^{1/3} + \frac{9}{2}\phi^{5/3} - 3\phi^2}. \quad (5.23)$$

The A_s parameter is a correction factor to the stream function that describes the distortion of the streamlines around a spherical particle including the effects of neighboring particles. The pressure drop per unit length of a packed bed is set equal to the drag force per particle divided by the cell volume, $4\pi b^3/3$, therefore:

$$-\frac{dp}{dx} = \frac{F}{\frac{4}{3}\pi b^3} = \frac{6\pi\mu a U A_s}{\frac{4}{3}\pi b^3} = \frac{\mu}{k_{HC}} U. \quad (5.24)$$

Expanding A_s and re-arranging gives

$$k_{HC} = \frac{3 - \frac{9}{2}\phi^{1/3} + \frac{9}{2}\phi^{5/3} - 3\phi^2}{18\phi(3 + 2\phi^{5/3})} d_m^2. \quad (5.25)$$

Noting the KC permeability coefficient can be written as $k_{KC} = \frac{(1-\phi)^3}{36K\phi^2} d_m^2$, we can extract from

Eq. 5.25 the effective Kozeny constant according to the HC model.

$$K_{HC} = \frac{(3 + 2\phi^{5/3})(1 - \phi)^3}{2\phi(3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2)}. \quad (5.26)$$

In the limit of low porosity ($\varepsilon \rightarrow 0$ so $\phi \rightarrow 1$), Probstein [27] showed Eq. 5.26 reduces to

$$k_{HC} = \frac{\varepsilon^3 d_m^2}{162} \approx \frac{\varepsilon^3 d_m^2}{180} = k_{KC}, \quad (5.27)$$

which is nearly identical to the Kozeny-Carman permeability coefficient. Replacing Carman's empirical Kozeny constant with the HC model constant makes the permeability

$$k_{HC} = \frac{\varepsilon^3 d_m^2}{36K_{HC}}, \quad (5.28)$$

and it can be seen that for porosity from 0 to 50% the Happel's Cell constant ranges from a low of 4.4. to a high of 4.7. Therefore, when multiplied by 36, the denominator ranges from a value

of 159 to 169 (Table 5.1). Finally, translating the HC permeability into the pore radius form gives

$$k_{HC} = \frac{\varepsilon r_p^2}{4K_{HC}}, \quad (5.29)$$

which is identical to the KC model equation except for the definition of K_{HC} . In Figure 5.2, we visualize all three models and summarize their forms in the Darcy equation.

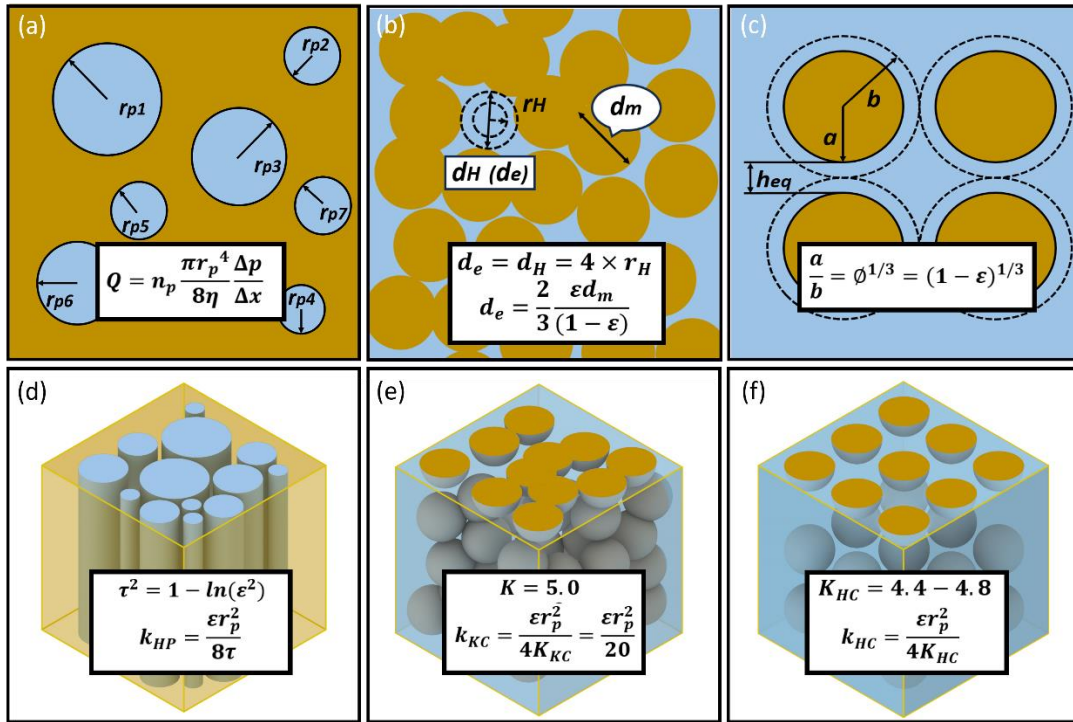


Figure 5.2. Illustration of three hydrodynamic models. Hagen-Poiseuille pore-flow model from (a) top and (d) axonometric view. Kozeny-Carman pore-flow model from (b) top and (e) axonometric view. Happel's Cell model from (c) top and (f) axonometric view.

Table 5.1. Happel's Cell model predictions of the Kozeny constant

Cell radius ratio $a/b = \phi^{1/3}$	Porosity $\varepsilon = 1 - \phi$	Kozeny constant K_{HC}
1.00	0.00	4.50
0.98	0.05	4.47
0.97	0.10	4.44
0.95	0.15	4.42
0.93	0.20	4.42
0.89	0.30	4.44
0.84	0.40	4.54
0.79	0.50	4.74
0.74	0.60	5.11
0.67	0.70	5.80
0.58	0.80	7.24
0.46	0.90	11.42
0.37	0.95	18.93

5.3 Materials and methods

5.3.1 Materials

Polysulfone (PSU, Ultrason S) and polyethersulfone (PES, Ultrason E) were generously supplied by BASF (Charlotte, North Carolina, USA). Polyvinylidene fluoride (PVDF, Kynar 761) was kindly provided by Arkema, Inc. (King of Prussia, Pennsylvania, USA).

Dimethylformamide (DMF, ACS reagent grade), polyethylene glycol (PEG, 100 kDa, powder), and polyethylene glycol (PEG, 20 kDa, powder) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA) and used as received. Polypropylene (PP, PC 15080) fabric was kindly provided by Hollingsworth-vose Inc. Commercial MF (PVDF, 0.1 μm) and UF (PS 20)

membranes were sourced from Solecta, Inc., (Oceanside, California, USA). Laboratory ultra-pure water (UPW) (Milli-Q Synthesis, Millipore, USA) was used in all experiments. All chemicals were used without any further purification.

5.3.2 Preparation of hand-cast flat-sheet membranes

Flat-sheet membranes were prepared by the non-solvent induced phase separation (NIPS) method[28], [29], [30]. Casting solutions of 12wt% and 20 wt% polymers were prepared by mixing PES, PSU or PVDF in DMF at 75 °C with continuously stirring at 250 rpm using an All-Purpose Mixer (MXD Process, Jeffersonville, Indiana, USA) until the solution became homogeneous. The dope solutions were cooled to ambient temperature (23 °C) and stored in the desiccator overnight for degassing. Thin polymer films were cast at room temperature (23 °C) on the PP nonwoven sheets by a casting knife (Gardco Co., Pompano Beach, Florida, USA) set at blade height of 200 μ m. The cast membrane was immediately immersed in a UPW coagulation bath for 10 min and then washed with the UPW (20 °C) five times to completely remove the residual solvents. Solidified membranes were stored in UPW at room temperature (23 °C) prior to testing and characterization. An additional set of PSU membranes were prepared from casting solutions comprising 14, 16, and 18 wt% in DMF using the identical procedure.

5.3.3 Membrane characterization

Membrane morphology: To determine the morphology of the membrane, surface and cross-section imaging was carried out with a field emission gun scanning electron microscope (Phenom Pharos G2 Desktop FEG-SEM, Thermo Fisher Scientific, Cleveland, OH). For the cross-section observation, membrane samples were fractured by the Indirect-Freeze-Fracture

(IFF) method [31]. All the membrane samples were secured on SEM stubs using double-sided carbon tape and sputter-coated (Ion beam sputtering/etching system, South Bay Technology, San Clemente, CA) with platinum for 3nm thickness prior to analysis. Scanning was performed at 10 kV. Top surface images for each membrane sample were taken at magnifications of 150,000×. Cross-section view images were first taken at magnifications of 3,000× to analyze the membrane structure and total thickness of polymer layer. Subsequently, the images were magnified up to 30,000× to observe intricate features, such as the skin layer. SEM images were analyzed by open-source ImageJ software (v1.8.0) to measure the skin layer thickness, polymer layer thickness, pore radius and surface porosity of membranes. For ImageJ analysis, the SEM images were converted to 8-bit mode to present. Automatic thresholding was then used to convert images to binary (black and white)[32]. Mean pore size was further calculated and plotted from the binary images. At high magnification (30,000×), one single cross-sectional image is insufficient to depict the entirety of the membrane. Accordingly, we vertically merged 4-8 images depending on the thickness of the polymer layer to present the overall morphology of membranes with more details.

Membrane swelling measurement: The thickness of each membrane was measured with a thickness gauge (ID-C112XBS, Mitutoyo Corp, Kawasaki, Japan). The sample size was 2.5 × 7.5 cm². UPW was used as the wetting agent. Membrane samples were soaked in water at room temperature overnight prior to analysis. The total porosity (ε_f) of the fully wetted fabric support was calculated from

$$\varepsilon_f = \frac{(m_{fw} - m_{fd})}{\rho_w AL_f}. \quad (5.30)$$

Here, m_{fw} is the weight of the wet fabric support (g), m_{fd} is the weight of the dry fabric support (g), ρ_w is the density of water (g/ml), A is the effective area (cm²), L_f is the total thickness (cm). The total porosities ($\varepsilon_{tot(wet)}$) of the fully wetted polymer layer of the supported composite membranes were calculated using

$$\varepsilon_{tot(wet)} = \frac{(m_w - m_d) - \rho_w A L_f \varepsilon_f}{\rho_w A (L - L_f)}. \quad (5.31)$$

Here, ε_f is the total porosity of the fully wetted fabric support (calculated from Eqn. 5.31), m_w and m_d are the weight of the wet composite membranes (g) and the weight of the dry composite membranes (g), respectively, and L is the total thickness of the composite membranes (cm). The total porosities ($\varepsilon_{tot(dry)}$) of the dry polymer layer of the supported composite membranes were calculated by

$$(m_d - m_{fd}) = (L - L_f)[(1 - \varepsilon_{tot(dry)})\rho_p + \varepsilon_{tot(dry)}\rho_{air}] \quad (5.32)$$

with the known bulk density (ρ_p) of PSU (1.24 g/cm³), PES (1.37 g/cm³), and PVDF (0.29 g/cm³) [33-35]. Since $\rho_{air} = 0$, Eqn. 5.30 and 5.32 can be simplified to

$$\varepsilon_{tot(dry)} = 1 - \frac{(m_d - m_{fd})}{A(L - L_f)\rho_p} \quad (5.33)$$

where $\varepsilon_{tot(dry)}$ is the total porosity of the polymer layer in the dry composite membrane and ρ_p is the bulk density of polymer. In this study, $\varepsilon_{tot,wet}$ and $\varepsilon_{tot,dry}$ are used to calculate membrane swelling ratio to obtain estimates of surface porosity of wet membranes from SEM porosity measurements of dry membranes. The conversion factor is used to transform surficial and cross-

sectional SEM porosities because it accounts for expansion of the existing structure of the membranes.

Membrane hydrophilicity: Contact angle measurements were conducted by using a contact angle goniometer (Model: 250, ramé-hart instrument co., Succasunna, NJ). The sessile drop (SD) method was applied to measure the contact angle of the membranes under completely dry conditions [34]. To guarantee statistical integrity, three samples were used for each type of membrane, and contact angle measurements were performed at twelve positions on each sample. The maximum and minimum values were removed, and the result was obtained by averaging the remaining 10 values.

Pure water permeability of membranes: The pure water flux (PWF, LMH) of the membranes was tested with dead-end filtration apparatus (50 ml, Amicon Stirred Cell) at room temperature (23 °C) using UPW water as the feed. The PWF tests were conducted with a sample diameter of 4.4 cm and a transmembrane pressure of 1.38 bar. All the membrane samples were compacted at 1.38 bar for 1 h to obtain a stable flux before the PWF tests. The PWF was calculated as follows:

$$J = \frac{V}{A_m \times t} \quad (5.34)$$

where the V is the volume of the collected permeate during the operation time.

Separation performance of membranes: The solute rejection by microfiltration (12 wt%) and ultrafiltration (14 wt%, 16 wt%, 18 wt%, and 20 wt%) membranes was determined using 100 kDa PEG at 1 g/L and 10 kDa PEG at 1 g/L, respectively. Solute concentrations in feed and

filtrate were analyzed with TOC-LCPH (total organic carbon) analyzer (Shimadzu Scientific Instruments, USA). The membrane solute rejection was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (5.35)$$

where C_p and C_f are the solute concentrations of the permeate solution and feed solution, respectively. Each type of membrane was tested 3 times to ensure accuracy. The stoke radius of the PEG solutes were calculated based on their molecular weights as follows [36]:

$$R = 16.73 \times 10^{-3} \times M^{0.557} \quad (5.36)$$

where R is the radius of the PEG (in nanometer), respectively. M represents the molecular weight of the particles (in Dalton). The solute rejection (R_s) was estimated from the solute-to-pore size ratio using the mechanical sieving model [37]:

$$R_s = [\lambda(2 - \lambda)]^2 \quad (5.37)$$

where $\lambda = (r_s/r_p)$ is the solute-to-pore size ratio, r_s is solute radius, and r_p is pore radius (Fig. 5.3).

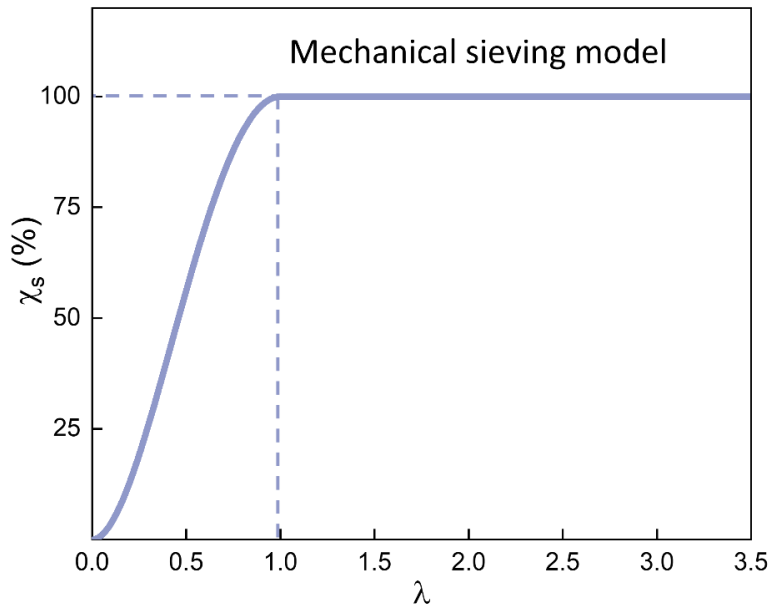


Figure 5.3. Illustration of mechanical sieving model.

5.4 Results and Discussion

5.4.1 Hydrodynamic simulations of the effect of surface porosity and pore size on water permeability of membranes

The water permeability of membranes by the HP, KC and HC models is presented in Fig. 5.4 and Fig. 5.5 as a function of two variables: (1) the pore radius and (2) the surface porosity. For all three models, permeability of membranes increases with pore size squared and porosity as expected, but to slightly varying degrees. In the HP equation, 8τ equals 20 when porosity is 7.2%. Further, 8τ ranges from about 25.6 to 12 for membrane porosities of 1 to 50 percent and from 25.6 to 17.6 for porosities of 1 to 15%, which is the range found in this study. So, as porosity approaches 1, the HP model will underestimate membrane permeability relative to the

KC model and as porosity exceeds 7.2% the HP model will overestimate membrane permeability, again relative to the KC model. In the HC model, the denominator ranges from about 17 to 19 across the range of porosities, which is much closer to the KC model, but overall, it will predict slightly higher permeability than the KC model. From our simulations, in the higher surface porosity range (from 15% to 50%), the permeability of HP model attains $1.62 \times 10^{-15} \text{ m}^2$ with the largest pore radius at $0.2 \text{ } \mu\text{m}$, whereas the KC and HC models produced permeabilities of $1.00 \times 10^{-15} \text{ m}^2$ and $1.05 \times 10^{-15} \text{ m}^2$, respectively. However, for surface porosity in the range of 0 to 15%, which is well-aligned with the typical surface porosity of UF membranes[34], [38], the simulated permeability of Happel's Cell model closely resembles that of Hagen-Poiseuille pore-flow model at $3.39 \times 10^{-16} \text{ m}^2$ and $3.43 \times 10^{-16} \text{ m}^2$, respectively, with both slightly higher than the Kozeny-Carman pore-flow model ($3.00 \times 10^{-16} \text{ m}^2$).

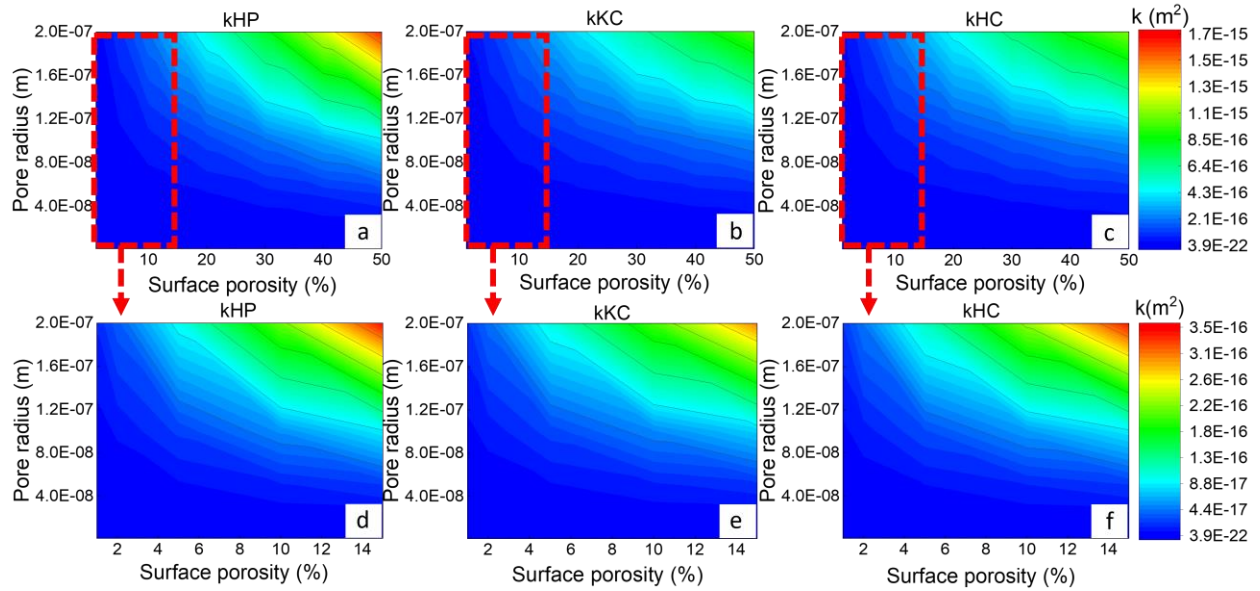


Figure 5.4. 2D contour plots showing the effects of pore radius (m) and surface porosity (%) on the permeability of three hydrodynamic models. Hagen-Poiseuille model at (a) 0-50% and (d) 0-15% surface porosity. Kozeny-Carman model at (b) 0-50% and (e) 0-15% surface porosity. Happel's Cell model at (c) 0-50% and (f) 0-15% surface porosity.

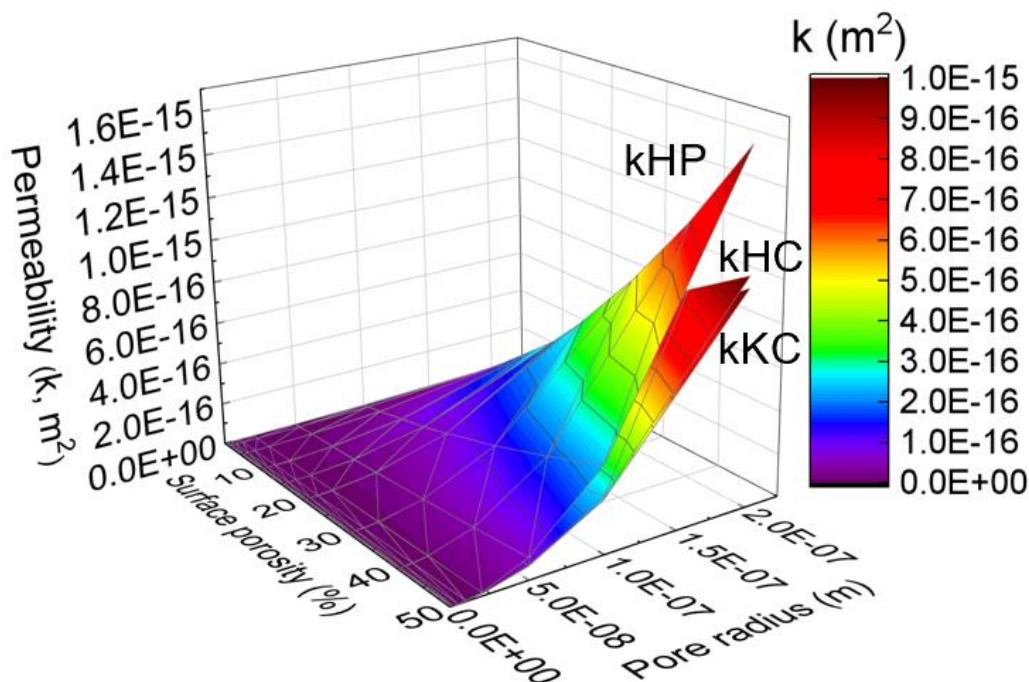


Figure 5.5. The 3D response surface: effects of pore radius (m) and surface porosity (%) on the permeability of three hydrodynamic models (Hagen-Poiseuille pore-flow model, Kozeny-Carman pore-flow model, and Happel's Cell model).

5.4.2 Characterizations of MF and UF membranes

In Fig. 5.6 and Fig. 5.7, it is clear that as the polymer concentration increased from 12% to 20%, both the mean pore size and surface porosity of PSU, PES, and PVDF membranes declined (Table 5.2). All pore size distribution (PSD) curves in Fig. 5.8 exhibit a reasonably “normal distribution” with minimal presence of excessively large or small pores. As the polymer concentration declines from 20% to 12%, the primary peaks of the distribution curves, indicative of the mean pore size of PSU, PES, and PVDF membranes, shift towards larger values: from 7.7 nm, 8.9 nm, and 6.8 nm to 23.1 nm, 18 nm, and 29.3 nm, respectively. Additionally, the commercial PS20 UF membrane, displays the smallest mean pore radius at 5 nm, but a relatively

high surface porosity (5.1%). Conversely, the commercial PVDF MF membrane had the largest mean pore size and surface porosity.

The skin layer thickness is effectively the pore-length; the water permeability is inversely proportional to the pore-length times the tortuosity factor [39]. Cross-sectional SEM images of membranes were captured at magnification of 30,000 X and post-processed by the ImageJ software to precisely define and measure thickness of the skin layer. Binary black and white images help illustrate the change in body porosity. We designate the skin layer thickness as the point at which the cross-sectional body porosity increases by 0.1% to provide an objective means for determining the end of the skin layer. (Fig. 5.6p-t and Fig. 5.7s-x). In Table 5.2, for a fixed polymer concentration of 12%, the skin layer thickness of membranes increased in the order of $\text{PSU} < \text{PES} < \text{PVDF}$, where the PVDF membrane had the thickest skin layer of $1.13\ \mu\text{m}$, while PSU had the thinnest skin layer at $0.33\ \mu\text{m}$. While the pore size and porosity clearly scaled with polymer concentration, the skin layer thickness did not show a clear trend.

Membrane body morphology and thickness (without fabric) were captured by cross-sectional SEM at lower magnification (3,000X). Fig. 5.9 demonstrates a positive correlation between increasing polymer concentration and the overall thickness of the membrane. Additionally, compared to the spongy-like structure of PSU membranes, the finger-like structure imparts varying degrees of void space within the PES and PVDF membranes. Consequently, with fixed polymer concentrations, the body thickness increases in the order of $\text{PSU} < \text{PVDF} < \text{PES}$. Moreover, PS20 exhibits a comparable dense sponge-like morphology to the hand-cast PSU membranes with higher polymer concentration, albeit with a skin layer thickness approximately tripled ($0.61\ \mu\text{m}$). In contrast, the commercial PVDF membrane presents a skin

layer resembling that of the hand-cast 12% PVDF membrane (1.2 μm), characterized by a distinct finger-like structure that imparts the thickest body layer.

The dry-to-wet conversion factor was obtained by conducting water uptake and membrane swelling measurements, which allows one to calculate the porosity, pore size, and skin layer thickness of wet membranes from dry membrane characterizations like SEM. Several studies have proved that the porosity of fully wetted polymeric membranes increases because the membranes swell by about 7 to 12% in water [40,41]. Our findings indicate that for PSU membrane, the extent of membrane swelling decreases (from 15% to 10%) with increasing polymer concentration. Likewise, a comparable pattern was observed in PES and PVDF membranes, wherein the swelling percentages decreased from 20% and 9% to 16% and 6%, respectively (Table 5.2). In addition, the swelling rates of PS20 and PVDF 0.1 membranes closely approximate those of the hand-cast 20% PSU membrane and 12% PVDF membrane (9.8% vs. 11.1% and 8.7% vs. 9.8%, respectively). We were unable separate the backing fabric from the commercial membrane materials (PS20 and PVDF 0.1 in this study), so we used the overall membrane density and thickness (including the fabric) for determining the water uptake and dry-to-wet swelling ratio.

At a fixed polymer concentration of 20%, the PES membrane was the most hydrophilic with a contact angle of 72° , followed by the PSU (77°) and PVDF (81°) membranes – both also at 20% (Table 5.2). Additionally, Fig. 5.8l shows the contact angle of membranes fabricated from identical polymers increases with increase in surface porosity, attributed to the presence of air (contact angle = 180°) within the pores [34].

Table 5.2: Properties of the MF and UF membranes

Membrane	Mean pore radius (nm)	Surface porosity (%)	Skin layer thickness (μm)	Total thickness* (μm)	$\frac{\varepsilon_{tot,dry}}{\varepsilon_{tot,wet}}$	Swelling ratio	Contact angle (o)
12% PSU	23.1 ± 1.2	7.6 ± 0.2	0.33 ± 0.05	34.1 ± 2.2	0.87	1.15	85.8 ± 1.2
14% PSU	13.7 ± 0.7	5.7 ± 0.3	0.19 ± 0.03	34.9 ± 3.0	0.88	1.14	83.5 ± 0.9
16% PSU	12.8 ± 1.1	3.9 ± 0.2	0.20 ± 0.03	38.5 ± 3.5	0.91	1.10	80.4 ± 1.5
18% PSU	9.1 ± 0.5	2.2 ± 0.2	0.27 ± 0.06	40.6 ± 1.3	0.90	1.11	78.2 ± 0.4
20% PSU	7.7 ± 0.7	1.2 ± 0.1	0.23 ± 0.04	42.7 ± 1.8	0.91	1.10	76.5 ± 0.7
12% PES	18 ± 1.1	8.2 ± 0.5	0.35 ± 0.03	37.6 ± 1.7	0.83	1.20	79.1 ± 1.0
20% PES	8.9 ± 1.0	1.7 ± 0.3	0.40 ± 0.05	69.5 ± 2.1	0.86	1.16	72.3 ± 1.7
12% PVDF	29.3 ± 1.5	13.3 ± 0.7	1.13 ± 0.12	35.1 ± 2.5	0.92	1.09	95.5 ± 1.5
20% PVDF	6.8 ± 0.9	0.8 ± 0.1	0.74 ± 0.08	53.8 ± 2.9	0.94	1.06	81.4 ± 1.2
PS 20	5.0 ± 0.8	5.1 ± 0.1	0.61 ± 0.05	41.3 ± 2.1	0.91	1.10	80.4 ± 0.4
PVDF 0.1 μm	31.1 ± 1.7	14.1 ± 0.6	1.2 ± 0.14	50.7 ± 2.4	0.92	1.09	98.6 ± 1.3

* Polymer layers only, not including PP fabric.

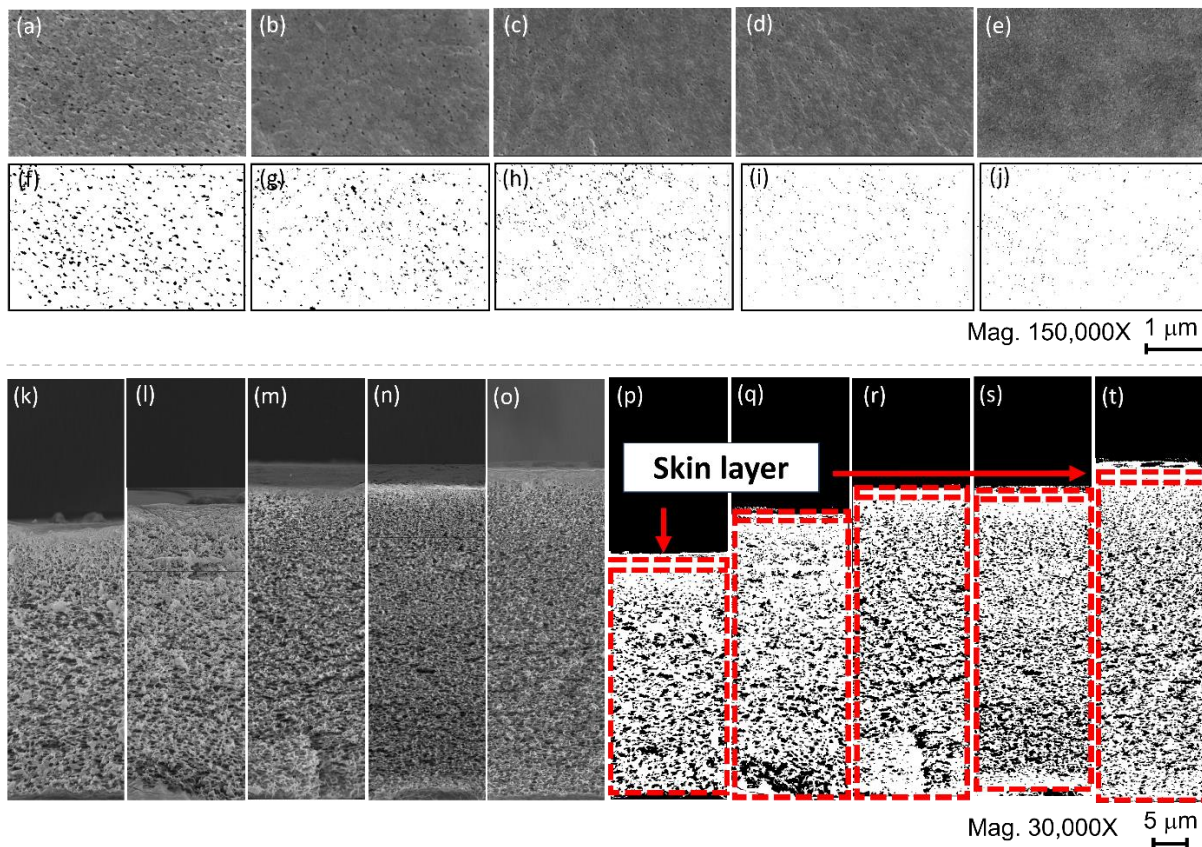


Figure 5.6. Surfacial and cross-sectional SEM images of PSU membranes with post-imaging analysis. (a-e) surfacial SEM images of 12-20% PSU membranes. (f-j) post-processed images of 12-20% PSU membranes. (k-o) cross-sectional SEM images of 12-20% PSU membranes at higher magnification (30,000X). (p-t) post-processed cross-sectional images of 12-20% PSU membranes.

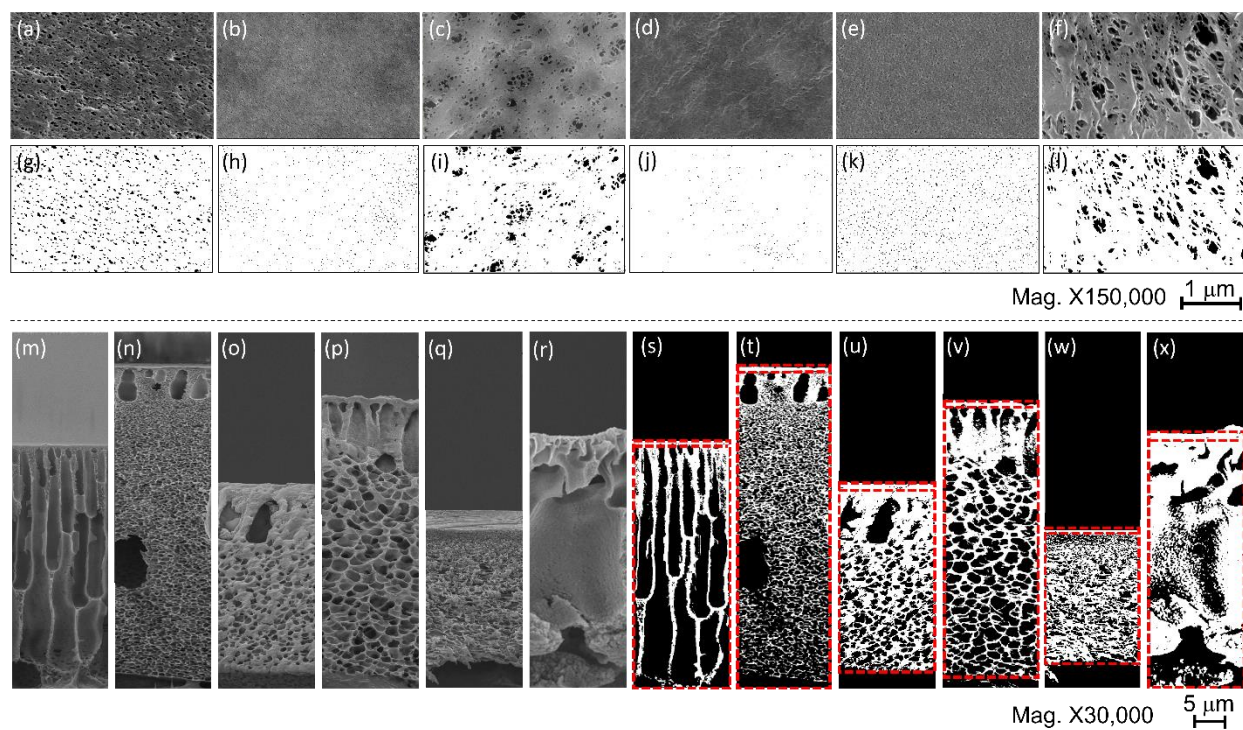


Figure 5.7. Surficial and cross-sectional (at higher magnification, 30,000X) SEM images of PES, PVDF, and commercial membranes with post-imaging analysis. (a, g, m, s) 12% PES. (b, h, n, t) 20% PES. (c, i, o, u) 12% PVDF. (d, j, p, v) 20% PVDF. (e, k, q, v) PS 20. (f, l, r, x) PVDF 0.1 mm.

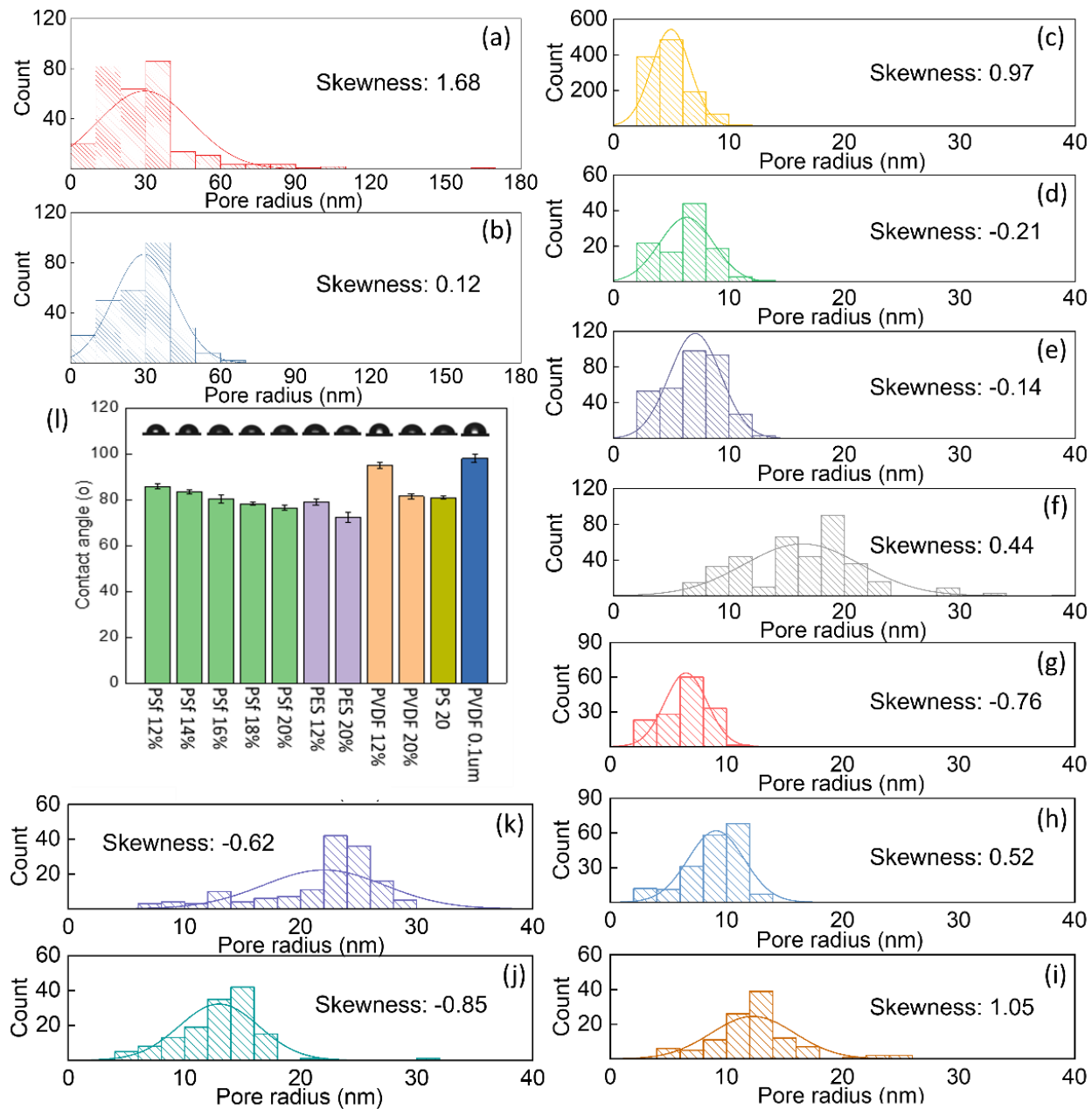


Figure 5.8. Pore size distribution of MF and UF membranes. (a) PVDF 0.1 mm. (b) 12% PVDF. (c) PS 20. (d) 20% PVDF. (e) 20% PES. (f) 12% PES. (g-k) 12%-20% PSU. And contact angle of MF and UF membranes (l).

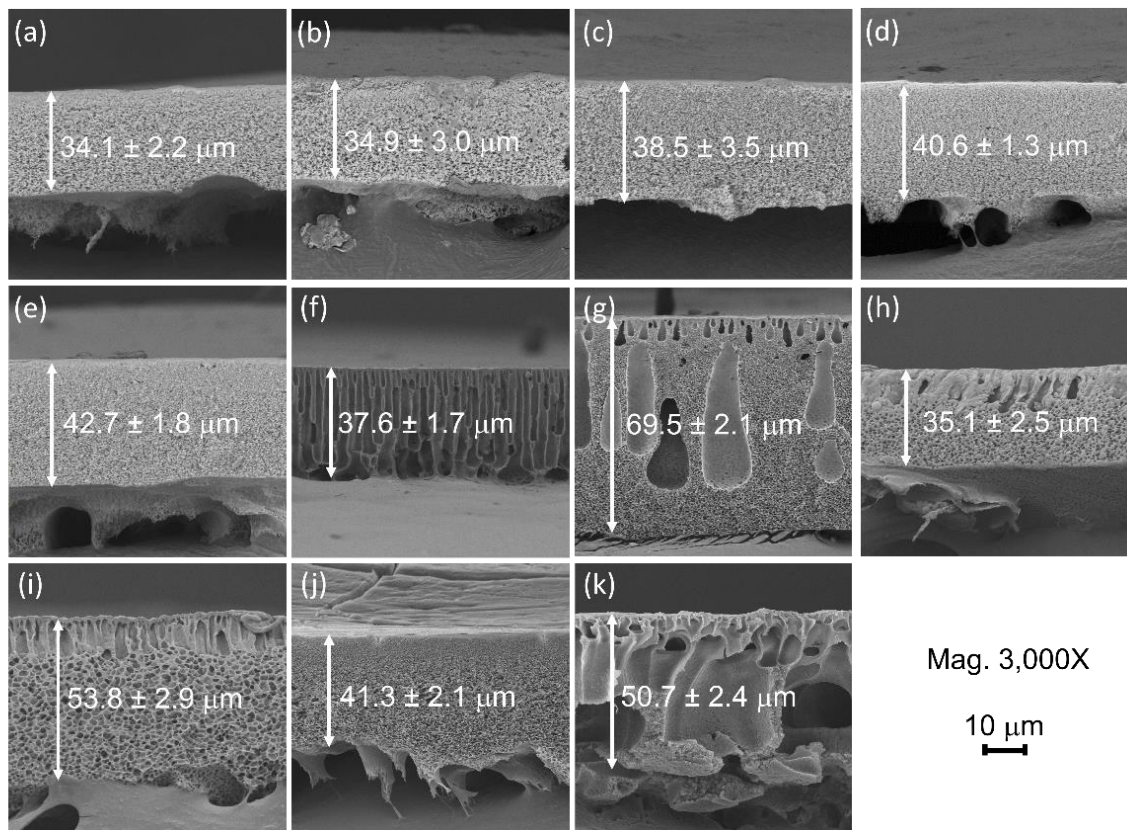


Figure 5.9. Membrane (without PP fabric) cross-sectional SEM images at lower magnification (3,000X). (a-e) 12-20% PSU. (f) 12% PES. (g) 20% PES. (h) 12% PVDF. (i) 20% PVDF. (j) PS 20. (k) PVDF 0.1 mm.

5.4.3 Comparative analysis of hydrodynamic and mechanical sieving models

We compared model-predicted water permeance values using dry (Fig. 5.10a) and wet (Fig. 5.10b) (swelling-corrected) membrane characterizations against experimental permeance values determined from filtration experiments (Table 5.3). Also, the slopes of all model-predicted permeance values are provided in Table 5.4. The dashed grey line in Fig. 5.10(a/b) represents the line of symmetry. In Fig. 5.10a, the Hagen-Poiseuille, the Kozeny-Carman, and the Happel's Cell models underestimate the experimental water permeance on average by about 25%, 30%, and 21%, respectively, based on the dry membrane characteristics. In the lower water

permeance range (0 to 200 lmh/bar), the slope of the dry membrane predictions by the HP model is 0.6082 ($R^2 = 0.9956$); in the higher water permeance range (200 to 3,500 lmh/bar), the slope was 0.7497 ($R^2 = 0.9914$). In contrast, the KC model produced slopes of 0.7607 ($R^2 = 0.9919$) and 0.7007 ($R^2 = 0.9985$) in the same low and high permeance ranges, respectively. The HC model yielded slopes of 0.8726 ($R^2 = 0.9987$) and 0.7866 ($R^2 = 0.9987$) in the low and high permeance ranges, respectively.

In Fig. 5.10b, model predictions using the wet membrane (dry-to-wet swelling corrected) characterization data were much closer to the line of symmetry. The deviation from experimental permeance data was reduced to 15%, 21% and 11% for the HP, KC, and HC models, respectively. The HP model deviated from experimental data by about 30% in the low water permeance range; however, it gave much better results in the high water permeance range (slope of 0.8454, $R^2 = 0.9951$). The KC model diverges from experimental data by 13% and 21% in the low and high water permeance ranges, respectively, which was opposite the trend of the HP model. One might conclude from these results that the KC model is a better fit for tighter UF membranes ($L_p < 200$ lmh/bar), whereas the HP model is a better fit for looser MF membranes ($L_p > 200$ lmh/bar). That said, the HC model fits the entire range as well as the high and low ranges better than both HP and KC. The slopes of the swelling-corrected predictions by the HC model at high and low water permeance were 0.8872 ($R^2=0.9988$) and 0.9811 ($R^2=0.9889$), respectively, which was the strongest correlation of the three models. Given that none of these models exactly describes the pre structure of a phase inverted polymeric membrane, which is neither a twisted pipe nor an assemblage of spherical particles, it is surprising that they produce such reasonable agreement with experimental data.

Fig. 5.10c shows the increase in solute rejection with polymer concentration, which is expected for any phase inverted polymer. Specifically, the selectivity of the PSU membranes for 100 kDa PEG increases from 32.4% to 97.3% as the concentration increases from 12% to 20% (Table 5.5). Moreover, the 12 and 20 wt.% PES and PVDF membranes exhibited similar behavior with 100 kDa PEG rejection increasing from 45.8% to 93.8% and from 20.2% to 98.5%, respectively. We note that the commercial PS20 and PVDF 0.1 mm membrane rejections were virtually identical to the hand-cast 20% PSU and PVDF 12% membranes, respectively. Model predicted rejections derived from “dry” mean pore sizes consistently overestimated solute rejection (on average by about 10%). The wet membrane swelling factor increased the membrane pore size, skin layer thickness and porosity values, which brought the predicted solute rejections very closely in line with experimentally measured rejections.

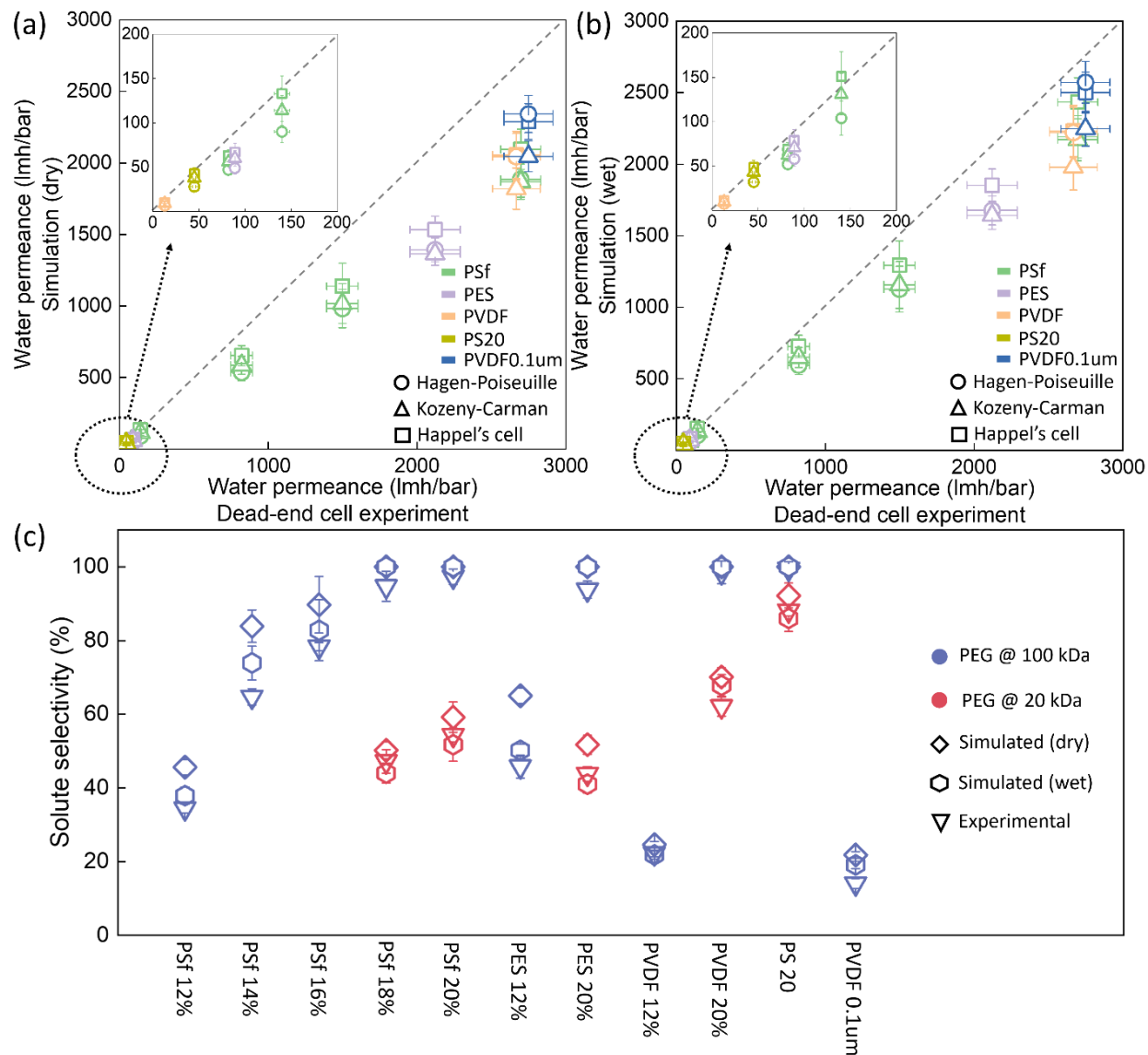


Figure 5.10. Comparison of the water permeance of membrane obtained by the dead-end filtration test and three hydrodynamic models under (a) dry and (b) wet conditions, and (c) comparison of model predicted and experimentally measured solute rejections.

Table 5.3. Water permeance of MF and UF membranes

Membrane	Water permeance (dry, lmh/bar)			Water permeance (wet, lmh/bar)			Water permeance (lmh/bar)
	HC**	HP***	KC****	HC**	HP***	KC****	Experimental
12% PSU	2096	1886	1869	2435	2191	2171	2697
14% PSU	1139	982	1017	1294	1126	1156	1498
16% PSU	653	536	585	726	595	649	821
18% PSU	133	90	114	151	104	131	140
20% PSU	63	47	56	69	52	62	82
20% PES	67	49	60	79	58	71	89
12% PES	1534	1393	1365	1853	1677	1643	2021
20% PVDF	10	7	9	11	8	10	13
12% PVDF	2055	2044	1820	2233	2221	1979	2667
PS 20*	43	28	38	48	32	43	45
PVDF 0.1 μm^*	2289	2342	2046	2503	2573	2248	2749

* Commercial type membranes.

**HC: Happel's Cell model.

***HP: Hagen-Poiseuille pore-flow model.

****KC: Kozeny-Carman pore-flow model.

Table 5.4. Linear regressions for three hydrodynamic models and experimental data

Water permeance (lmh/bar)	Condition	Hydrodynamic model					
		Hagen-Poiseuille		Kozeny-Carman		Happel's Cell	
		Slope	R ²	Slope	R ²	Slope	R ²
0 to 200	dry	0.6082	0.9956	0.7607	0.9919	0.8726	0.9987
	wet	0.7004	0.9952	0.8728	0.9918	0.9811	0.9889
200 to 3,500	dry	0.7497	0.9914	0.7007	0.9985	0.7866	0.9987
	wet	0.8454	0.9951	0.7911	0.9985	0.8872	0.9988
0 to 3,500	dry	0.7486	0.9914	0.7007	0.9985	0.7867	0.9987
	wet	0.8452	0.9951	0.7912	0.9985	0.8873	0.9987

Table 5.5. Solute selectivity of MF and UF membranes

Membrane	Solute selectivity (100 kDa PEG, %)			Solute selectivity (20 kDa PEG, %)		
	Simulated**		Experimental	Simulated**		Experimental
	dry	wet		dry	wet	
12% PSU	47.6	39.9	32.4	-	-	-
14% PSU	83.9	74.9	64.7	-	-	-
16% PSU	89.7	84.8	78.3	-	-	-
18% PSU	100	100	94.7	53.2	43	46.2
20% PSU	100	100	97.3	59.2	50.7	52.3
12% PES	65	52.2	45.8	-	-	-
20% PES	100	100	93.8	53.7	40	42.8
12% PVDF	24.6	22.8	20.2	-	-	-
20% PVDF	100	100	98.5	72.1	68.8	60.1
PS 20*	100	100	99.4	93.2	88	85.1
PVDF 0.1 μm^*	23.8	20.1	12	-	-	-

* Commercial type membranes.

** Simulated by the mechanical sieving model

5.5 Conclusions

In this chapter, we investigated classical hydrodynamic models of membrane permeability and solute rejection. A range of porous polymeric membranes were fabricated from three different polymers and different polymer concentrations to produce a wide range of mean pore sizes and surface porosities. As polymer concentration increased, membrane thickness increased, while body porosity, surface porosity and mean pore size decreased, but no clear trend in skin layer thickness; thus, water permeability decreased, and solute rejection increased. The hydrodynamic models were used to predict (without any fitting parameters) the water permeability and solute rejection of all membranes. Three hydrodynamic models of water permeability and a mechanical sieving model of solute rejection all agreed very well with experimentally measured values, but a few key take-aways stood out. First, when characterizing

membrane pore size and porosity, one must apply the “dry-to-wet membrane swelling ratio” to estimates derived from dry membrane characterizations (e.g., SEM); this reproduces a membrane’s fully wetted and swollen state, which increases pore size, porosity and skin layer thickness. Hence, increases permeability and decreases rejection. Second, Happel’s Cell model agrees best with experimental permeability data ($\sim 10\%$ deviation) across the entire spectrum of water permeances considered (from 0 to 3,500 lmh/bar), while the Hagen-Poiseuille and Kozeny-Carman models were less accurate, deviating by 15% and 21%, respectively. Finally, we also considered uncharged tracer solutes, so Ferry’s steric exclusion model worked reasonably well to predict rejections. However, for charged solutes one may need to consider Donnan and Borne exclusion as well.

5.6 References

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Chapter 6 Tailoring Pore Size Distribution of Phase Inverted Porous Polymeric Membranes

6.1 Introduction

In applications of low-pressure membrane filtration, the primary performance indicators are the rejection of the target solute and the permeability of water [1,2]. In Chapter 2, the computational fluid dynamics (CFD) model and other classic simulations were investigated to analyze and elucidate the influence of the shape of membrane pore size distribution on the performance of the membranes, emphasizing the significance of cutting down the right tail of the pore size distribution curve, specifically by decreasing the portion of larger pores, in order to enhance the selectivity of the membrane.

Chapter 3 highlighted the critical role of sample preparation and imaging parameters on SEM imaging of polymeric membranes. We established that that a platinum coating thickness of 3 nm optimizes scanning electron microscopy (SEM) imaging of microfiltration and ultrafiltration membranes by ensuring sufficient conductivity without compromising surface detail or porosity analysis. Additionally, an accelerating voltage of 10 kV was found to yield high-resolution images while preserving the integrity of the polymer structure. Furthermore, we outlined preferred cross-sectioning techniques: indirect freeze-fracture for situations where the fabric layer is not analytically significant, and direct freeze-fracture for cases where the morphology of the fabric layer is of interest, which offered comprehensive guidance and standardized procedures for membrane characterizations via scanning electron microscopy (SEM). Building on this foundation, Chapter 4 further established and verified a novel method

for quantifying surface porosity of porous membranes by integrating SEM characterization results with the data derived from contact angle (CA) measurements. More importantly, this chapter proposed the dry-to-wet conversion factor, identified as a crucial parameter in the performance simulations in subsequent chapters, by measuring the water uptake of membranes.

Chapter 5 investigated classical hydrodynamic models of membrane permeability and solute rejection. Our result indicated that the Happel's Cell model agrees best with experimental permeability data across the entire spectrum of water permeances considered (from 0 to 3,500 lmh/bar), while the Hagen-Poiseuille and Kozeny-Carman models were less accurate. Additionally, this chapter also proved that the Ferry's steric exclusion model worked reasonably well to predict rejections of uncharged tracer solutes. So far, the characterization methods and theoretical simulations for membrane pore size distribution and membrane performance have been comprehensively investigated.

In this chapter, a series of porous membranes are fabricated via nonsolvent induced phase separation (NIPS) with different recipe and conditions to tailor pore size and pore size distribution of membranes. We systematically evaluate the separation performance and water permeance of membranes. Surface and body morphology (surface porosity, mean pore size, pore size distribution, body structure, and skin layer thickness) of membrane samples are captured by image analysis of SEM images. Finally, we conduct a comprehensive analysis of each recipe aimed at manipulating membrane pore size and pore size distribution, drawing from both membrane performance, herein water permeance and solute rejection, and intuitive characterization outcomes.

6.2 Materials and methods

6.2.1 Materials

Polysulfone (PSU, Ultrason S) was generously supplied by BASF (Charlotte, North Carolina, USA). Chlorinated polyvinyl chloride (CPVC) was kindly provided by Lubrizol® Corporation. Nano-bubble water (NBW) was kindly provided by Moleaer Inc (Carson, California, USA). N, N-dimethylformamide (DMF, ACS reagent grade), N-Methyl-2-pyrrolidone (NMP, ACS reagent grade), polyethylene glycol (PEG, 100 kDa, powder), polyethylene glycol (PEG, 40 kDa, powder) and polyvinylpyrrolidone (PVP, 40 kDa, powder) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA) and used as received. Polyester (PET, 05TH-80W) nonwoven fabric was kindly provided by Hirose Paper Mfg Co., Ltd. Laboratory ultra-pure water (UPW) (Milli-Q Synthesis, Millipore, USA) was used in all experiments. All chemicals were used without any further purification.

6.2.2 Preparation of flat-sheet membranes

General procedure: Flat-sheet ultrafiltration membranes were prepared by non-solvent induced phase separation (NIPS)[3,4]. Casting solutions of were prepared by mixing polymers in the organic solvent at 75 °C with continuously stirring at 250 rpm using an All-Purpose Mixer (MXD Process, Jeffersonville, Indiana, USA) until the solution became homogeneous. The dope solutions were cooled to ambient temperature (23 °C) and stored in the desiccator overnight for degassing. Thin polymer films were cast at room temperature (23 °C) on the fabric by a casting knife (Gardco Co., Pompano Beach, Florida, USA) set at blade height of 200 µm. The cast

membrane was then immersed in a coagulation bath for 10 min and then washed with the UPW (20 °C) five times to completely remove the residual solvents. The time interval between the casting process and immersion was 5 seconds. Solidified membranes were stored in UPW at room temperature (23 °C) prior to testing and characterization.

Table 6.1 Membrane composition and preparation conditions.

Polymer		Solvent		Pore forming agent		Coagulation bath				Time interval (s)
Type	Conc (wt%)	Type	Conc (wt%)	Type	Conc (wt%)	Type	Temp (C)	Additive		
								Type	Conc (wt%)	
CPVC	16	DMF	84	-	-	UPW	20	-	-	5
			83.2	PEG @40kDa	0.8			-	-	
			82.4		1.6			-	-	
			80.8		3.2			-	-	
			83.2		0.8			-	-	
			82.4	PVP @40kDa	1.6			-	-	
			80.8		3.2			-	-	
				-	-		5	-	-	10
				-	-		10	-	-	
				-	-		35	-	-	
				-	-			-	-	
				-	-			-	-	
				-	-			-	-	
				-	-			-	-	
				84	-		-		2	5
				-	-			DMF	4	
				-	-				6	
				-	-				5	
				-	-			NaCl	10	
				-	-				5	
				-	-			Na2CO3	10	

Table 6.1 Continued. Membrane composition and preparation conditions.

Polymer		Solvent		Pore forming agent		Coagulation bath				Time interval (s)
Type	Conc (wt%)	Type	Conc (wt%)	Type	Conc (wt%)	Type	Temp (C)	Additive		
								Type	Conc (wt%)	
CPVC	16	DMF: NMP @3:1	63+21	-	-	UPW	20	-	-	5
		DMF: NMP @1:1	42+42	-	-			-	-	
		DMF: NMP @1:3	21+63	-	-			-	-	
		NMP	84	-	-			-	-	
				-	-			UPW	-	
PSU	12		88	-	-	NBW	-	-		
				-	-	UPW	-	-		
			86	-	-	NBW	-	-		
	14	DMF		-	-		35	-	-	
			85.3	PVP @40kDa	0.7	UPW		-	-	
			84.6		1.4			-	-	
				-	-		20	IPA	25	
16		84	-	-	NBW	-	-			

6.2.3 Membrane testing and characterizations

Membrane morphology: To determine the morphology of the membrane, surface and cross-section imaging was carried out with a field emission gun scanning electron microscope (Phenom Pharos G2 Desktop FEG-SEM, Thermo Fisher Scientific, Cleveland, OH). For the cross-section observation, membrane samples were fractured by the Indirect-Freeze-Fracture (IFF) method [5]. All the membrane samples were secured on SEM stubs using double-sided carbon tape and sputter-coated (Ion beam sputtering/etching system, South Bay Technology, San Clemente, CA) with platinum for 3nm thickness prior to analysis. Scanning was performed at 10 kV. Top surface images for each membrane sample were taken at magnifications of 150,000 $\times$. Cross-section view images were first taken at magnifications of 3,000 $\times$ to analyze the membrane structure and total thickness of polymer layer. SEM images were analyzed by open-source ImageJ software (v1.8.0) to measure the skin layer thickness, polymer layer thickness, pore radius and surface porosity of membranes. For ImageJ analysis, the SEM images were converted to 8-bit mode to present. Automatic thresholding was then used to convert images to binary (black and white)[6]. Mean pore size was further calculated and plotted from the binary images.

Membrane hydrophilicity: Contact angle measurements were conducted by using a contact angle goniometer (Model: 250, ramé-hart instrument co., Succasunna, NJ). The sessile drop (SD) method was applied to measure the contact angle of the membranes under completely dry conditions [7]. To guarantee statistical integrity, three samples were used for each type of membrane, and contact angle measurements were performed at twelve positions on each sample.

The maximum and minimum values were removed, and the result was obtained by averaging the remaining 10 values.

Pure water permeability of membranes: The pure water flux (PWF, LMH) of the membranes was tested with dead-end filtration apparatus (50 ml, Amicon Stirred Cell) at room temperature (23 °C) using UPW water as the feed. The PWF tests were conducted with a sample diameter of 4.4 cm and a transmembrane pressure of 1.38 bar. All the membrane samples were compacted at 1.38 bar for 1 h to obtain a stable flux before the PWF tests. The PWF was calculated as follows:

$$J = \frac{V}{A_m \times t} \quad (6.1)$$

where the V is the volume of the collected permeate during the operation time.

Separation performance of membranes: The solute rejection was determined using 100 kDa PEG at 1 g/L. Solute concentrations in feed and filtrate were analyzed with TOC-LCPH (total organic carbon) analyzer (Shimadzu Scientific Instruments, USA). The membrane solute rejection was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (6.2)$$

where C_p and C_f are the solute concentrations of the permeate solution and feed solution, respectively. Each type of membrane was tested 3 times to ensure accuracy. The stoke radius of the PEG solute was calculated based on molecular weights as follows [8]:

$$R = 16.73 \times 10^{-3} \times M^{0.557} \quad (6.3)$$

where R is the radius of the PEG (in nanometer). M represents the molecular weight of the particles (in Dalton). The hydrodynamic radius of PVP at 40 kDa was 5.2 nm [9]. The solute rejection (R_s) was estimated from the solute-to-pore size ratio using the mechanical sieving model [10]:

$$R_s = [\lambda(2 - \lambda)]^2 \quad (6.4)$$

where $\lambda = (r_s/r_p)$ is the solute-to-pore size ratio, r_s is solute radius, and r_p is pore radius.

6.3 Results and discussion

6.3.1 Characteristics of CPVC membrane with different temperature of coagulation bath

Fig. 6.1 illustrates how the temperature of coagulation bath affects the characteristics of a membrane's surface, particularly showing that both mean pore size and surface porosity decrease as the temperature decreases. Notably, the contact angle of membranes fabricated from identical polymers (CPVC) increases from 74.9° to 82.0° with increase in surface porosity, attributed to the presence of air (contact angle = 180°) within the pores [7] (Table 6.2). In Fig. 6.2, it is clear that as the temperature decreases from 35 °C to 5 °C, the thickness of the spongy polymer layer diminishes from 50.5 μm to 23.8 μm, implying a densification of the layer, which aligns with the characterization findings of the surface. In addition, in comparison to membranes fabricated at 20 °C, those processed at higher and lower temperatures exhibited diminished skewness values (1.6 vs. 1.3), suggesting a slightly closer shape to a normal distribution of the pore size distribution curve (Fig. 6.2a). Moreover, the increase in membrane surface porosity and mean pore size resulting from elevated temperature of coagulation bath augments water permeance.

However, this increment in pore size concurrently decreases the solute rejection rate, from 78% at 5 °C to 52% at 35 °C.

Table 6.2 Mean pore size, surface porosity, and contact angle of CPVC membranes with different temperature of coagulation bath.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC @ 5 °C	6.1 ± 0.4	0.37 ± 0.08	74.9 ± 0.9
16% CPVC @ 10 °C	6.6 ± 0.2	0.74 ± 0.10	75.6 ± 0.7
16% CPVC @ 20 °C	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC @ 35 °C	9.1 ± 1.2	5.45 ± 0.17	82.0 ± 1.1

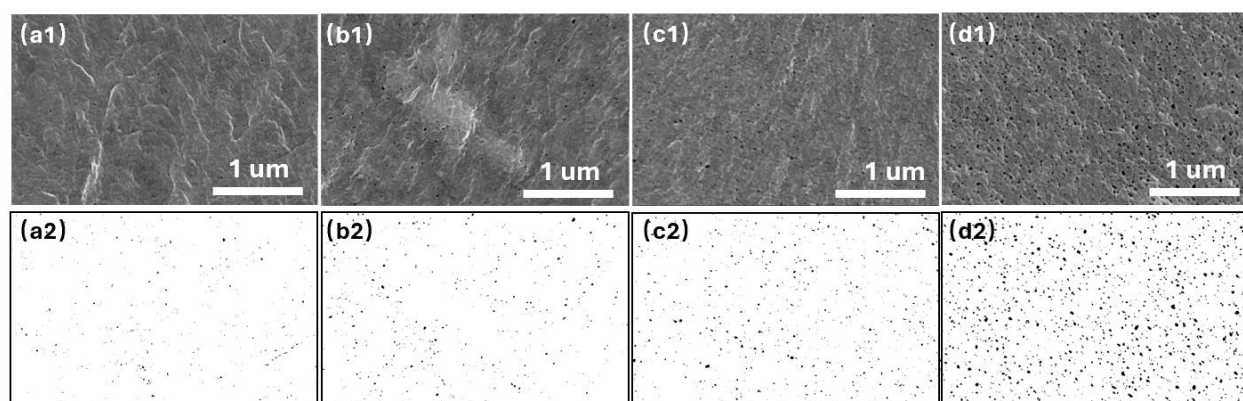


Figure 6.1 Surfacial SEM images and threshold processed images of 16% CPVC membrane with 5 °C (a1, a2), 10 °C (b1, b2), 20 °C (c1, c2), and 35 °C (d1, d2).

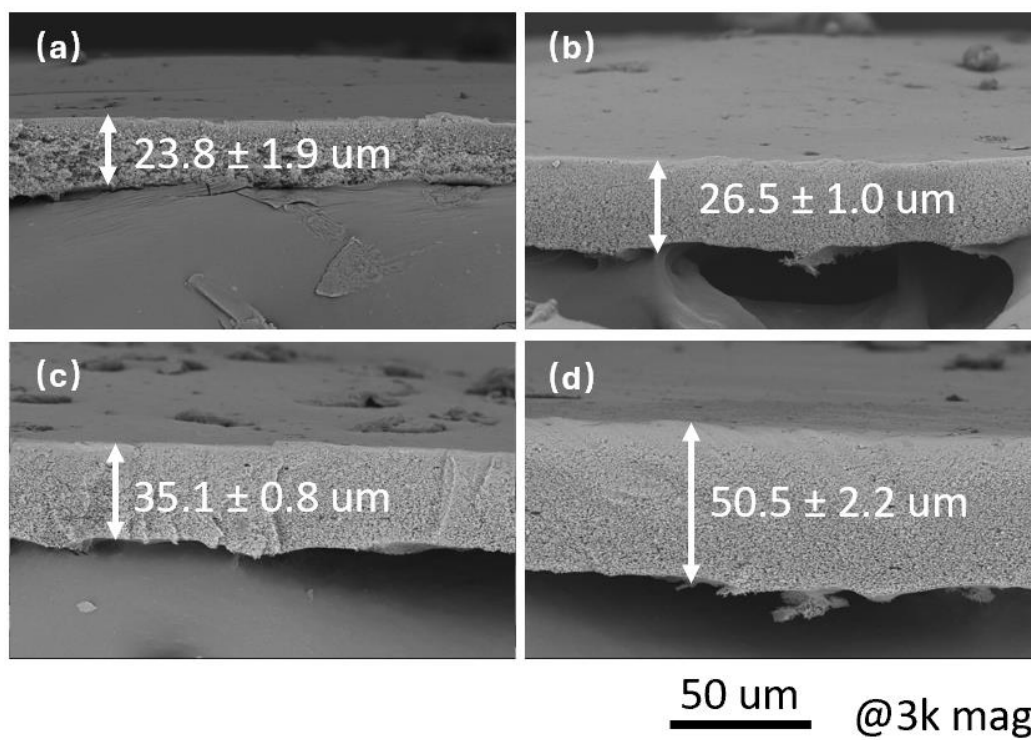


Figure 6.2 Cross-sectional SEM images of 16% CPVC membrane with 5 °C (a), 10 °C (b), 20 °C (c), and 35 °C (d).

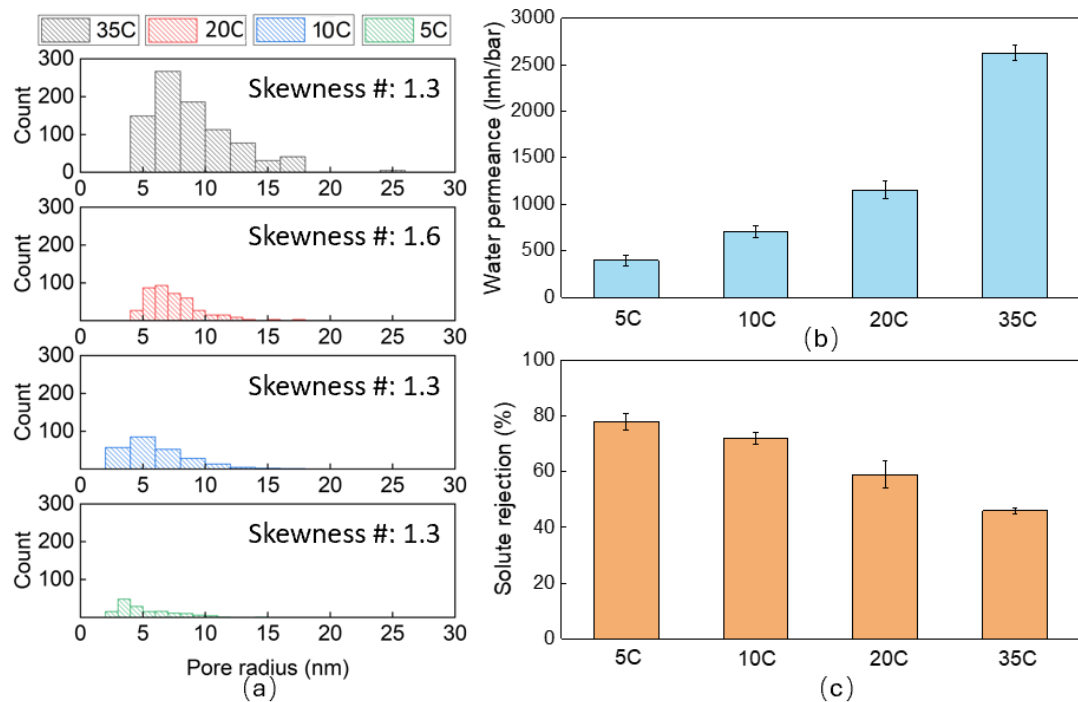


Figure 6.3 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membranes with different temperature of coagulation bath.

Fig. 6.4 delves into the impact of the time intervals between casting and phase inversion process on the membrane fabrication. With the extension of the interval from 5 seconds to 60 seconds, the membrane's surface porosity, mean pore size, and polymer layer thickness decrease from 2.02% and 7.4 nm to 0.68% and 6.1 nm, respectively (Table 6.3). However, the spongy polymer layer thickness increases with the lengthening of the interval time, indicating that longer intervals can yield a membrane with dense surface and porous interior (Fig. 6.5). The results depicted in Fig. 6.6b, c align with the surface characterizations. As interval time increases, water permeance drops while solute selectivity improves due to the decrease in pore size, which highlights the decisive impact of the skin layer on the permeability and selectivity of porous

membranes. Additionally, the skewness number of pore size distributions decreases to varying degrees as the interval time increases (Fig. 6.6a).

Table 6.3 Mean pore size, surface porosity, and contact angle of CPVC membranes with different time interval between casting process and immersing in coagulation bath.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC @ 5 s	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC @ 10 s	7.2 ± 0.4	1.40 ± 0.31	76.0 ± 0.9
16% CPVC @ 30 s	7.0 ± 0.2	0.92 ± 0.14	74.8 ± 0.6
16% CPVC @ 60 s	6.1 ± 0.5	0.68 ± 0.09	74.0 ± 1.0

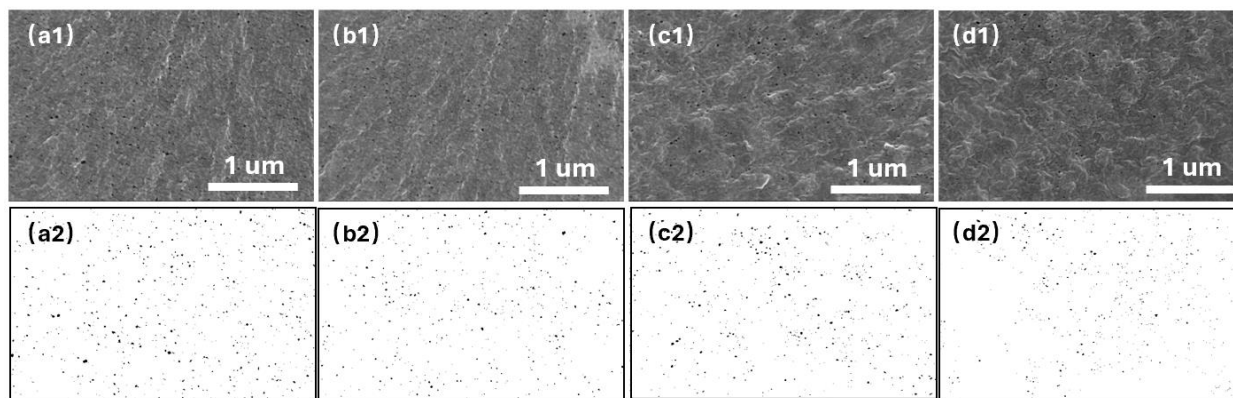


Figure 6.4 Surfacial SEM images and threshold processed images of 16% CPVC membrane with different time interval between casting process and immersing in coagulation bath: 5s (a1, a2), 10s (b1, b2), 30s (c1, c2), and 60s (d1, d2).

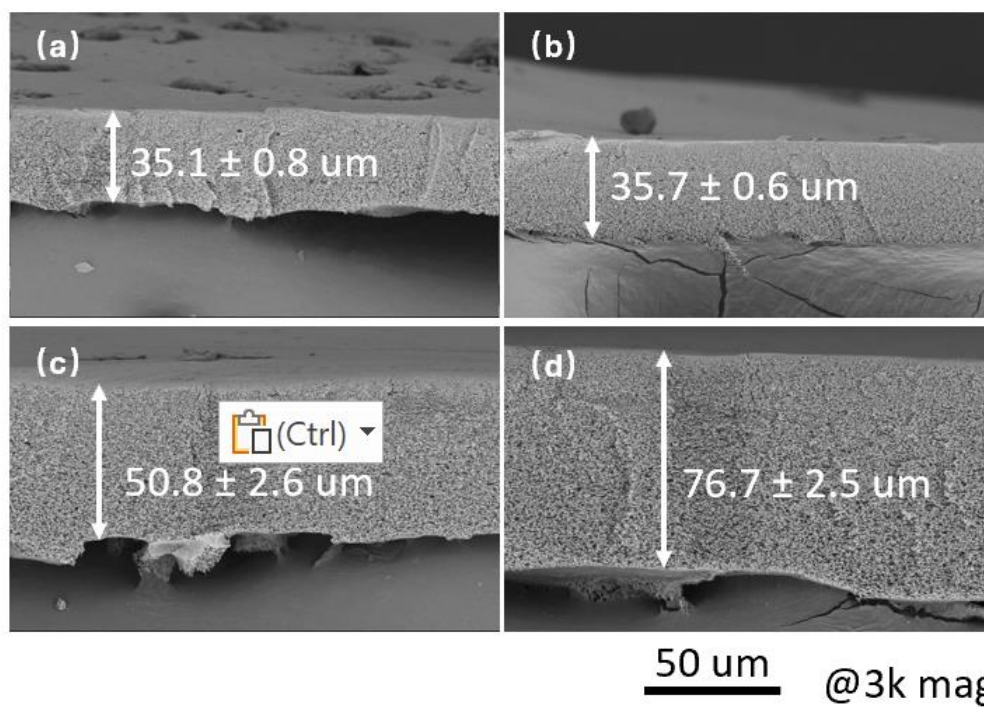


Figure 6.5 Cross-sectional SEM images of 16% CPVC membrane with different time interval between casting process and immersing in coagulation bath: 5s (a), 10s (b), 30s (c) ,and 60s (d).

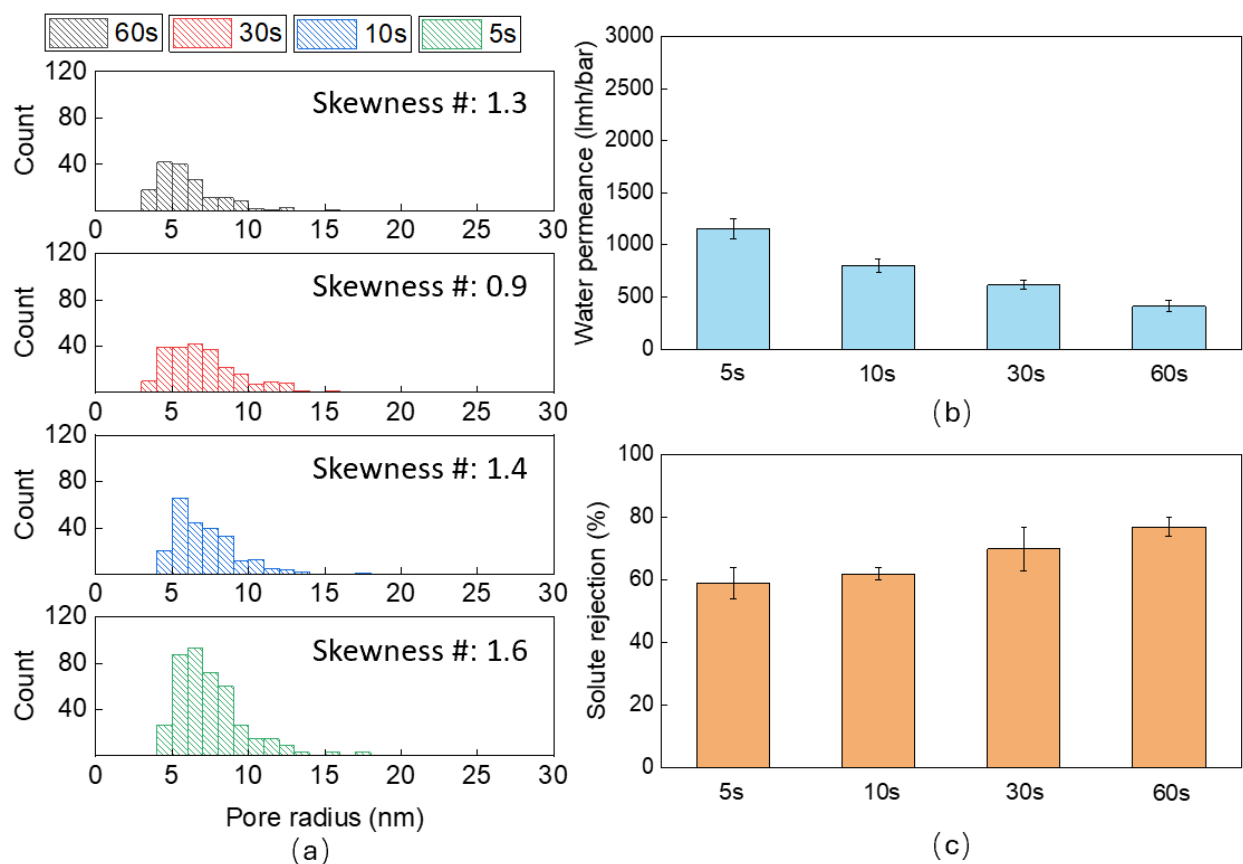


Figure 6.6 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with different time interval between casting process and immersing in coagulation bath.

Fig. 6.7 reveals the effect of using PEG and PVP as pore formers on the membrane surface morphology. Compared to the membrane with no additives, the addition of 0.8% PEG and PVP significantly increased the number of pores, thereby enhancing the membrane surface porosity from 2.02% to 2.89% and 3.48%, respectively (Table 6.4). However, when the concentration of pore formers increases to 1.6%, the pore formers start to aggregate. The black and white images processed by the ImageJ software clearly exhibit a significant reduction in the number of pores, along with a decrease in surface porosity. Additionally, larger black dots appear in the images, representing larger pores, which leads to an increase in the mean pore size. As the concentration

of pore formers goes up to 3.2%, the emergence of the extremely large pores contributes to an additional increase in the mean size of the pores. Meanwhile, the continued reduction in pore count accounts for the further decline in surface porosity.

The cross-sectional SEM images from Fig. 6.8 indicate that the addition of pore forming agents, herein PEG and PVP, has fundamentally changed the structure of the membrane body, transforming the original spongy structure into a fully finger-like structure. The presence of larger macrovoids, characteristic of finger-like structures, results in an increased thickness of polymer layer.

Fig. 6.9a and Fig. 6.10a intuitively demonstrates the impact of different concentrations of pore formers, herein PEG and PVP @40kDa, on membrane pore size and pore size distribution. Compared to the membrane without additives, which has the pore size concentrated between 5-9 nm, the use of 0.8% PEG and PVP as pore formers doesn't significantly alter the distribution curve, except for increasing the number of pores with radii of 4-8 nm and eliminated pores with radii greater than 15 nm, which truncating the right tail of the distribution curve. The increase in both water flux and solute rejection rate further indicates that appropriate amounts of PEG and PVP as pore formers can improve the performance of membranes. However, excessively high concentrations (1.6% and 3.2%) of PEG and PVP tend to aggregate in the dope solution. Although this also enhances water permeance, the resulting pores with radius of 17-25 nm significantly extend the right tail of the distribution curves and compromise the selectivity of membranes (Fig. 6.9b and Fig. 6.10b).

Table 6.4 Mean pore size, surface porosity, and contact angle of CPVC membranes 16% CPVC membrane with pore forming agents.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC with no pore former	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC with 0.8% PEG*	6.9 ± 0.3	2.89 ± 0.14	78.5 ± 1.1
16% CPVC with 1.6% PEG*	7.8 ± 0.4	2.78 ± 0.17	77.6 ± 0.8
16% CPVC with 3.2% PEG*	8.5 ± 0.4	3.86 ± 0.21	80.0 ± 1.0
16% CPVC with 0.8% PVP**	6.8 ± 0.5	3.48 ± 0.16	78.2 ± 0.5
16% CPVC with 1.6% PVP**	7.2 ± 0.2	3.18 ± 0.27	77.3 ± 0.3
16% CPVC with 3.2% PVP**	9.1 ± 0.5	3.07 ± 0.29	77.3 ± 0.7

* PEG @ 40kDa; ** PVP @ 40kDa

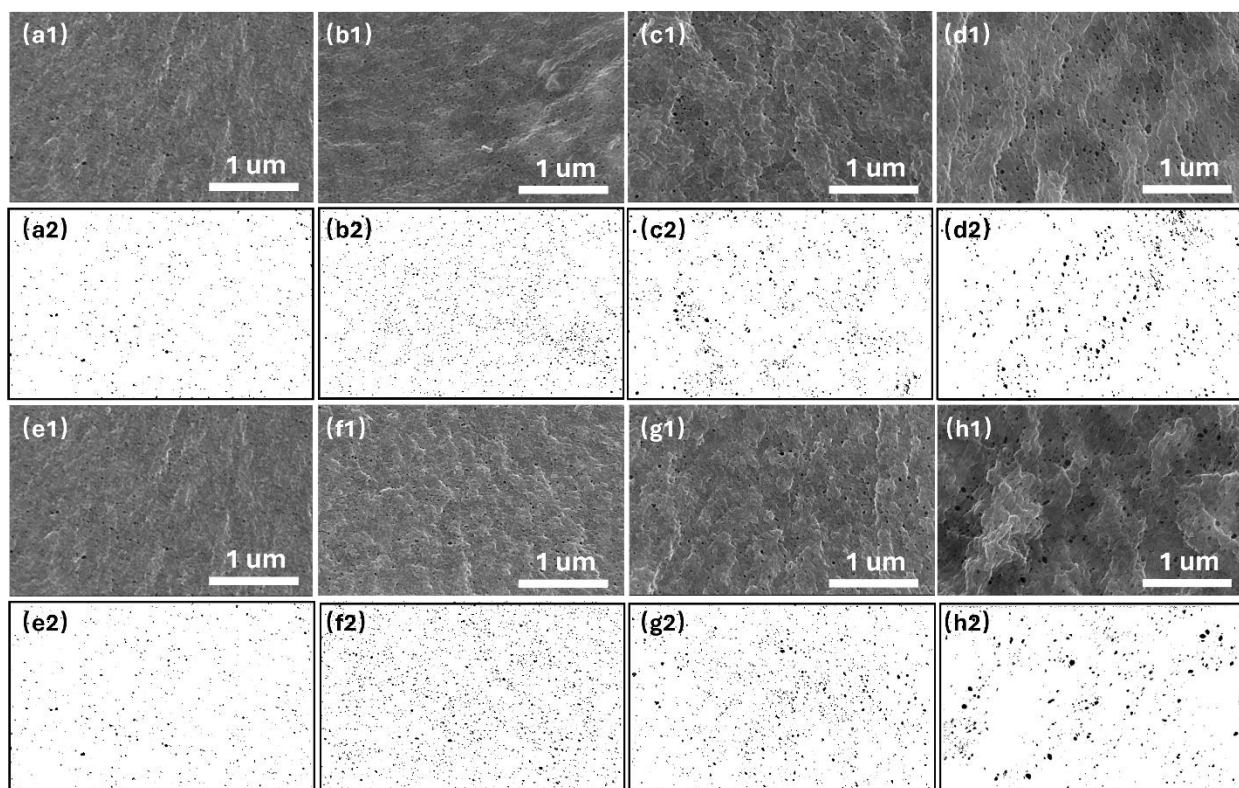


Figure 6.7 Surficial SEM images and threshold processed images of 16% CPVC membrane with pore forming agents: 0%, 0.8%, 1.6%, and 3.2% PEG @ 40kDa (a1-d1 and a2-d2, respectively), 0%, 0.8%, 1.6%, and 3.2% PVP @ 40kDa (e1-h1 and e2-h2, respectively).

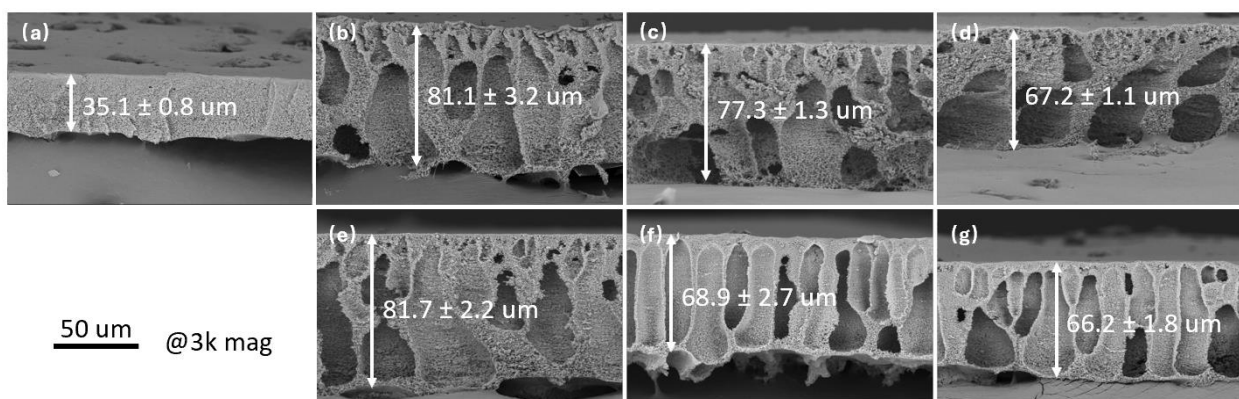


Figure 6.8 Cross-sectional SEM images of 16% CPVC membrane with pore forming agents: no pore former (a), 0.8%, 1.6%, and 3.2% PEG @ 40kDa (b-d), 0%, 0.8%, 1.6%, and 3.2% PVP @ 40kDa (e-g).

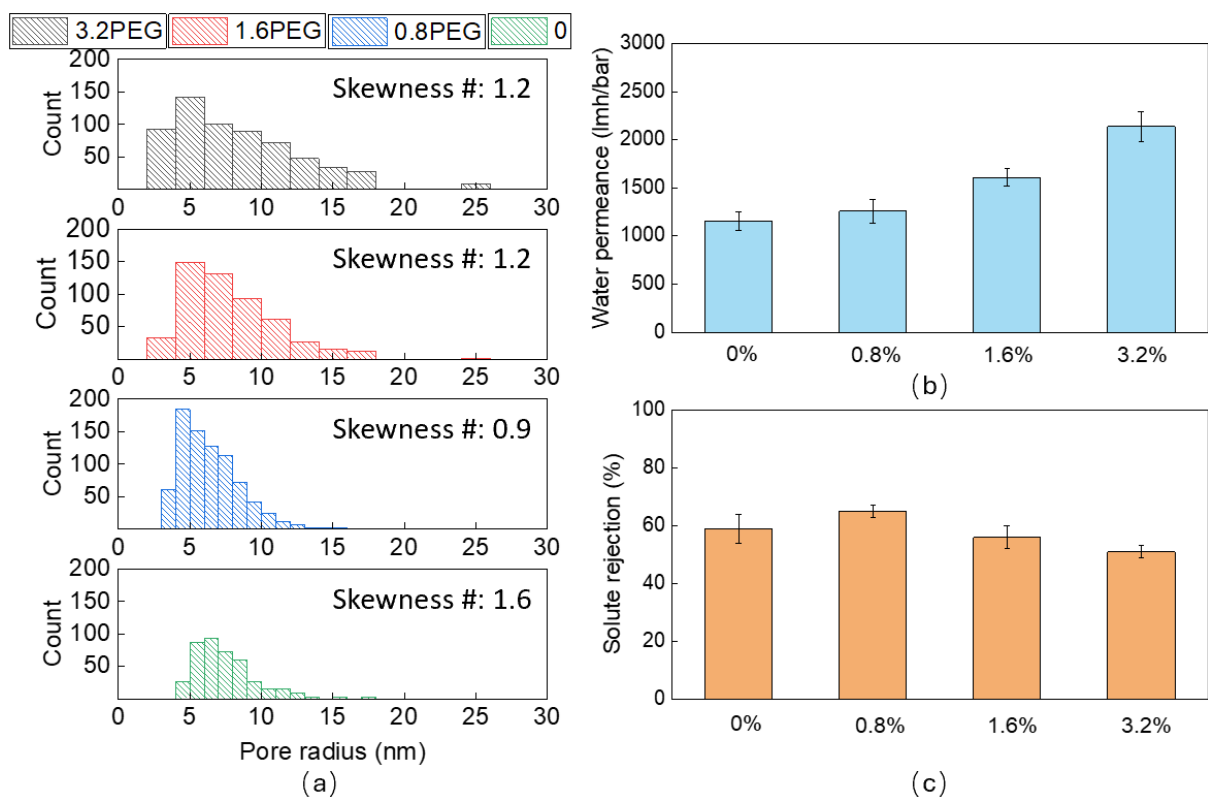


Figure 6.9 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with CPVC membrane with pore forming agent (PEG@40kDa).

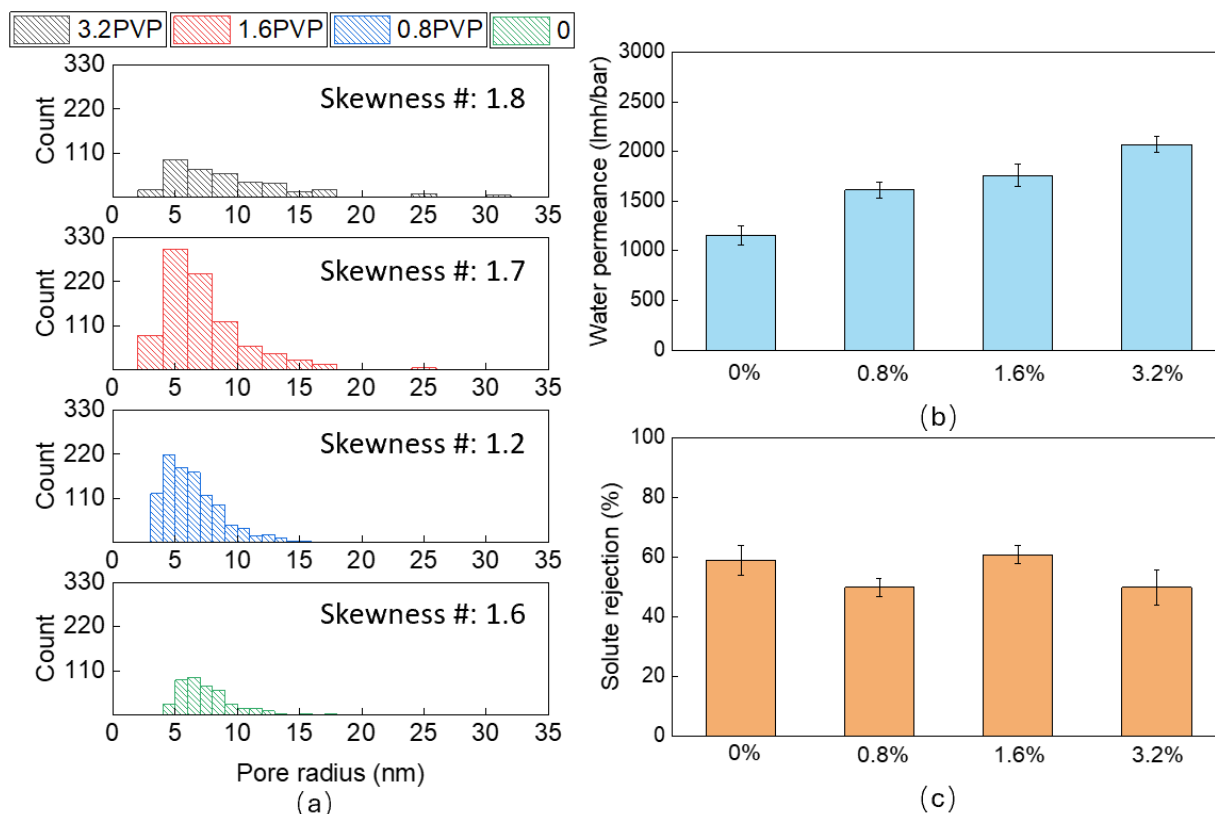


Figure 6.10 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with CPVC membrane with pore forming agent (PVP@40kDa).

Fig. 6.11 reveals that blending the solvent (DMF) in the coagulation bath results in a looser membrane surface. As the content of DMF increased from 0 to 6%, the mean pore size increased from 7.4 nm to 10.4 nm, and the surface porosity elevated from 2.02% to 10.25%, which drives the increase in contact angle (Table 6.5). Conversely, it is evident from Fig. 6.12 that the thickness of the polymer layer is inversely proportional to the DMF content in the coagulation bath.

Notably, the number of pores in the UPW-DMF membranes is significantly greater than that in UPW membrane. Moreover, the looser membrane surface not only shifts the main peak of the pore size distribution curve to the right, reducing the skewness number from 1.6 to 1.1, 1.1,

and 1.3, respectively, but also elevates the water permeance of the UPW-DMF membranes (Fig. 6.13a, b). However, a common issue with increasing mean pore size is the compromise in selectivity. The rejection rate of UPW-2%DMF membrane, UPW-4%DMF membrane, and UPW-6%DMF membrane decreased by 17%, 13%, and 40%, respectively, compared to the UPW membrane (Fig. 6.14).

Table 6.5 Mean pore size, surface porosity, and contact angle of CPVC membranes with solvent, herein DMF, blending in coagulation bath.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC-UPW	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC-2% DMF	8.6 ± 0.8	4.16 ± 0.27	79.0 ± 1.3
16% CPVC-4% DMF	8.0 ± 0.6	6.56 ± 0.19	82.5 ± 0.5
16% CPVC-6% DMF	10.4 ± 1.1	10.25 ± 0.48	84.1 ± 1.1

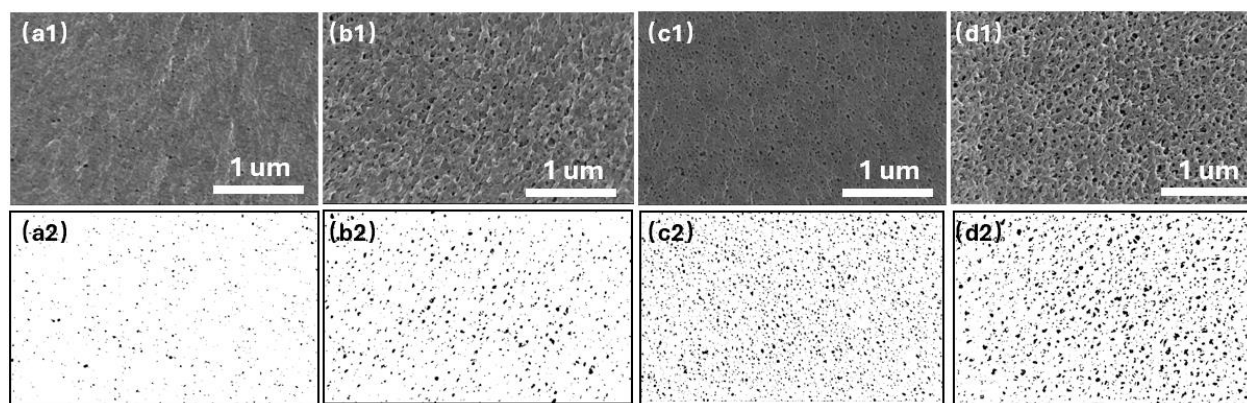
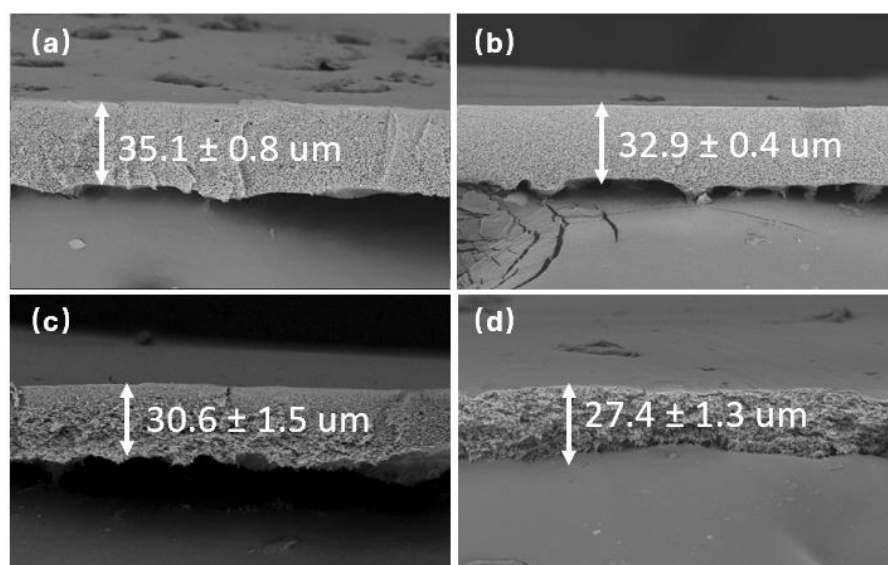


Figure 6.11 Surfacial SEM images and threshold processed images of 16% CPVC membrane with solvent, herein DMF, blending in coagulation bath: 0% (a1, a2), 2% (b1, b2), 4% (c1, c2), and 6% (d1, d2).



50 μm @3k mag

Figure 6.12 Cross-sectional SEM images of 16% CPVC membrane with solvent, herein DMF, blending in coagulation bath: 0% (a), 2% (b), 4% (c), and 6% (d).

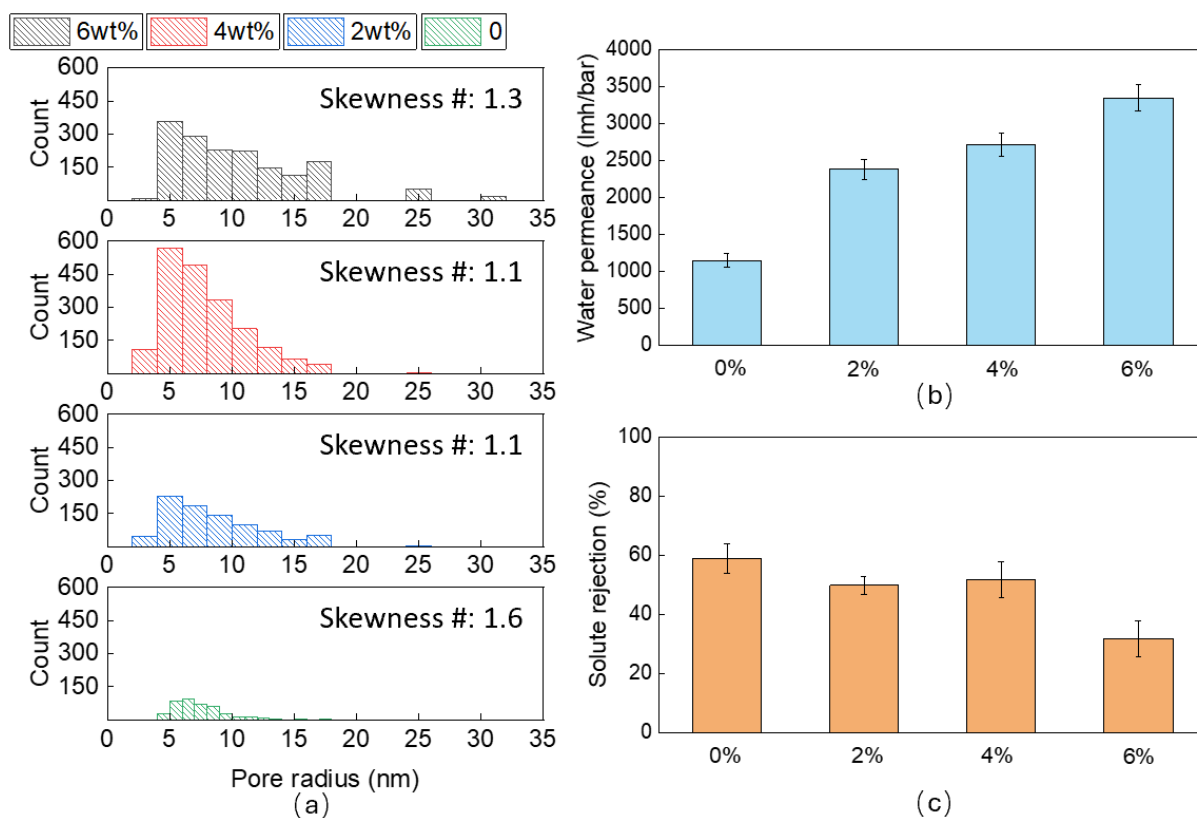


Figure 6.13 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with solvent, herein DMF, blending in coagulation bath.

Fig. 6.14 exhibits surficial SEM images that illuminate the impact of mixing salts (NaCl and Na_2CO_3) in the coagulation bath on the surface morphologies of 16% CPVC membranes. The threshold processed images indicate that both NaCl and Na_2CO_3 can effectively densify the membrane surface. A clear trend is also observed: as concentration of NaCl and Na_2CO_3 increases from 5% to 10%, the mean pore size decreased from 7.4 nm to 4.5 nm and 5.8 nm, while the surface porosity decreased from 2.02% to 0.49% and 0.33%, respectively. (Table 6.6). The cross-sectional SEM images from Fig. 6.15 indicate that the introduction of NaCl and Na_2CO_3 into the coagulation bath does not alter the sponge-like structure of the membrane;

rather, it results in a reduction in the thickness of the polymer layer as the salt concentration increases.

Fig. 6.16 validates the conclusions drawn from surface characterizations through a comparative analysis of pore size and pore size distribution curve of the membranes. NaCl and Na₂CO₃, involved in the phase inversion process within the coagulation bath, shifting the main peaks of the pore size distribution curves to the left. Furthermore, it notably diminishes the extent of the right-sided tail of the distribution curves. The maximum pore radius eventually decreases from 18 nm (no salt) to 8 nm (10% NaCl) and 11 nm (10% Na₂CO₃), respectively (Fig. 16a). In comparison to the UPW membrane, UPW-10% NaCl and UPW-10% Na₂CO₃ membrane exhibited a reduction in water permeance by 82% and 87%, respectively, attributable to surface densification, while the selectivity was greatly improved due to the reduction of the mean pore size and the elimination of extremely large pores. Our findings provide valuable insights into the fabrication of dense porous membranes.

Table 6.6 Mean pore size, surface porosity, and contact angle of CPVC membranes with salts blending in coagulation bath.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC with no salt	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC with 5% NaCl	6.3 ± 0.3	0.77 ± 0.08	75.7 ± 1.0
16% CPVC with 10% NaCl	4.5 ± 0.5	0.49 ± 0.05	73.8 ± 1.4
16% CPVC with 5% Na ₂ CO ₃	6.5 ± 0.7	1.11 ± 0.17	76.3 ± 0.7
16% CPVC with 10% Na ₂ CO ₃	5.8 ± 0.5	0.33 ± 0.04	74.5 ± 0.6

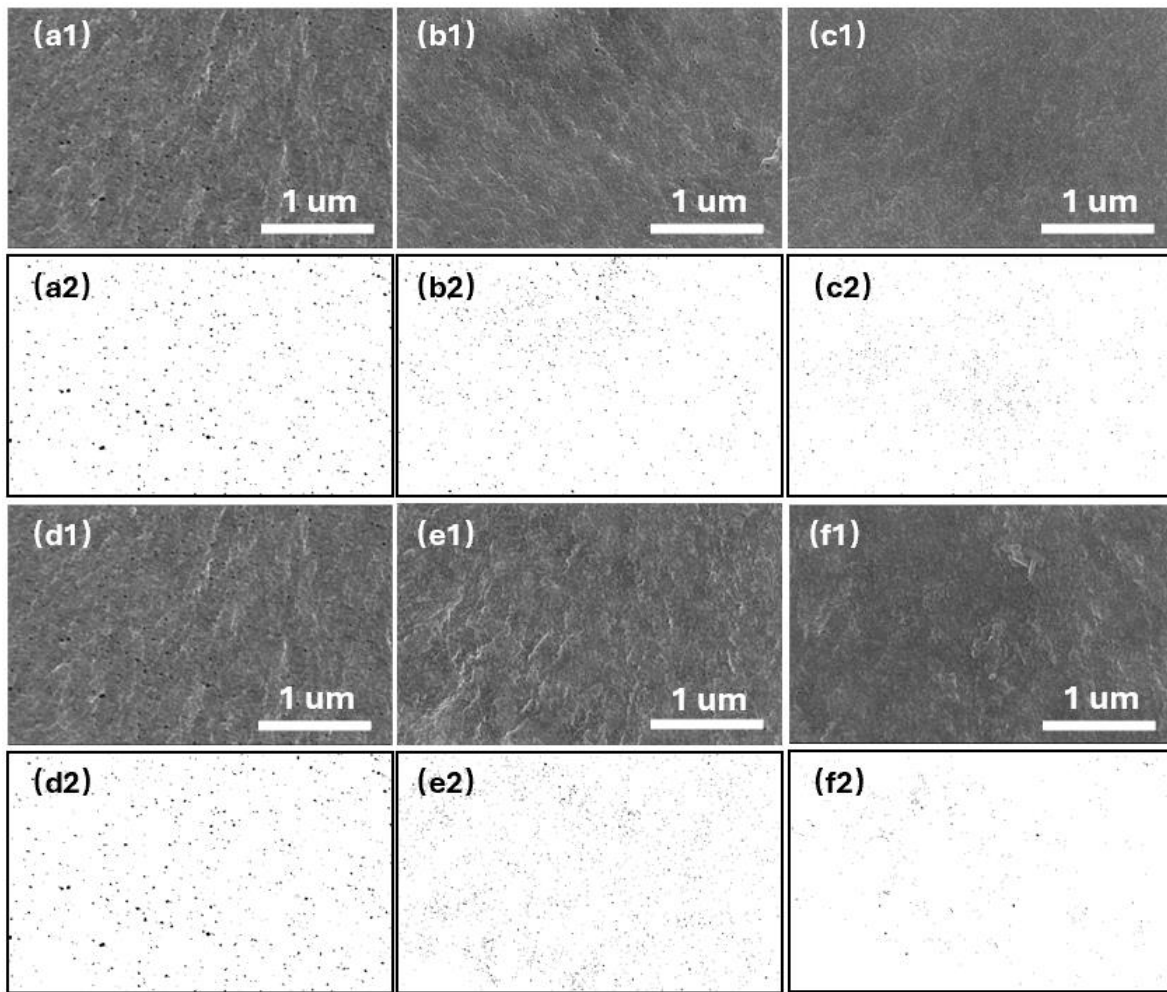


Figure 6.14 Surficial SEM images and threshold processed images of 16% CPVC membrane with salts blending in coagulation bath: 0%, 5%, and 10% NaCl (a1-c1 and a2-c2, respectively), 0%, 5%, and 10% Na₂CO₃ (d1-f1 and d2-f2, respectively).

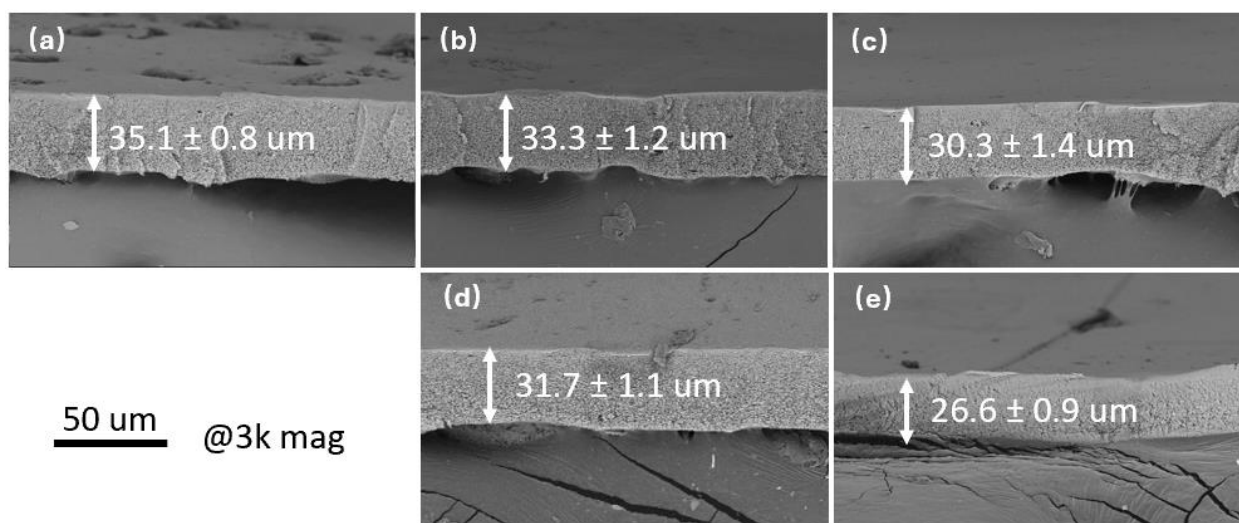


Figure 6.15 Cross-sectional SEM images of 16% CPVC membrane with salts blending in coagulation bath: no salt (a), 5% and 10% NaCl (b, c), 5% and 10% Na_2CO_3 (d, e).

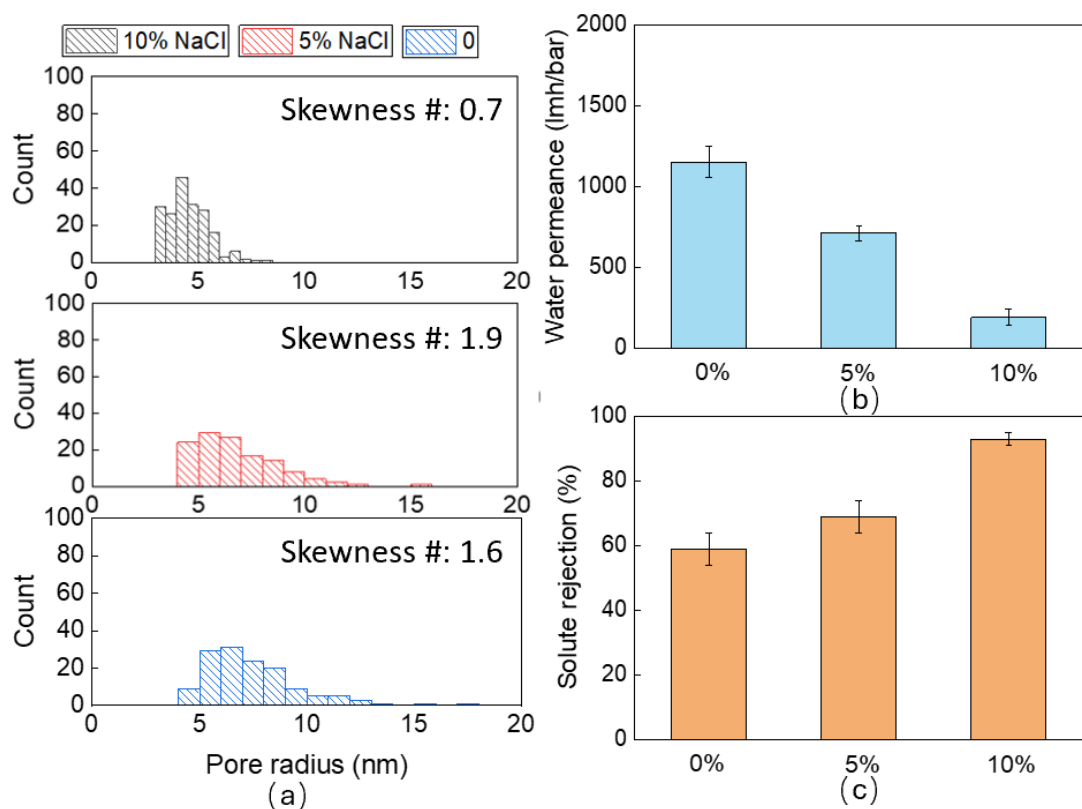


Figure 6.16 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with NaCl blending in coagulation bath.

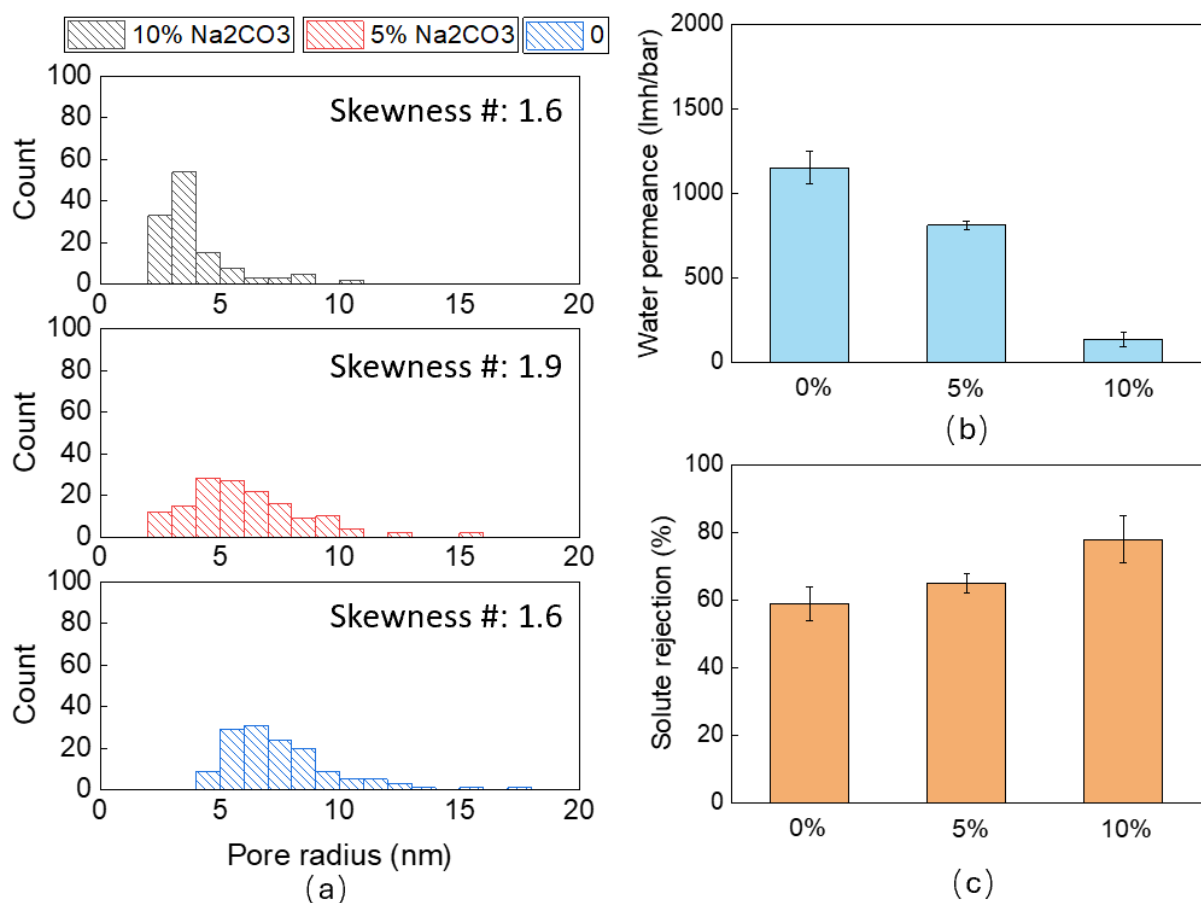


Figure 6.17 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with Na_2CO_3 blending in coagulation bath.

Fig. 6.18 exhibits surface SEM images that illuminate the impact of solvent (DMF) to co-solvent (NMP) ratios on the surface morphologies of 16% CPVC membranes, particularly showing that both pore size and surface porosity are significantly influenced by variations in the ratio of solvent to co-solvent. Table 6.7 presents the 5 distinct solvents to co-solvent ratios investigated in this chapter, which are 1:0, 3:1, 1:1, 1:3 and 0:1, respectively. Our findings indicates that 25% NMP facilitates the loosest membrane surface, characterized by the largest mean pore radius at 9.7nm and highest surface porosity at 6.13%. The surface morphology of 50% NMP membrane and 75% NMP membrane exhibits notable similarity, with slightly smaller

mean pore radius compared to the pure DMF membrane (6.8 nm and 6.6nm, respectively). However, due to a considerable increase in the number of pores per unit membrane area, the surface porosity of 50% NMP membrane and 75% NMP membrane surpasses that of the pure DMF membrane by 1.5% and 1.1%, respectively. Furthermore, the CPVC membrane fabricated with pure NMP as solvent exhibits the smallest mean pore size and lowest surface porosity among all solvent to co-solvent ratios.

When further examining the influence of the solvent to co-solvent ratio, it appears that this factor also has a crucial effect on the body properties of the membranes. A distinct trend is observed in Fig. 6.19: as the ratio of solvent to co-solvent decreases from 100% to 0%, the structure of membranes becomes significantly less compact as sponge, with the distinctive finger-like cavities becoming more prominent from Fig. 6.19b to Fig. 6.19d and completely dominant in Fig. 6.19e. Moreover, the thickness of the polymer layer increases as the ratio of solvent to co-solvent decreases, from 35.1 μm to 77.3 μm .

Fig. 6.20 highlights the impact of different ratios of solvent and co-solvent on the pore distribution, water permeance, and solute rejection rate of membranes. The observations and experimental results are consistent with the surface characterizations: Blending 25% NMP as co-solvent not only enlarges the size but also increases the number of the pores, as evidenced by the rightward shift of the main peaks in the pore size distribution curve. Consequently, the water permeance of this membrane is significantly elevated, albeit with a reduction in selectivity as the trade-off. Although the mean pore size of 50% NMP membrane and 75% NMP membrane is slightly smaller than that of the pure DMF membrane, their greater number of pores increases the water permeance by 117% and 54%, respectively. Additionally, the smaller mean pore size

contributes to the higher solute rejection rate, thereby markedly improving the performance of the membranes.

Table 6.7 Mean pore size, surface porosity, and contact angle of CPVC membranes with mixed solvent.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
16% CPVC-DMF	7.4 ± 0.5	2.02 ± 0.22	77.5 ± 1.2
16% CPVC-DMF: NMP@3:1	9.7 ± 0.7	6.13 ± 0.31	82.8 ± 1.6
16% CPVC-DMF: NMP@1:1	6.8 ± 0.3	3.55 ± 0.20	79.5 ± 0.9
16% CPVC-DMF: NMP@1:3	6.6 ± 0.4	3.08 ± 0.24	77.1 ± 1.0
16% CPVC- NMP	6.0 ± 0.3	1.74 ± 0.19	76.6 ± 0.7

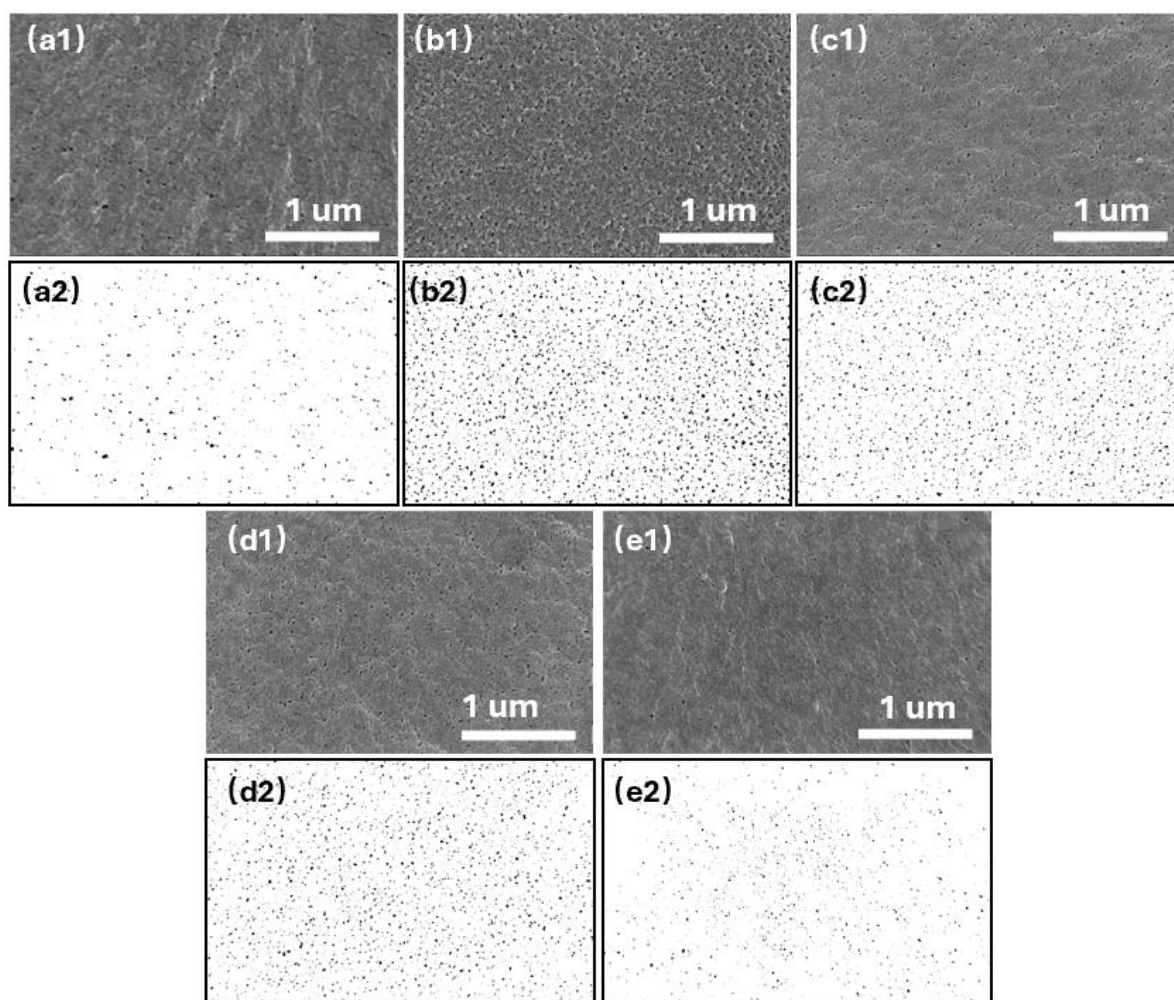


Figure 6.18 Surfacial SEM images and threshold processed images of 16% CPVC membrane with mixed solvent: DMF only (a1, a2), DMF: NMP@3:1 (b1, b2), DMF: NMP@1:1 (c1, c2), DMF: NMP@1:3 (d1, d2), NMP only (e1, e2).

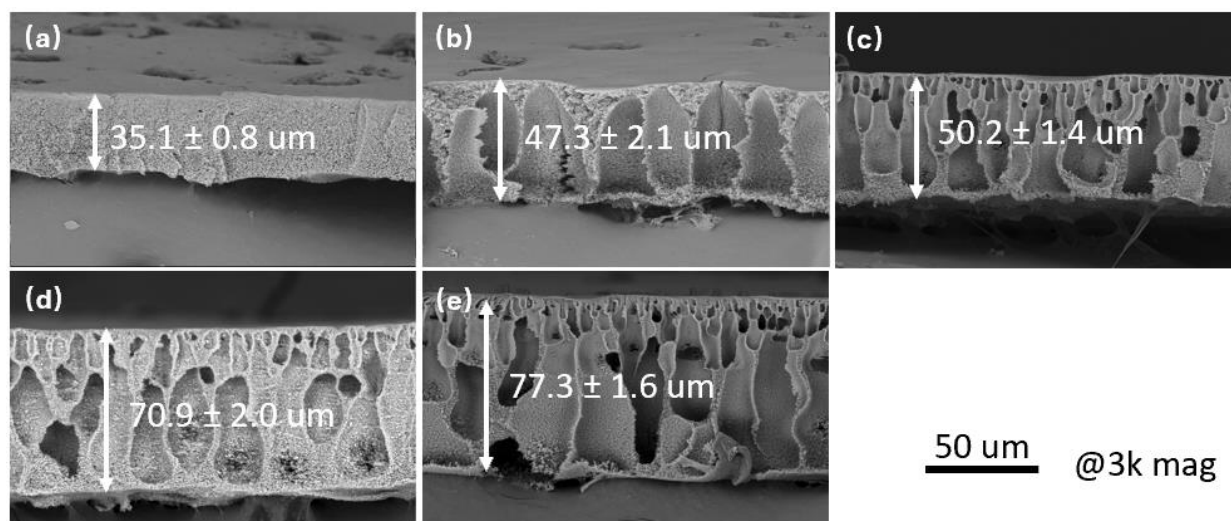


Figure 6.19 Cross-sectional SEM images of 16% CPVC membrane with mixed solvent: DMF only (a), DMF: NMP@3:1 (b), DMF: NMP@1:1 (c), DMF: NMP@1:3 (d), NMP only (e).

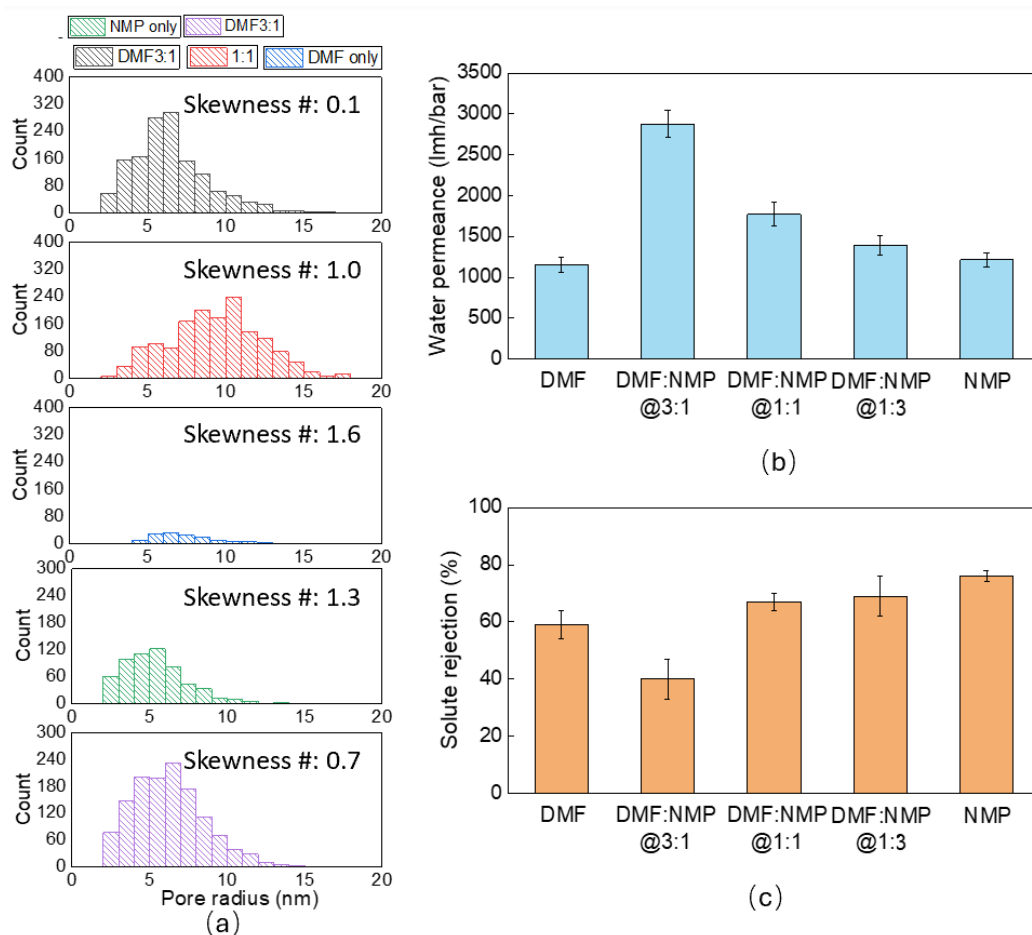


Figure 6.20 Pore size distribution (a), water permeance (b), and solute rejection (c) of 16% CPVC membrane with mixed solvent.

Fig. 6.21 presents surficial SEM images that emphasize the impact of polymer concentration and types of non-solvent on membrane fabrications. It is evident that: as polymer concentration increases from 12% to 16%, with UPW as a non-solvent, the membrane surface becomes denser, with the distinctive smaller and fewer pores, drives to the reduction of surface porosity ranging from 8.43% to 3.85% (Table 6.8). Similarly, a clear trend is observed from images Fig. 6.21d through Fig. 6.21f: with NBW as a non-solvent, the membrane becomes denser as the polymer concentration increases.

Fig. 6.22 showcases cross-sectional SEM images that illuminate the impact of using NBW as non-solvent in phase inversion process on the architecture of PSU membranes. With a fixed non-solvent, the thickness of the polymer layer increases with the increase of polymer concentration. Additionally, the polymer layer thickness of the membrane fabricated with NBW is significantly greater than that of the membrane prepared using UPW, indicating a relative looser body structure.

The pore analysis from Fig. 6.23a provides a intuitive testament to the impacts of polymer concentration and the use of NBW as a non-solvent on the pore size and pore size distribution of PSU membranes. The increase in polymer concentration shifts the main peaks of the membrane pore size distribution curve to the left, which combined with decreasing surface porosity, progressively reduces the water permeance while significantly increasing the solute rejection rate (Fig. 6.23b). Notably, with the same polymer concentration, the PSU-NBW membranes exhibit a significantly higher number of pores in the 16-19 nm range (in radius) compared to PSU-UPW membranes. More importantly, this phenomenon remained unaffected by variations in polymer concentration. Therefore, we hypothesize that the increased number of pores within this specific radius range is attributable to the NBW, serving as the non-solvent in the phase inversion process. Consequently, this chapter proposes that the pore size and pore size distribution of the polymeric porous membrane can be further refined and precisely manipulated by adjusting and regulating the size of nanobubbles.

Table 6.8 Mean pore size, surface porosity, and contact angle of PSU membranes with UPW or NBW as non-solvent.

Membrane	Mean pore size (r, nm)	Surface porosity (%)	Contact angle (°)
12% PSU-UPW	23.2 ± 1.5	8.43 ± 0.43	74.5 ± 1.8
12% PSU-NBW	21.7 ± 0.9	9.13 ± 0.51	77.3 ± 1.3
14% PSU-UPW	17.2 ± 1.3	6.37 ± 0.40	71.5 ± 1.1
14% PSU-NBW	17.7 ± 1.1	8.15 ± 0.37	73.4 ± 0.9
16% PSU-UPW	13.6 ± 0.7	3.85 ± 0.33	70.1 ± 0.8
16% PSU-NBW	17.1 ± 1.0	5.03 ± 0.18	72.6 ± 1.0

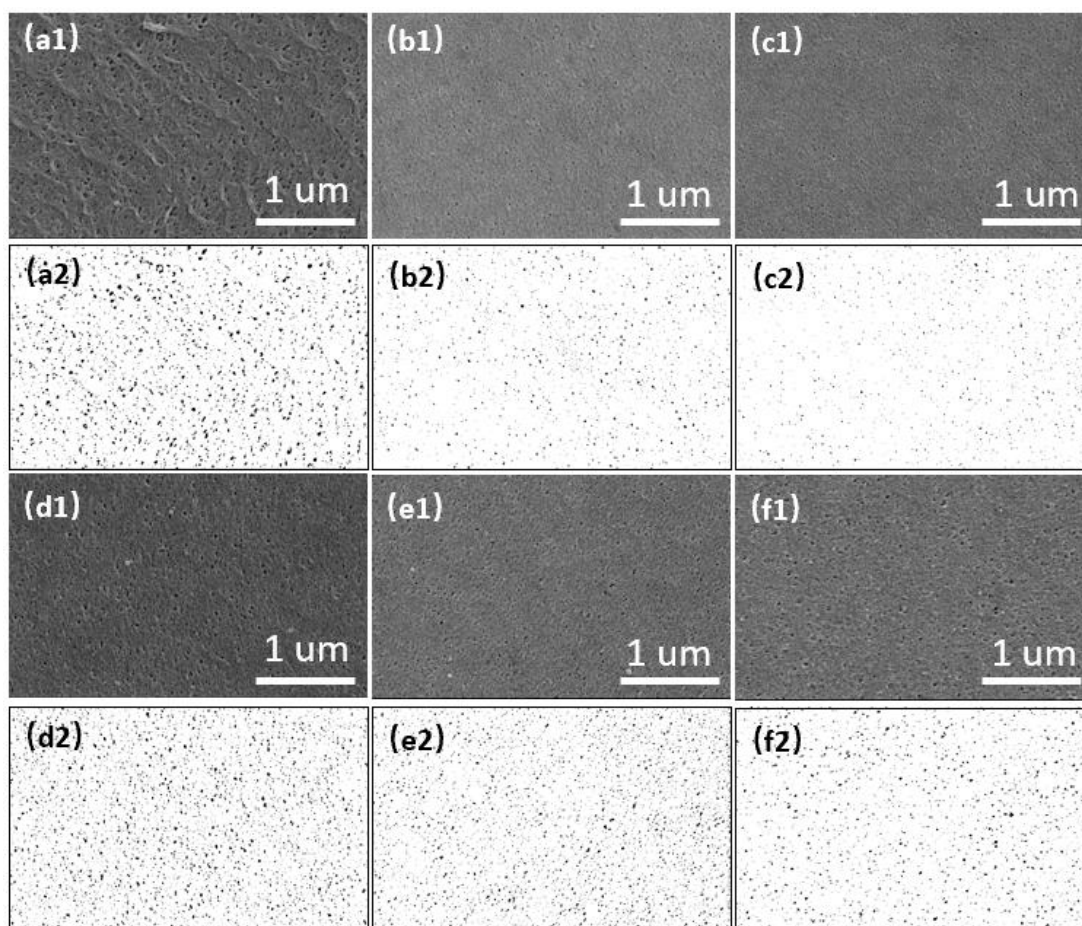


Figure 6.21 Surficial SEM images and threshold processed images of PSU membranes with UPW or NBW as non-solvent: 12% PSU-UPW (a1, a2), 14% PSU-UPW (b1, b2), 16% PSU-UPW (c1, c2), 12% PSU-NBW (d1, d2), 14% PSU-NBW (e1, e2), and 16% PSU-NBW (f1, f2).

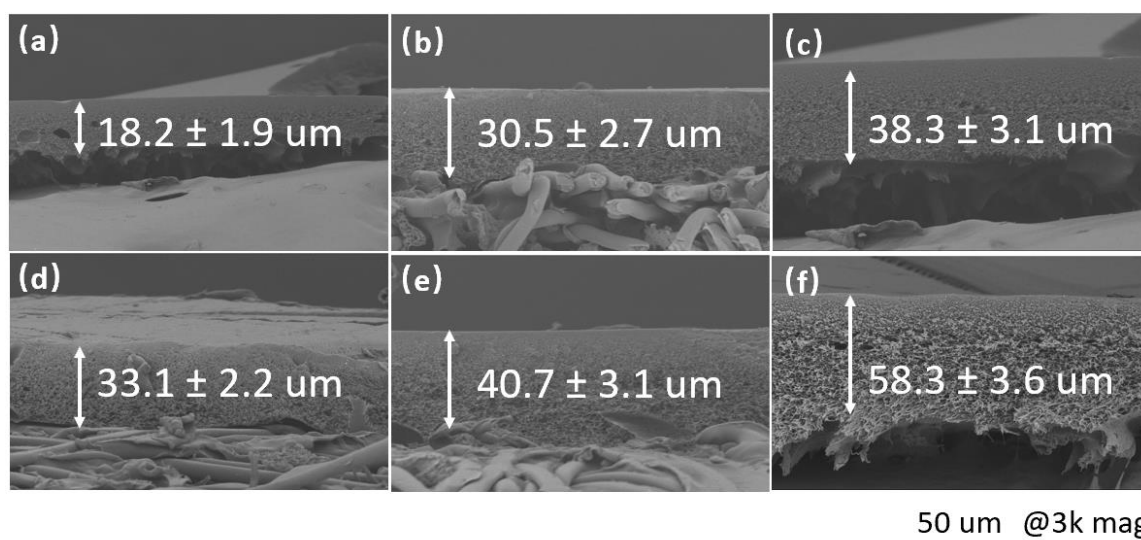


Figure 6.22 Cross-sectional SEM images of PSU membranes with UPW or NBW as non-solvent: 12% PSU-UPW (a), 14% PSU-UPW (b), 16% PSU-UPW (c), 12% PSU-NBW (d), 14% PSU-NBW (e), and 16% PSU-NBW (f).

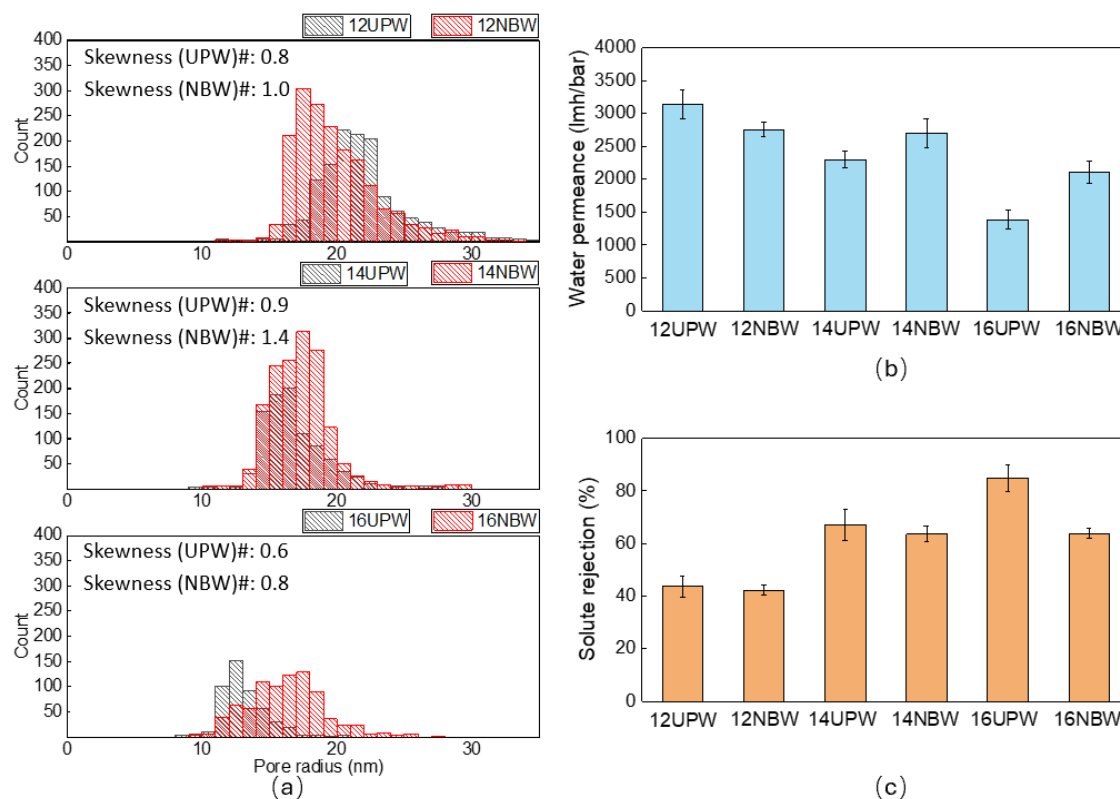


Figure 6.23 Pore size distribution (a), water permeance (b), and solute rejection (c) of PSU membranes with UPW or NBW as non-solvent.

The cross-sectional SEM images from Fig. 6.25 provide a visual testament to the impacts of various fabrication conditions on the structure of 14% PSU membranes. Our results indicate that raising the temperature of the coagulation bath to 35 °C and substituting NBW for UPW as the non-solvent increases the thickness of the polymer layer (from 32.5 μm to 37.4 μm and 44.7 μm, respectively) without altering the spongy body structure of the membranes. However, the membrane transformed into a fully finger-like morphology by adding PVP as the pore former. The larger macrovoids, generated by the finger-like structure, substantially increased the thickness of the polymer layer, which is consistent with the previous characterizations for CPVC membranes with PEG and PVP as pore forming agents. The PSU membrane with mixed non-solvent (IPA-UPW) exhibits a hybrid morphology with a sponge-like structure in the upper region and a finger-like structure in the lower region.

Table 6.9 Mean pore size, surface porosity, and contact angle of PSU membranes with different methods to manipulate pore size and pore size distribution.

Membrane	Mean pore size (r, μm)	Surface porosity (%)	Contact angle (°)
14% PSU-UPW	17.2 ± 1.3	6.37 ± 0.40	71.5 ± 1.1
14% PSU-NBW	17.7 ± 1.1	8.15 ± 0.37	73.4 ± 0.9
14% PSU with 1.4% PVP*	18.0 ± 1.5	6.71 ± 0.40	72.2 ± 0.8
14% PSU-NBW	20.4 ± 1.4	6.55 ± 0.34	71.0 ± 1.0
16% PSU- UPW: IPA@3:1**	31.8 ± 2.1	12.16 ± 0.47	82.8 ± 1.3
16% PSU-35°C	26.4 ± 1.6	10.13 ± 0.52	81.3 ± 1.1

* PVP @40 kDa; ** UPW: IPA@3:1 as non-solvent

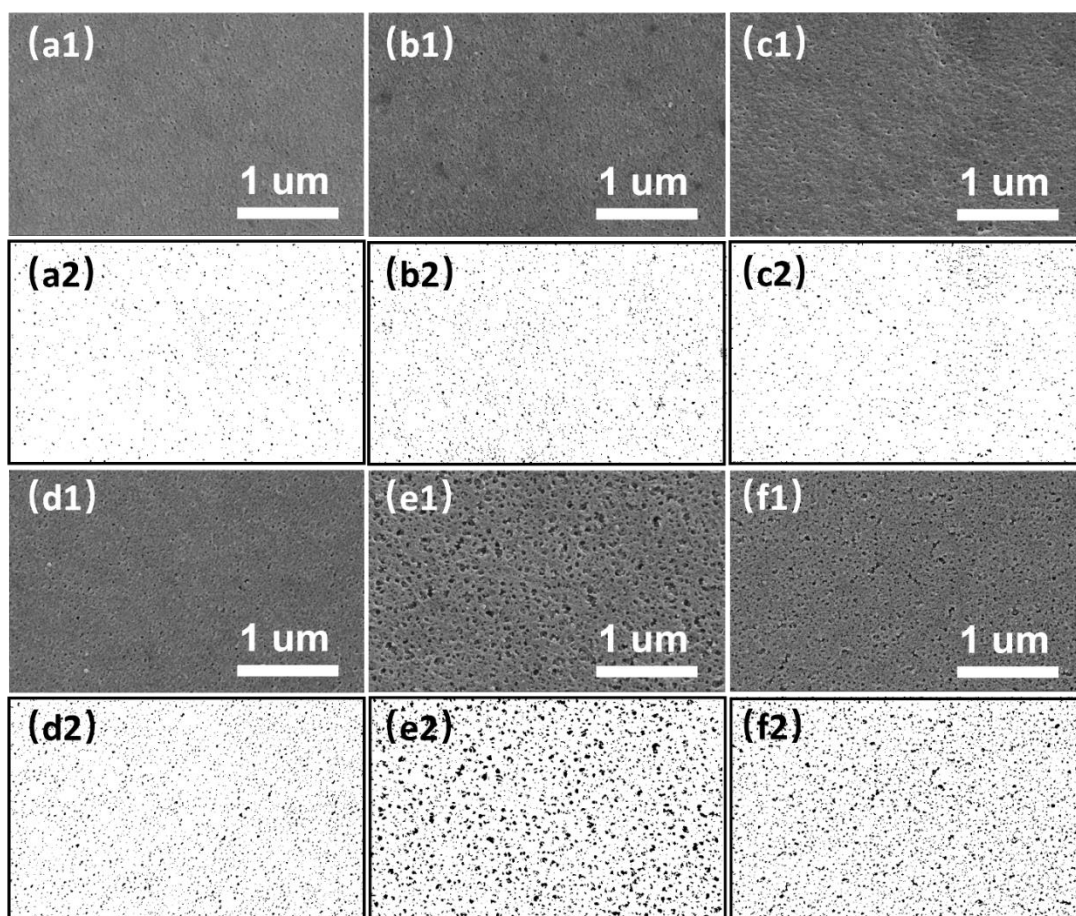


Figure 6.24 Surficial SEM images and threshold processed images of PSU membranes: 14% PSU-UPW (a1, a2), 14% PSU with 0.7% PVP@40 kDa as pore former (b1, b2), 14% PSU with 1.4% PVP@40 kDa as pore former (c1, c2), 14% PSU-NBW (d1, d2), 14% PSU-UPW:IPA@3:1 as non-solvent (e1, e2), and 14% PSU-35°C (f1, f2).

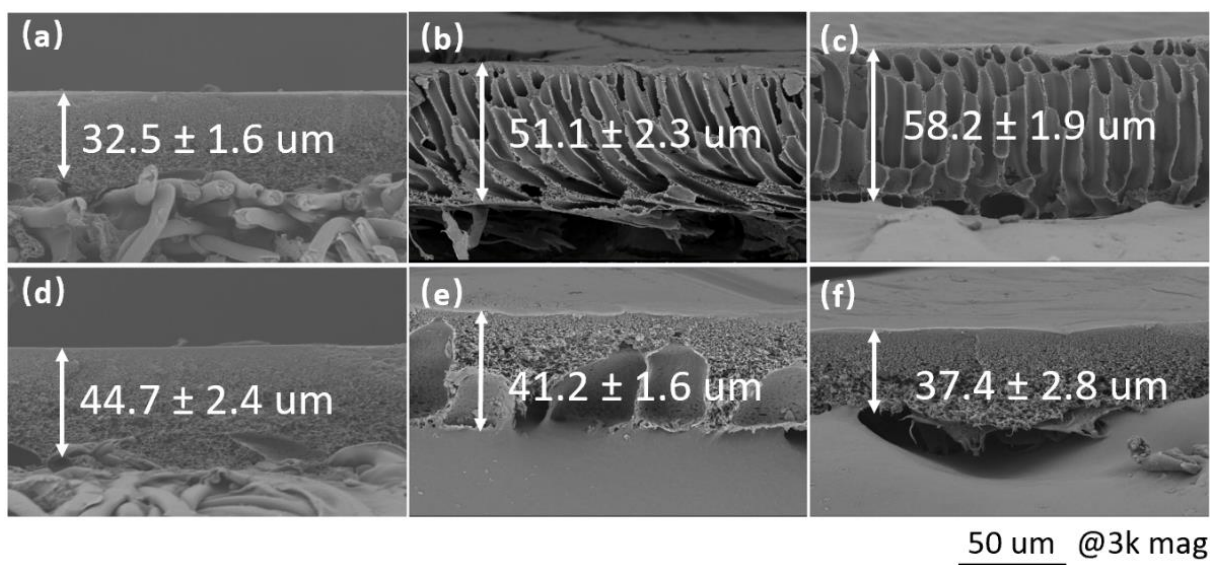


Figure 6.25 Cross-sectional SEM images of PSU membranes: 14% PSU-UPW (a), 14% PSU with 0.7% PVP@40 kDa as pore former (b), 14% PSU with 1.4% PVP@40 kDa as pore former (c), 14% PSU-NBW (d), 14% PSU-UPW: IPA@3:1 as non-solvent (e), and 14% PSU-35°C (f).

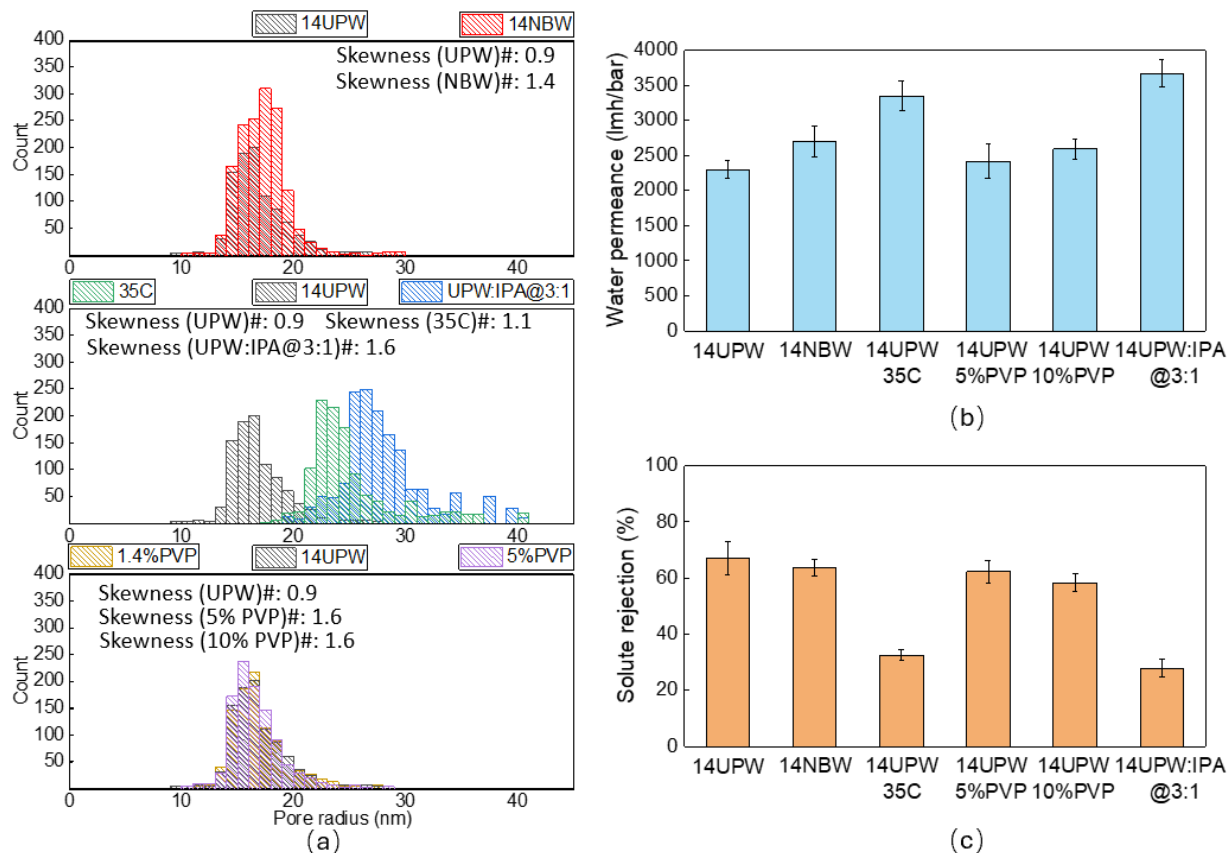


Figure 6.26 Pore size distribution (a), water permeance (b), and solute rejection (c) of PSU membranes: 14% PSU-UPW, 14% PSU with 0.7% PVP@40 kDa as pore former, 14% PSU with 1.4% PVP@40 kDa as pore former, 14% PSU-NBW, 14% PSU- UPW: IPA@3:1 as non-solvent, and 14% PSU-35°C.

6.4 Conclusions

This chapter's exploration into polymeric porous membrane fabrications underscores the integral relationship between membrane structure, especially surface morphology and membrane performance. By manipulating the phase inversion process, it is possible to fine-tune the pore size and pore size distribution of membranes. The evolution of membrane fabrication, driven by the incorporation of pore-forming agents, the inclusion of isopropanol (IPA) in coagulation baths, the precise control of coagulation bath temperature, the use of blended salts and solvents

in the coagulation bath, and the strategic application of co-solvents, plays a critical role in fabricating membranes with high water permeance without compromising solute selectivity.

In this chapter, our experimental results demonstrate that pore size and surface porosity of membranes increase as temperature of coagulation bath increases, leading to higher water permeance and a lower rejection rate. Incorporating a small amount of pore forming agents (PEG and PVP, 0.8% and 1.6%, respectively) into the fabrication system increases membrane surface porosity without altering mean pore size of membranes, thereby enhancing membrane performance with no compromise. However, when the concentration of pore forming agents reaches 3.2%, aggregation occurs, leading to the formation of bigger pores and a reduction in surface porosity. Additionally, by blending IPA and solvent in the coagulation bath, the surface porosity of the membrane can be elevated. However, this also results in the appearance of bigger pores, which significantly decreases the rejection rate. Moreover, the use of salts, herein NaCl and Na₂CO₃, in the coagulation bath and the extension of intervals between casting and phase inversion notably diminish surface porosity and pore size, facilitating the fabrication of denser membranes. In this study, we innovatively incorporated nanobubble water (NBW) into membrane fabrication via phase inversion process. Our findings indicate that membranes prepared with NBW as the non-solvent exhibit elevated surface porosity. More importantly, the rejection rate of the membranes can be precisely regulated by finely modulating the pore size and pore size distribution in accordance with the dimensions of the nanobubbles.

In summary, this chapter investigated and evaluated a variety of methods for tailoring pore size and pore size distribution of polymeric porous membranes. Through a deep understanding of the phase inversion process, these methods offer a comprehensive theoretical

and experimental framework for fabricating porous membranes with improved performance, characterized by higher water permeance and comparable or enhanced solute selectivity. Notably, the use of nanobubble water (NBW), rather than conventional ultra-pure water (UPW), as the non-solvent in the phase inversion process for fabricating porous membranes is distinguished by excellent environmental sustainability (no chemical additives) and superior performance in water permeance and solute rejection.

6.5 References

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Chapter 7 Conclusion

7.1 Major conclusions

In this dissertation, the culmination of extensive research across six critical chapters on the significance of precisely tailoring and characterizing membrane pore size and pore size distribution with NIPS method, along with the development of theoretical simulation models and experimental methodologies.

In Chapter 2, various hypothetical PSDs were constructed based on the empirical PSD data to analyze the effects of PSD mean, shape and scale on membrane performance, herein, water permeance and solute rejection, using both classical analytical models and computational fluid dynamics (CFD), which demonstrated the relationship between mean pore size and membrane performance, elucidating the phenomenon wherein the water permeance and rejection of membranes change due to the presence of excessively large or small pores.

Chapter 3 revealed that surface morphology analysis via SEM is significantly affected by coating thickness and accelerating voltage, while cross-sectional images (typically, at much higher magnification) exhibit little difference in morphology. However, improper preparation can damage membranes, compromising cross-sectional imaging, which can create significant biases in SEM analyses of microfiltration, ultrafiltration membranes. This chapter also established a suite of refined protocols designed for broad adoption, which can ensure the precise and consistent characterization of membrane materials.

Chapter 4's in-depth analysis, integrating SEM and two basic contact angle measurements, developed a simple analytical model to obtain wet and dry membrane surface porosity. The results indicated that the surface porosity calculated from both wet and dry contact

angle data correlates strongly with the surface porosity calculated from SEM values. However, wet contact angles of the membranes with high porosities produce significantly higher porosity values, which also emphasizes the importance of membrane swelling in determining membrane porosity for aqueous filtration applications.

The subsequent chapter shifted focus to three classical hydrodynamic pore-flow models, emphasizing the mechanisms governing transport across polymeric porous membranes. By elucidating concepts such as flow path, viscosity, porosity, and pressure drop and integrating the analytical insights derived from membrane characterizations, three classical hydrodynamic pore-flow models (Hagen-Poiseuille (HP), Kozeny-Carman (KC), and Happel's cell (HC)) facilitate a comprehensively understand and precisely predict membrane permeability.

Finally, Chapter 6 exhibited a framework for the precise control of membrane pore size and pore size distribution through the fabrication and characterization of a series of polymeric porous membranes. These membranes are characterized using the techniques described in Chapters 3 and 4 and the experimental results of permeance and rejection are integrated with the simulation models introduced in Chapter 5. This comprehensive and systematic approach offers strategies to enhance membrane performance, herein, water permeance and solute rejection, through precise manipulation of pore size and distribution. It also acknowledged the potential for casting high porosity polymeric membrane with nano-bubble water, which paves the way for advancement of porous membrane fabrication for a wide range of both academic and industrial applications.

7.2 Implications and future research

The thesis concludes with a reflection on the broader implications of this work. This study establishes robust and accurate methodologies for membrane characterizations. Furthermore, it demonstrates the use of various techniques to precisely manipulate membrane pore size and pore size distribution. This work not only provides novel insights but also contributes systematically to the field, offering foundational knowledge and innovative approaches for the fabrication of polymeric porous membranes.

In future research, efforts will focus on improving the system of membrane characterizations and integrating additional advanced techniques, such as atomic force microscopy (AFM) with scanning electron microscopy (SEM) and contact angle measurement. This approach aims to further validate the methodologies presented in this thesis (chapter 3) while introducing new concepts for simplified and precise membrane characterizations. In addition, recently, there has been widespread news coverage regarding the potential ban on polyvinylidene fluoride (PVDF) as one of thousands of per- and poly-fluoroalkyl compounds by the European Union, the United States and several U.S. states including California (the 5th largest economy in the world). This could greatly impact the membrane manufacturing industry as well as its downstream users in biopharma, automotive, water, dairy, food and beverage industries. I will conduct research on novel polymeric materials to identify potential alternatives that may address prospective future crises.