Cellulose Nanocrystals/Polydimethylsiloxane Composite Membranes for Air Dehydration With the Aim of Energy-use Reduction in Wood Kiln Drying

Nasim Alikhani
University of Maine, nasim.alikhani@maine.edu

Follow this and additional works at: https://digitalcommons.library.umaine.edu/etd

Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation
https://digitalcommons.library.umaine.edu/etd/3871

This Open-Access Dissertation is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.
CELLULOSE NANOCRYSTALS/POLYDIMETHYLSILOXANE COMPOSITE MEMBRANES FOR AIR DEHYDRATION WITH THE AIM OF ENERGY-USE REDUCTION IN WOOD KILN DRYING

By

Nasim Alikhani

B.A. Iran University of Science and Technology, 2011
M.A. Isfahan University, 2017

A DISSERTATION
Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (In Forest Resources)

The Graduate School
The University of Maine
August 2023

Advisory Committee:

Ling Li, Assistant Professor of Sustainable Bioenergy Systems, Advisor
Jinwu Wang, Research Forest Products Technologist, Forest Products Laboratory
Douglas J. Gardner, Professor of Sustainable Materials Technology
Doug W. Bousfield, Calder Professor, Department of Chemical & Biomedical Engineering
Mehdi Tajvidi, Associate Professor of Renewable Nanomaterials
This dissertation project addressed the manufacture and evaluation of a small polydimethylsiloxane (PDMS) hollow fiber membrane system in the kiln drying of lumber in an attempt to explore air dehydration and reduced energy usage. Temperature and vacuum pressure exert the most pronounced influence on membrane efficiency. Under optimal conditions, the PDMS membrane module demonstrates a remarkable 66% efficiency in removing water vapor from a moist air stream. Based on the parameters of the lab system and its operational performance, a finite element model was developed to simulate its scaleup for a lab-scale lumber drying kiln to remove moisture from the exhaust air such that the dehydrated air can be recirculated into the kiln to dry the lumber. Traditional kiln drying methods consume substantial energy and experience heat loss through the expulsion of the high-humidity exhaust air and drawing in fresh outside dry air. To address these challenges, a closed moisture removal system was designed and simulated, where a membrane removes moisture from moist air without any phase change, enabling the recycling of warm air and retention of thermal energy, therefore, reducing the energy consumption of the kiln. The simulation has demonstrated that this novel membrane system has significant potential for energy-saving applications in wood drying and other industries with similar drying processes. By conserving heat energy within the system, it can reduce energy consumption by up to 20% depending on weather conditions and drying schedules.
Because membranes are a key component of the membrane separation technology, sustainable cellulose nanocrystals (CNCs) are incorporated into PDMS to create a composite membrane with enhanced thermal and mechanical stability, as well as water vapor permeability. The hydrophilic nature and agglomeration issues of CNCs within PDMS were addressed through silylation, resulting in a composite membrane consisting of silylated CNCs and PDMS. The silylated CNC (SCNC)/PDMS composite membrane exhibits an increase in water vapor permeability compared to pure PDMS and a significant increase in selectivity compared to both pure PDMS and unmodified CNC/PDMS membranes. Thermo-mechanical analysis indicates a decrease in the coefficient of thermal expansion (CTE) of the PDMS membrane upon the addition of both CNC and SCNC. This research highlights the challenges and potential benefits of incorporating nanocellulose in membrane materials for high-temperature applications.

Overall, this study presents a promising approach to revolutionize kiln drying processes, offering energy efficiency and sustainability through the utilization of membrane-based air dehydration with nanocellulose-modified membranes.
DEDICATION

➢ I’d like to dedicate this dissertation to my parents for always believing in me and because of all the efforts they made to put me on the path to success.

➢ I would also like to dedicate this dissertation to my husband Masoud Ataei for always supporting me, believing in me, and encouraging me during these years.
ACKNOWLEDGEMENTS

➢ I’d like to thank my advisor Dr. Ling Li for all the support and help during this dissertation. It was a great honor to work under her supervision and being a part of her research group.

➢ I also want to thank my committee members: Dr. Jinwu Wang, Dr. Douglas J. Gardner, Dr. Douglas W. Bousfield, and Dr. Mehdi Tajvidi for all the help, support, comments, and suggestions during this dissertation.

➢ I would like to thank Sungjun Hwang for collaboration in Chapter 5 with providing spray dried CNC. It was a great help to my work.

➢ I also want to acknowledge the staff and graduate students at the School of Forest Resources and Advanced Structures and Composites Center, great people who have helped and supported me during my years at UMaine.

➢ Special thanks to the wonderful people at the Office of International Programs (OIP) for their full support through these years.
# TABLE OF CONTENTS

DEDICATION ................................................................................................................................. ii  

ACKNOWLEDGEMENTS ........................................................................................................... iii  

LIST OF TABLES .......................................................................................................................... ix  

LIST OF FIGURES ....................................................................................................................... xi  

1 INTRODUCTION ....................................................................................................................... 1  
   1.1 Overview of Energy-Saving Methods in Dry Kiln Systems .................................................. 2  
   1.2 Isothermal Membrane-based Dehumidification (IMAD) ..................................................... 5  
   1.3 Dense Membranes .................................................................................................................. 6  
   1.4 Polymeric Membranes .......................................................................................................... 8  
   1.5 Air Dehydration with Membranes ......................................................................................... 9  
   1.6 Modification of Polymeric Dense Membrane using Nanoparticles .................................. 11  
   1.7 Structure of this dissertation ............................................................................................... 13  
   1.8 References ........................................................................................................................... 16  

2 EXPLORATION OF MEMBRANE-BASED DEHUMIDIFICATION SYSTEM  
TO IMPROVE THE ENERGY EFFICIENCY OF KILN DRYING PROCESSES:  
FACTORS THAT AFFECT THE MOISTURE REMOVAL EFFICIENCY .................................. 22  
   2.1 Chapter Summary .................................................................................................................. 22  
   2.2 Introduction ......................................................................................................................... 23  
   2.3 Materials and Methods ....................................................................................................... 25
2.3.1 Water Vapor Separation Mechanism of Membranes .................................................. 25
2.3.2 Selection of Membrane Material ................................................................................. 26
2.3.3 Experimental Setup ..................................................................................................... 27
2.3.4 Experimental Design .................................................................................................... 29
2.4 Results and Discussion .................................................................................................... 31

2.4.1 The Reduction of RH with Time .................................................................................. 31
2.4.2 Effects of Test Variables on the Efficiency of Moisture Vapor Removal ............... 32
2.4.3 Analysis of Variance (ANOVA) and a Regression Model of Efficiency of Moisture Vapor Removal ................................................................................................. 38
2.4.4 Verification of the Regression Model ........................................................................... 41
2.5 Conclusions ..................................................................................................................... 41
2.6 References ....................................................................................................................... 43

3 NUMERICAL SIMULATION OF THE WATER VAPOR SEPARATION OF A MOISTURE-SELECTIVE HOLLOW-FIBER MEMBRANE FOR THE APPLICATION IN WOOD DRYING PROCESSES ................................................................. 46

3.1 Chapter Summary ............................................................................................................ 46
3.2 Introduction ...................................................................................................................... 47
3.3 Materials and Methods ................................................................................................... 49

3.3.1 Materials .................................................................................................................... 49
3.3.2 Methods ...................................................................................................................... 50
3.3.3 Finite Element Analysis Modeling .................................................................52

3.3.4 Correlation of Sh–Re–Sc .............................................................................56

3.4 Results and Discussion .....................................................................................57

3.4.1 Experimental Results ..................................................................................57

3.4.2 FEA Modeling Results ................................................................................58

3.4.3 Model Validation .........................................................................................60

3.4.4 Correlation Relationship of Sh–Re–Sc Numbers ..........................................61

3.5 Conclusions ....................................................................................................62

3.6 References .....................................................................................................65

4 INFLUENCE OF CELLULOSE NANOCRYSTAL (CNC) IN POLYDIMETHYLSILOXANE (PDMS) MEMBRANES FOR WATER VAPOR/AIR SEPARATION AT ELEVATED TEMPERATURES .................................................................69

4.1 Chapter Summary ............................................................................................69

4.2 Introduction ....................................................................................................70

4.3 Materials and Methods ..................................................................................72

4.3.1 Materials .....................................................................................................72

4.3.2 Methods .....................................................................................................73

4.4 Results ...........................................................................................................78

4.4.1 Appearance and Morphology of CNC/PDMS Membrane Samples ............78

4.4.2 ATR - FTIR Analysis ..................................................................................80
4.4.3 Permeability of Water Vapor ................................................................. 82
4.4.4 Permeability of Nitrogen Gas ................................................................. 82
4.4.5 Selectivity of Water Vapor and Nitrogen .............................................. 84
4.4.6 Coefficient of Thermal Expansion (CTE) of Membranes ...................... 84

4.5 Discussion ............................................................................................... 85
4.5.1 Influence of CNC Agglomeration on Membrane Appearance and Properties ...... 85
4.5.2 Effects of Temperature on Permeability of Water Vapor and Nitrogen Gas ........ 86
4.5.3 Effectiveness of CNC as a Nanofiller on Water Vapor and Nitrogen Gas Permeability ........................................................................................................ 87

4.6 Conclusions ............................................................................................. 89
4.7 References ............................................................................................... 90

5 SILYLATED CNC/PDMS COMPOSITE MEMBRANES WITH IMPROVED SELECTIVITY FOR H₂O/AIR SEPARATION ............................................................... 95

5.1 Chapter Summary .................................................................................... 95
5.2 Introduction ............................................................................................. 96
5.3 Materials and Methods ............................................................................ 99
5.3.1 Materials .............................................................................................. 99
5.3.2 Methods .............................................................................................. 100
5.4 Results .................................................................................................... 103
5.4.1 Morphology of CNCs and SCNCs ....................................................... 103
LIST OF TABLES

Table 1.1: Water vapor permeabilities and water vapor/nitrogen selectivities for various organic polymers at 30 °C ........................................................................................................................................11

Table 2.1: Factors and levels of each factor ........................................................................................................................................30

Table 2.2: Analysis of variance of test variables and their interactions .................................................................................................38

Table 3.1: Geometric information of the hollow fiber membrane module and single hollow fiber and physical properties of PDMS membrane material........................................................................50

Table 3.2: Experimental design of operating hollow-fiber membrane air dehumidification system. ........................................................................................................................................51

Table 3.3: Summary of experimental and modeling results. ...............................................................................................................................58

Table 3.4: Abbreviation ..................................................................................................................................................................................63

Table 4.1: Kinetic diameter and critical temperature of molecules ........................................................................................................87

Table B.1: Overall 2-way ANOVA results for the effect of concentration and temperature on water vapor permeability ........................................................................................................................................140

Table B.2: Concentrations means comparison for the water vapor permeability results ..................141

Table B.3: Overall 2-way ANOVA results for the effect of concentration and temperature on Nitrogen gas permeability........................................................................................................................................141

Table B.4: Concentrations means comparison for the Nitrogen gas permeability results ..........142

Table B.5: Overall 2-way ANOVA results for the effect of concentration and temperature on selectivity ........................................................................................................................................142

Table B.6: Overall one-way ANOVA results for the effect of concentration on CTE .................142

Table B.7: Concentrations means comparison for the CTE results ........................................................................................................................................143
Table C.1: Overall 2-way ANOVA results for the effect of type of membrane and temperature on water vapor permeability ........................................................................................................143

Table C.2: Type of membrane means comparison for the water vapor permeability results ......144

Table C.3: Overall 2-way ANOVA results for the effect of type of membrane and temperature on nitrogen gas permeability ........................................................................................................144

Table C.4: Type of membrane means comparison for the nitrogen gas permeability results ........................................................................................................................................145

Table C.5: Overall 2-way ANOVA results for the effect of type of membrane and temperature on selectivity ........................................................................................................................................145

Table C.6: Type of membrane means comparison for the selectivity results .........................................145

Table C.7: Overall ANOVA results for the effect of type of membrane on CTE ..........................146

Table C.8: Type of membrane means comparison for the CTE results .........................................146
# LIST OF FIGURES

Figure 1.1: Schematic diagram for heat exchanger .................................................................3
Figure 1.2: a) Schematic diagram and b) external view of the experimental setup for
investigating drying of lumber with the use of a heat pump ..................................................4
Figure 1.3: Schematic diagram for open absorption system installed at a wood dryer ..........4
Figure 1.4: Schematic diagram for IMAD ...........................................................................6
Figure 1.5: Schematic diagram for permeation through a dense membrane according to
solution-diffusion .................................................................................................................7
Figure 2.1: Schematic of a membrane-based energy recovery system being applied in dry
kiln .......................................................................................................................................25
Figure 2.2: Gas separation mechanism of dense polymer membrane ..................................26
Figure 2.3: Water vapor permeability and H$_2$O/N$_2$ selectivity of various polymer-based
membranes [10] ...................................................................................................................27
Figure 2.4: (a) View of a hollow fiber PDMS membrane, (b) a cross-section of one single
tube and (c) a schematic of gas separation .............................................................................28
Figure 2.5: Schematic of a membrane dehumidification system .........................................29
Figure 2.6: General curves of the reduction of RH at the outlet with time at representative
testing conditions ................................................................................................................32
Figure 2.7: Main effects of the four factors on the efficiency of moisture vapor removal ....33
Figure 2.8: Effects of the interactions between two factors on the efficiency of moisture
vapor removal .........................................................................................................................37
Figure 2.9: Plots of residuals in the regression analysis ........................................................40
Figure 3.1: Schematic of a lab-scale membrane air dehumidification system .................51
Figure 3.2: Schematic of a hollow fiber membrane module and the three domains of a hollow fiber membrane. ................................................................. 53
Figure 3.3: Schematic of a segment of the half longitudinal section of a single fiber mesh distribution. ................................................................................. 56
Figure 3.4: Distribution of concentration of water vapor in three domains of a hollow fiber membrane .......................................................................................................................... 59
Figure 3.5: Axial concentration distribution of water vapor in the tube domain of hollow fiber membrane .......................................................................................................................... 59
Figure 3.6: The concentration of water vapor in dehumidified air at outlet of PDMS membrane ................................................................................................................................. 61
Figure 3.7: Correlation among Re, Sc and Sh numbers ................................................................................................................................. 62
Figure 4.1: Schematic of the WVTR test setup on a dynamic vapor sorption instrument .......... 75
Figure 4.2: Schematic of a single gas transmission cell ................................................................................................................................. 76
Figure 4.3: Appearance of the membrane Samples ................................................................................................................................. 78
Figure 4.4: SEM images of composite membrane materials of CNC/PDMS: (a) 0%, (b) 2%, (c) 4%, and (d) 6% ................................................................................................................................. 79
Figure 4.5: 3D images of AFM results of composite membrane materials (a) Pure PDMS, (b) 2% CNC/PDMS, (c) 4% CNC/PDMS, and (d) 6% CNC/PDMS. ......................................................................................... 80
Figure 4.6: FTIR spectra of all membrane samples and control groups ................................................................................................................................. 81
Figure 4.7: Water vapor permeability at elevated temperatures and a humidity differential of 60% ................................................................................................................................. 81
Figure 4.8: Nitrogen permeability at the elevated temperatures ................................................................................................................................. 83
Figure 4.9: Selectivity of H₂O/N₂ at elevated temperatures ................................................................................................................................. 84
Figure 4.10: The CTE values for different samples

Figure 5.1: a) diagram of the fabrication method of SCNC/PDMS membrane, b) chemical formula of silylated CNCs and SCNC/PDMS membrane

Figure 5.2: SEM images of CNC powder and SCNC powder and Si mapping images

Figure 5.3: FT-IR spectra of CNC powder and SCNC powder

Figure 5.4: XRD patterns of CNC powder and SCNC powder

Figure 5.5: SEM images of composite membrane materials of CNC/PDMS: (a) Pure PDMS, (b) 2% CNC/PDMS, (c) 2% SCNC/PDMS. Polarized light results of composite membrane materials of CNC/PDMS: (d) Pure PDMS, (e) 2% CNC/PDMS, (f) 2% SCNC/PDMS

Figure 5.6: Appearance of the membrane samples

Figure 5.7: Height images of AFM results of the top surface of the composite membrane materials (a) Pure PDMS, (b) 2% CNC/PDMS, and (c) 2% SCNC/PDMS.

Figure 5.8: Water vapor permeability of the membrane samples

Figure 5.9: Nitrogen gas permeability of the membrane samples

Figure 5.10: Schematic illustration of pure PDMS and PDMS nanocomposite films

Figure 5.11: Selectivity of the membrane samples

Figure 5.12: The CTE values for different samples

Figure A.1: Schematic of a single hollow fiber

Figure C.1: Schematic diagram of a spray-dry encapsulation process and image of Mini-spray dryer picture

Figure C.2: Particle size distribution of spray dried CNCs

Figure C.3: Particle shapes and size distributions of the spray dried CNCs
Figure C.4: DMA results of membranes ................................................................. 151
1 INTRODUCTION

The conventional method of kiln drying is a wood drying process that consumes a significant amount of energy. This process involves the use of hot air at controlled velocity, temperature, and relative humidity to facilitate the evaporation of moisture from lumber [1]. The process involves arranging lumber in stacked layers with narrow gaps between them to facilitate the flow of air. As the air passes through these layers, it absorbs moisture from the wood, leading to a decrease in the dry-bulb temperature while maintaining the wet-bulb temperature. Heat energy is supplied by a steam-based system to a circulated air stream, which serves to elevate the temperature of both the lumber and the kiln, facilitate the evaporation of moisture from the wood, and compensate for heat loss resulting from the temperature difference between the kiln and the outside environment. The heat required for conventional kiln drying serves various purposes, including increasing the wood's temperature, overcoming hygroscopic forces, raising the temperature of any remaining water inside the wood, evaporating the removed water, elevating the temperature of incoming ventilation air, and compensating for system losses.

A notable aspect of the conventional kiln drying process is the common practice of expelling high-humidity air as exhaust while introducing fresh, low-temperature air. Unfortunately, this exchange of air results in a significant loss of heat from the system [1]. However, it is important to highlight that there is potential for recycling and reusing this heat within the system [2]. Harvesting and reusing this heat energy in kiln drying can improve the entire energy efficiency of the kiln.

To develop an energy-saving system for kiln drying, which is the overarching goal of this dissertation project, a membrane-based air dehydration system employing advanced nanocellulose-modified membrane materials was investigated in this dissertation project. The performance of a polydimethylsiloxane (PDMS) hollow fiber membrane module was evaluated
through experimental testing (Chapter 2) and simulation (Chapter 3). To enhance thermal and mechanical stability, as well as the water vapor permeability of the membrane, sustainable cellulose nanocrystals (CNCs) were incorporated into PDMS to create a composite mixed matrix membrane (Chapter 4). To address the hydrophilic nature and agglomeration issues of CNCs within PDMS, silylation of spray-dried CNCs in an anhydrous system was conducted, resulting in a composite membrane consisting of silylated CNCs and PDMS (Chapter 5). Below is a background of energy-saving methods in kiln drying and using Isothermal membrane-based dehumidification (IMAD) for energy saving. Furthermore, the background of IMAD systems and different polymers for this application are reviewed. The benefits of adding CNCs to the membrane and the silylation of CNCs are explained.

1.1 Overview of Energy-Saving Methods in Dry Kiln Systems

Currently, there are several approaches to increasing the energy efficiency of kilns such as heat exchangers, mechanical heat pumps, and open absorption systems [3]. More information about these methods is as follows:

1) One of the commonly employed heat recycling methods in kilns involves the use of an air/air heat exchanger for heat recovery as shown in Figure 1.1. By installing heat exchangers in kiln vents, heat energy is exchanged between the hot humid air inside the kiln and the fresh air from outside. This system utilizes the evacuation air to heat the incoming drying air, resulting in increased efficiency ranging from 4% to 10%. This preheats the fresh air by utilizing thermal energy in the evacuation air obtained from the hot stream. The advantages of this system include low initial investment and variable operational costs. However, it is important to note that the overall efficiency of this method is relatively low [4], [5].
2) In certain rare cases, heat pumps are utilized in kiln drying processes. However, the high cost of electricity in comparison to heat often limits the profitability of heat pumps. Mechanical heat pump dehumidifiers offer a potential solution by reducing energy consumption by up to 50% when compared to conventional kiln drying methods. Figure 1.2 a and b, show a schematic diagram and external view of the experimental setup for investigating the drying of lumber with the use of a heat pump. This process involves directing hot, moist air from the drying chamber over cold evaporator coils within the dehumidification unit. The moisture present in the air condenses on the coils, and the resulting water is drained from the system. The heat extracted from the air is recycled through the use of a refrigerant fluid, which is compressed and employed to heat the incoming air from the evaporator. Dehumidification kilns typically operate within the temperature range of 60 to 70°C, with heat being recovered from both the exhaust air and the ambient air. The energy balance of this system encompasses the electrical energy consumption of the heat pump (comprising the compressor and blower) and the multiple-speed dryer fan. Additionally, it includes the thermal energy (both sensible and latent) recovered from the dryer and returned to it by the heat pump. The thermal energy recovered from the dryer reduces the overall energy requirement for drying, and the electrical input of the heat pump is fully reused as drying energy [5].
3) Another approach is the implementation of an open absorption system, which involves the following sequential steps. Initially, water evaporates from the lumber within the kiln and is carried by the flowing air to the absorber unit. Subsequently, the absorption solution present in the absorber unit absorbs the water vapor present in the humid air, leading to the generation of dry air. This dry air is then reintroduced into the kiln, eliminating the need for outdoor air supply. A schematic diagram for the open absorption system installed at a wood dryer is illustrated in Figure 1.3. However, low efficiency and the need for regeneration of the adsorption liquid are the drawbacks of this method [8], [9].

Figure 1.2: a) Schematic diagram and b) external view of the experimental setup for investigating drying of lumber with the use of a heat pump. (1. upper drying chamber; 2. lower drying chamber; 3. heat pump evaporator; 4. heat pump condenser; 5. heat pump compressor; 6. condenser of the evacuation system; 7. vacuum pump; 8. expanding valve) (Adopted from [7])

Figure 1.3: Schematic diagram for open absorption system installed at a wood dryer (Adopted from [8])
1.2 Isothermal Membrane-based Dehumidification (IMAD)

Traditional dehumidification methods may be adopted and cost-effective, but they encounter difficulties in terms of regeneration and low efficiency. However, these challenges can be addressed by employing innovative strategies and implementing new technologies. Among these emerging technologies, isothermal membrane-based dehumidification (IMAD) offers a promising solution [6]. IMAD represents a thermodynamically efficient gas separation process that has the potential to enhance energy efficiency by more than 50% [10], [11]. IMAD has a dense membrane which is a selective layer allowing some certain components to pass through but stops others, separating the components from the mixture. The membranes used for IMAD separates vapor gas from the humid air. The driving force for vapor transfer is the chemical potential gradient between the feed side and the permeate side of the selective membrane. The permeability and selectivity are two critical characteristics that determine the vapor separating performance of the IMAD [12].

A Schematic diagram for IMAD is shown in Figure 1.4. IMAD exhibits superior energy and economic performance in comparison to conventional dehumidification methods, making it highly applicable in various domains such as food processing, water treatment, electrochemistry, air drying, and gas separation. IMAD has superior energy and economic performance compared to the conventional dehumidification methods due to the following reasons:

1) It is an isothermal system that does not need any cooling or heating process;

2) No need to use energy to regenerate the desiccant; and

3) The IMAD can remove moisture with good efficiency of more than 50% which is higher than moisture removal of desiccant dehumidification [3], [6], [10], [13]-[15].
Based on the findings from previous studies, a 50% or higher energy efficiency gain over a conventional vapor compression system was attainable when the selectivity for water vapor to air was above 200 [16]. However, the application of the membrane for thermal energy savings in wood-drying processes has not been addressed. In this study, IMAD technology was used to enhance the energy efficiency of wood drying. Because of the need for reducing the heat energy loss in kiln drying through opening vents, in this research, for the first time, a closed system was introduced where an air dehumidification membrane can remove the moisture from saturated air without any phase change, thereby allowing the warm air to be recycled into the system, retaining thermal energy, and returning dehumidified air into the kiln to run another cycle of drying. This thereby reduces the energy required to heat another cold air stream coming into the kilns from the environment. [17].

1.3 Dense Membranes

A membrane functions as a discerning transport barrier separating two contiguous phases. It facilitates the traversal of certain molecules (referred to as the permeate) while excluding others (known as the retentate) through the utilization of a driving force, such as pressure or disparities in concentration [18]. As the partial pressure difference of the crucial component between the feed
and permeate sides of the membrane increases, the driving force for permeation correspondingly increases [19].

In general, the permeation of a gas through a dense membrane is governed by the solution diffusion mechanism. And permeability is considered the multiplication of diffusivity and solubility. Consequently, gas separation through membranes can be broadly classified into two categories: diffusivity-based separation and solubility-based separation [20]. A schematic diagram for permeation through a dense membrane according to the solution-diffusion mechanism is illustrated in Figure 1.5. Several assumptions are made when considering this mechanism which are as follows:

1) The polymer membrane is treated as a liquid continuum.
2) Chemical equilibrium is assumed to exist at the boundaries between the feed/membrane and membrane/permeate phases.
3) No interaction is considered between different gas species.
4) The solubility of gas components in the membrane follows Henry's law [21], [22].

Dense polymeric membranes exhibit significant potential for gas separation processes because of their cost-effectiveness and low operating expenses [23].
1.4 Polymeric Membranes

The efficiency of gas separation technology relies heavily on the choice of membrane materials [24]. Polymer membranes have wide applications in various industrial separation processes, including both gas and liquid separations. However, a notable drawback in polymeric membranes is the inherent trade-off between permeability and selectivity, known as the "polymer upper bound limit." In 1991, Robeson conducted a comprehensive analysis of numerous polymers, revealing an intrinsic connection between the selectivity and permeability of polymer membranes. This relationship demonstrates that as selectivity increases, permeability decreases, and vice versa [25].

In the past, commercial polymer membranes were fabricated using rubbery and glassy polymers, such as polyamides, polyetherimides, polypropylene, polyvinyl chloride, and polyvinyl fluoride. However, traditional polymer membranes have encountered certain limitations, including inadequate resistance to contaminants, low chemical stability, and limited thermal stability [26].

Rubbery membranes function above their glass transition temperature, allowing the polymer chains to undergo significant rearrangements within a relatively short period. These membranes are typically in a state of thermodynamic equilibrium. Examples of common rubbery membranes include polydimethylsiloxane (PDMS), polyethylene glycol, and silicone rubber. Selectivity in rubbery membranes is primarily achieved through variations in solubility [27].

Glassy membranes, in contrast, operate below the glass transition temperature, resulting in polymer chain rearrangement occurring over an extremely long timescale. As a result, these membranes do not reach thermodynamic equilibrium. The polymer chains are imperfectly packed, leading to the presence of excess free volume in the form of microscopic voids within the polymeric matrix. These voids facilitate the Langmuir adsorption of gases, enhancing the solubility of gases within the membrane [20]. Examples of glassy membranes include polysulfone and
polyimide. The significant presence of free volume, attributed to the existence of micro voids, within glassy polymeric membranes typically governs that this membrane class is governed by diffusivity selectivity [27]. The significant presence of free volume within glassy polymeric membranes, attributed to the existence of micro voids, typically means that this membrane class is governed by diffusivity selectivity.

Glassy polymeric membranes exhibit remarkable permeability; however, they are hindered by the drawbacks of costly raw materials, harsh synthesis conditions, and limited chemical stability [28]. In contrast, rubbery polymers offer favorable characteristics, with poly(dimethylsiloxane) (PDMS) standing out as one of the most gas-permeable rubbery polymers. This can be attributed to its flexible siloxane linkages and satisfactory H₂O/N₂ selectivity which makes it a promising candidate for air dehydration [24], [28], [29].

1.5 Air Dehydration with Membranes

Several polymer-based membrane materials such as poly(dimethylsiloxane) (PDMS), polyether-block-amide (PEBAX), and sulfonated poly(ether ether ketone) (SPEEK) have been found suitable as dense membranes for eliminating water vapor from air or gas streams. As a result, these membranes have been employed in certain air conditioning units to enhance the energy-saving capabilities of building systems [30]-[32].

In a study [16], the water vapor and nitrogen permeability behavior of various polymers was compiled. The data in Table 1.1, adapted from [16] and [33], represent extrapolated values of water vapor permeability and H₂O/N₂ selectivity at zero water activity, with many values derived from pure gas permeability and ratios calculated for mixtures. The permeabilities are expressed in Barrer.
Many of the values for permeability reported in Table 1.1 were obtained from pure gas permeability by calculating the ratios for the mixtures. However, in real mixtures, the presence of water can cause membrane swelling, making it uncertain how it affects the slower species. Generally, for binary mixtures of permanent gases, higher selectivity corresponds to lower permeability. However, this relationship does not hold for water vapor in mixtures with permanent gases, where highly selective polymers often exhibit very high permeability. The selectivity can vary over seven orders of magnitude, while permeability can vary over five orders of magnitude. The impact of polymer structure on performance is variable. Completely non-polar membranes, such as those based on natural rubber, polystyrene, polypropylene, and polyethylene, tend to have poorer permeabilities. Poly(vinyl alcohol) or PVA, which is widely used in commercial membranes, exhibits low permeability despite its prevalence in this field [34]. The presence of polarity, such as ether or sulphonate groups, is considered advantageous in membrane materials. Introducing sulphonate or carboxylate groups into the structure of poly(vinyl alcohol) (PVA) appears to be a worthwhile modification [35].

Among these materials, PDMS dense membrane is the most common membrane for air dehumidification and is also commercially available. PDMS offers numerous advantages, including low cost, chemical stability, nontoxicity, ease of scale-up, good processability, and a high surface area-to-volume ratio [17], [29]. Particularly, PDMS membranes in hollow-fiber form offer a high surface area-to-volume ratio and scalability. Moreover, PDMS is acknowledged as one of the most permeable rubbery polymers, due to its flexible siloxane linkages, resulting in exceptional water vapor permeability. Additionally, PDMS exhibits a satisfactory H₂O/N₂ selectivity, typically around 140 [17], [24], [29].
Table 1.1: Water vapor permeabilities and water vapor/nitrogen selectivities for various organic polymers at 30°C (adapted from [16], [33]).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Water Permeability, Barrer</th>
<th>Selectivity, H₂O/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>19</td>
<td>33,300</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>68</td>
<td>227</td>
</tr>
<tr>
<td>Poly (vinyl chloride)</td>
<td>275</td>
<td>12,500</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>275</td>
<td>11,000</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>300</td>
<td>1,880,000</td>
</tr>
<tr>
<td>Polyimide</td>
<td>640</td>
<td>5,330,000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>970</td>
<td>388</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1,400</td>
<td>4,670</td>
</tr>
<tr>
<td>Polysulphone</td>
<td>2,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>2,600</td>
<td>299</td>
</tr>
<tr>
<td>Poly (ether sulphone)</td>
<td>2,620</td>
<td>10,500</td>
</tr>
<tr>
<td>Poly (phenylene oxide)</td>
<td>4,060</td>
<td>1,068</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>6,000</td>
<td>24,000</td>
</tr>
<tr>
<td>Sulphonated poly(ether sulphone)</td>
<td>15,000</td>
<td>214,000</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>20,000</td>
<td>6,060</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>40,000</td>
<td>143</td>
</tr>
<tr>
<td>Sulphonated poly (ether ether ketone)</td>
<td>61,000</td>
<td>10,200,000</td>
</tr>
<tr>
<td>PBT/PEO block copolymer b</td>
<td>85,500</td>
<td>40,500</td>
</tr>
<tr>
<td>PEBAX® 1074 a</td>
<td>160,000</td>
<td>200,000</td>
</tr>
</tbody>
</table>

a PEBAX® 1074 is a blend of polyether block amide (nylon 12) and poly (ethylene oxide)

b (Polybutylene terephthalate)/poly (ethylene oxide) block copolymer

1.6 Modification of Polymeric Dense Membrane using Nanoparticles

Most polymeric membranes, including PDMS, are recommended for use in working conditions with temperatures less than 50°C because of thermal and mechanical degradability as well as a reduction in gas separation efficiency. However, in most softwood drying processes, the temperature of the air increases up to about 82°C [1]. Similarly, in other industries, the gas streams often exhibit high temperatures that exceed the tolerance of the membranes used. For instance, in the study of flue gas dehydration using PEBAX®1074 and sulfonated SPEEK membrane
materials, field tests were carried out when the temperature of flue gas was cooled below 50°C [33]. In another study, feed gas streams were cooled solely to accommodate a membrane gas separation process and subsequently heated back up [36]. However, the practice of reducing gas temperature and subsequently reheating it introduces additional costs and energy consumption in the process [36], [37]. Therefore, for the purpose of energy saving with membranes in these processes, it is necessary to modify membranes that can operate at elevated temperatures.

To enhance the thermal and mechanical properties, as well as the vapor/gas separation performance of membranes, a promising approach is to develop mixed matrix membranes that combine the favorable characteristics of both polymeric and nanomaterials [38]-[40]. Various nanoparticles are employed to enhance the performance of polymeric membranes. Examples include ZnO [41], TiO$_2$ [42], SiO$_2$ [43], titanate nanotubes (TNTs) [44], Zeolite [45], [46], and more. These nanoparticles are incorporated into polymeric membranes to improve their thermal and mechanical properties, as well as their permeability. However, it is important to note that some of these nanoparticles may have non-sustainable origins and could be petroleum-based.

Cellulose nanocrystals (CNC) are a class of nanomaterials derived from lignocellulosic biomass. They have dimensions of 100-300 nm in length and 5-70 nm in diameter. These nanocrystals possess several attractive characteristics, including a large specific surface area, high tensile strength and stiffness, an abundance of surface hydroxyl groups, an extremely low coefficient of thermal expansion, and more [47]-[50]. Because of these properties, CNCs have been utilized as substitutes for inorganic nanoparticles like TiO$_2$ and Al$_2$O$_3$ in film-type composites. They serve as reinforcement fillers to enhance the strength, thermal stability, optical properties, permeability, and other characteristics of the composites. Nanocellulose's unique physical and mechanical properties make it an excellent choice for reinforcement in composite materials. [40], [51], [52].
When hydrophilic materials, such as CNCs, are added to hydrophobic polymers, poor compatibility of the two phases is always a challenge, which impacts a wide range of the polymer properties. To address this issue, various techniques have been investigated to enhance CNC dispersion and compatibility with the matrix, including graft polymerization using hydrophobic polymers, low molecular weight esters, and silane coupling agents [53]. These approaches lead to the modification of CNCs, imparting improved hydrophobicity and favorable compatibility with hydrophobic polymer matrices [53]. Some existing studies investigated their impacts on the mechanical properties of polymeric materials. One study found that the modified CNCs resulted in an increase in the tensile strength of silicone rubber by increasing the concentration of modified CNCs from 0 to 3 wt.% [54]. Another study revealed that the addition of 4 wt.% silylated CNCs to PDMS led to improved mechanical stability [52]. However, there is very limited research on how CNCs or modified CNCs can affect the vapor/gas separation performance of polymetric dense membranes, including PDMS.

1.7 Structure of this dissertation

Chapter 1 is an overview of the dissertation project, which addresses the challenges facing the wood drying industry, the overarching goal of this dissertation project, a literature review of possible solutions, and the structure of this dissertation.

Chapter 2 focuses on investigating the viability of utilizing a PDMS membrane-based dehumidification system to achieve energy savings in kiln drying processes. A laboratory-scale model was established to examine the impact of operational parameters on the efficacy of a hollow fiber PDMS membrane module. The experiment was designed and analyzed using response surface methodology. The findings revealed that temperature and vacuum pressure exerted the most pronounced influence on membrane efficiency. At optimal conditions, the PDMS membrane
module demonstrated a remarkable 66% efficiency in removing water vapor. This chapter is published as a journal article.

**Chapter 3** developed a computational fluid dynamics (CFD) model to simulate the PDMS membrane separation process for air dehydration. A simplified two-dimensional axisymmetric finite element analysis (FEA) model was developed using COMSOL Multiphysics® software to simulate water vapor and nitrogen gas separation in a moisture-selective hollow-fiber membrane. Firstly, the appropriate geometry and boundary conditions, input values for the air flow rate, vacuum pressure, and initial relative humidity (RH) at different levels were defined. The membrane output temperature, RH, and pressure profiles were then obtained as the simulation results. The experimental results in Chapter 2 were used to validate this CFD model. It was found that the simulation results agreed with the experimental data. Then, the experimentally validated model was used to calculate the mass transfer coefficient of water vapor and the Sherwood number. Using the modeling results, a correlation of Sh–Re–Sc (Sherwood-Reynolds-Schmidt numbers) was established. In addition, comparing the correlation obtained from this FEA model with the correlations from previous studies showed that there is good agreement with the literature. The correlation obtained here is not material dependent. Therefore, the CFD model and the correlation can be used by other researchers working under similar operating conditions and provide information for scale-up of the membrane system and new membrane material development. This chapter is also published as a journal article.

**Chapter 4** discusses the feasibility of adding CNCs to PDMS for improving the water vapor and nitrogen gas separation performance of PDMS at elevated temperatures from room temperature to 80°C, particularly for wood drying applications. The choice of CNCs was based on two hypotheses: First, the presence of surface hydroxyl groups on CNCs could enhance the water vapor
permeability of PDMS membranes. Second, the low thermal expansion property of CNCs could effectively mitigate the thermal expansion of PDMS at elevated temperatures. The optimization of CNC concentration in composite membranes was conducted, and the permeability of water vapor and nitrogen was investigated at 25°C, 50°C, and 80°C and relative humidity of 60%. Characterization tests, however, indicated that the dispersion of CNC nanoparticles within the PDMS matrix varied, with random dispersion or small agglomerations observed depending on the CNC concentrations. Achieving a homogeneous dispersion of cellulose nanocrystals (CNCs) within hydrophobic polymer matrices is a widely recognized challenge stemming from the hydrophilic nature of CNCs, which is attributed to the abundant presence of hydroxyl groups. Consequently, achieving suitable compatibility between the reinforcing phase and polymer matrix is often problematic [53], [54].

Chapter 5 addresses the challenge found in Chapter 4 by studying the effectiveness of a silylation technique to modify the surface of spray-dried CNC powder and achieve better compatibility and dispersion of the modified CNCs within a PDMS matrix. Since modifying CNCs in aqueous suspensions, such as 1% to 11.8% solid concentrations, with silylation presented some challenges in the following membrane manufacturing process, an anhydrous process was used. Spray-dried CNC powder was selected and subjected to silylation. The surface modification of CNCs was carried out through the reaction between hydroxyl groups of the CNCs and the silylation agent. Then, the silylated CNCs (SCNCs) were added to the PDMS/curing agent mixture and the resulting silylated CNC/PDMS composite membrane showed promising results, including improved water vapor permeability, improved water vapor/N₂ selectivity and improved thermal and mechanical properties. Therefore, the new silylated CNC/PDMS composite membrane developed shows potential for air dehydration applications.
1.8 References


2 EXPLORATION OF MEMBRANE-BASED DEHUMIDIFICATION SYSTEM TO IMPROVE THE ENERGY EFFICIENCY OF KILN DRYING PROCESSES: FACTORS THAT AFFECT THE MOISTURE REMOVAL EFFICIENCY

2.1 Chapter Summary

Green wood drying through a steam kiln drying technology is an energy-demanding process. This process consumes a large amount of energy to evaporate water from wood and discharge it to the atmosphere through venting. The thermal energy loss from the venting of dry kilns takes up to 20% of total energy consumed by the whole wood drying operation because a considerably large amount of thermal energy is stored in the exhaust air. Harvesting and reusing such waste thermal energy would improve the energy efficiency of the kiln drying process. Advanced moisture selective membranes have been used to dehydrate humid air or gas steam because of the advantages of low energy requirements, the simplicity of operation, and high specificity. However, the application of membrane in wood drying processes has not been addressed. Therefore, this study aims to investigate the feasibility of using a moisture selective membrane system to dehydrate the warm moist exhaust air to achieve an energy saving purpose. The membrane material was polydimethylsiloxane (PDMS) with high-water vapor permeability. A small membrane-based dehumidification system was constructed to evaluate the effects of four factors (temperature, air flow rate, initial relative humidity (RH), and vacuum pressure) on the efficiency of moisture vapor removal. Statistical analysis in terms of response surface methodology was carried out. The major findings include 1) increasing the temperature and vacuum pressure caused a significant increase in the efficiency of moisture vapor removal; 2) the initial RH had little influence on the efficiency of moisture vapor removal; 3) increasing the air flow rate had a negative impact on the efficiency
of moisture vapor removal; and 4) the regression model can be used to predict the efficiency of moisture vapor removal. This PDMS membrane would be a possible solution for a pre-drying process at relatively low operation temperatures (<45°C), i.e., dehumidification process.

### 2.2 Introduction

Green wood usually has high moisture contents (MCs) in a wide range; that range being from 60% to 120% on a dry weight basis. The kiln drying process is a key process in drying lumber/boards fast to reduce their MCs to the required final MCs for various applications. The conventional steam drying kiln is the most commonly used kiln type in North America. In this particular process, steam is circulated in heating coils to heat air and in spraying lines to adjust the relative humidity (RH) of the air based on a specified drying schedule. Free water and bound water in wood evaporate into the air in the kiln. Gradually, the air becomes saturated with moisture and loses its drying power [1]. The humid and hot air is typically ventilated to the environment regularly. Because the air moisture holding capacity increases exponentially with the temperature [2], relatively cold and dry air is brought into the kiln to absorb the water vapor that is escaping from lumber. Although the kiln drying process greatly decreases the time required to produce dry wood, it consumes a large amount of heat energy to lower the MC of wood [3]. During the kiln drying process, energy is consumed by several elements such as latent heat of evaporating water, heat loss from kiln structures (walls, doors), heat loss from venting air, and sensible heat to warm lumber, air, water, and kiln structures, etc., most of which are irreversible. The heat loss can only be partially recovered through ventilation to serve an energy-saving purpose. It was reported that about 20% of heat energy loss in conventional dry kilns was ascribed to the ventilation of exhaust air [4]. There have been several energy recovery systems that have been applied to conventional dry kilns. One of them employs heat exchangers to capture the sensible heat of exhaust air and transfer it to
the incoming fresh cold air. The efficiency of energy recovery of these systems varies with environmental conditions, for example, the differential in temperature between the air inside the kiln and incoming fresh air in summer is less than that in winter. In addition, the RH of the incoming air is affected by environmental conditions as well, for example, moist air in rainy/snowy days.

With the rapid development of membrane technology during recent decades, it has been shown that a type of moisture selective membrane can effectively and efficiently remove moisture from the air. An example of this application is in certain air conditioning units used in the HVAC system of buildings [5-6]. Overall, membrane-based dehumidification systems have numerous advantages: less energy consumption because the moisture vapor is removed through diffusion without undergoing a phase change (i.e., moisture vapor showing at the permeate side), unlike the heat pump dehumidification system via condensation; simplicity in maintenance and operation; high selectivity; ease of scale up; and low initial cost [7-9]. The membrane dehumidification technology shows promising potential for the wood industry’s need to reduce energy consumption. A hypothesis is that energy saving could be achieved when dry air is separated from the humid and hot exhaust air and the dry, hot air is rerouted back into the kiln thereby reducing the energy required to heat another cold air stream coming into the kilns from the environment, as shown in Figure 2.1.
In order to investigate the feasibility of using a moisture selective membrane module to develop a closed energy recovery system that can improve the energy efficiency of the wood drying process, a small lab unit was set up to study the effects of temperature, air flow rate, initial relative humidity, and vacuum pressure on the moisture separation efficiency of the system.

2.3 Materials and Methods

2.3.1 Water Vapor Separation Mechanism of Membranes

Water vapor in air can be separated by dense polymer-based membranes [10]. Such dense membrane separates mixed gas components in terms of the differences in solubility and diffusivity of the components in the membrane material. A solution-diffusion process, as shown in Figure 2.2, which is driven by the difference in pressure between the two sides of the membrane, is briefly described below [11]:

1) Under applied high-pressure, water vapor molecules in a gas mixture first absorb on the membrane surface;

2) Then the water vapor molecules diffuse through the thickness of the membrane, which is facilitated by the concentration gradient of water vapor (Fick’s law); this generates a net flow toward the low concentration side; and
3) The water vapor molecules desorb at the low-pressure side of the membrane (i.e., the opposite side of the feed gas).

![Gas separation mechanism of dense polymer membrane](image)

*Figure 2.2: Gas separation mechanism of dense polymer membrane (adapted from [12])*

### 2.3.2 Selection of Membrane Material

Literature review reveals that many polymer-based membrane materials can be used for the removal of water vapor from air or gas streams, as seen in Figure 2.2 [13-24]. Water vapor permeability and H$_2$O/N$_2$ selectivity are two primary parameters in selecting membranes for various applications. Considering medium-size to large-size steam drying kilns, large volumetric moisture vapor would be expelled from the vents regularly. It then requires that the membrane have a high-water vapor permeability to quickly remove the excess water vapor in the air. Likewise, the H$_2$O/N$_2$ selectivity should be high enough to effectively separate the moisture vapor from the air.

In this study, a membrane material of polydimethylsiloxane (PDMS) was selected. A hollow-fiber membrane module made of PDMS was purchased from PermSelect-MedArray Inc. Based on the factsheet provided by the material supplier, the water vapor permeability is 36,000 Barrer (1 Barrer = $3.35 \times 10^{-16}$ mol·m·m$^{-2}$·s·Pa$^{-1}$) and the H$_2$O/N$_2$ selectivity is 129 as shown in Figure 2.3. The supplier recommended operating the membrane module below 60°C to obtain the optimum result.
However, considering that most softwood drying processes are conducted in a conventional temperature range, i.e., 45°C to 82°C, the temperature limitation of the PDMS membrane should be overcome prior to targeting the application on the conventional kiln drying processes. The PDMS will be modified in future investigations, focusing on the operational capability of the system under higher temperatures. Nevertheless, this PDMS membrane would be a possible solution for a pre-drying process, i.e., dehumidification process. Also, the experimental results of the PDMS membrane obtained in this study will be used as a benchmark to compare with the modified PDMS membrane.

![Figure 2.3: Water vapor permeability and H₂O/N₂ selectivity of various polymer-based membranes [10]](image)

2.3.3 Experimental Setup

A hollow fiber PDMS membrane module with a surface area of 1.0 m², in Figure 2.4 (a), was used for fabricating the dehumidification system due to the compact size. The Scanning Electron Microscopy (SEM) image, in Figure 2.4 (b), shows the cross section of a single fiber with an approximate 55-µm-thick wall. As illustrated in Figure 2.4 (c), the feed gas mixture flows in one end of the lumen of the fiber and exhausts from the other end. Most water vapor molecules permeate across the thickness of the PDMS fiber to the shell side, forming a cross flow mode.
As shown in the schematic of the membrane dehumidification system, Figure 2.5, the small-scale membrane system was placed in a temperature- and RH-controlled environmental chamber. The humid air entered the membrane module through inlet 1. The air flow rate was controlled by an air blower and monitored by a mass/volume flow meter. The humid air passed through the lumen of hollow fibers and the dehumidified air came out of outlet 2, which was collected in a closed airtight container for the measurement of RH and temperature. The moisture vapor that permeated through the wall of hollow fibers came out of outlet 3 and outlet 4 and expelled to the outside of the environmental chamber through a vacuum pump. The vacuum pump equipped with a vacuum regulator and moisture trap. Port 5 was blocked during the whole testing process.
The temperature and RH of humid air and dehumidified air were monitored and recorded with time at an interval of 10 secs by temperature and humidity sensors and a data logging system, which were used to calculate the efficiency of water vapor removal, Eq. (2.1)

\[
\text{Efficiency}(\%) = \frac{(\text{RH}_{\text{in}} - \text{RH}_{\text{out}})}{\text{RH}_{\text{in}}} \times 100
\]  

where, 

\(\text{RH}_{\text{in}}\) is the initial RH of humid air entering inlet 1 (Figure 2.5); and 

\(\text{RH}_{\text{out}}\) is the RH of dehumidified air coming out of outlet 2 (Figure 2.5).

It is worth noting that the \(\text{RH}_{\text{out}}\) was the value of the level-off stage when a steady-state was reached as shown in Figure 2.6.

2.3.4 Experimental Design

2.3.4.1 Selection of four factors

Four factors were investigated including temperature, air flow rate, RH, and vacuum pressure. Temperature (dry bulb), RH, and air flow rate were selected because they are three key parameters of the wood drying process, which vary with the drying schedule of different wood species. Since
a vacuum pump was used to generate a pressure difference between the two sides of the membrane in this study, the vacuum pressure was chosen as a factor. Table 2.1 lists the four factors and three levels of each factor.

Table 2.1: Factors and levels of each factor

<table>
<thead>
<tr>
<th>Factors</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Temperature (T), °C</td>
<td>25</td>
</tr>
<tr>
<td>Initial RH (RH), %</td>
<td>65</td>
</tr>
<tr>
<td>Air flow rate (FR), cm³/min</td>
<td>600</td>
</tr>
<tr>
<td>Vacuum Pressure (P), kPa</td>
<td>68</td>
</tr>
</tbody>
</table>

The temperatures of moist air were set in a low range of 25°C to 45°C due to the temperature limitation of the environmental chamber used in the lab and the maximum operating temperature for the air flow meter is 50°C. The levels of volumetric air flow rate were determined by the cross-sectional area of the inlet of the small PDMS membrane module and air velocity commonly circulated in the kiln, e.g. 23 m/min for drying Douglas fir.

2.3.4.2 Response surface methodology (RSM)

A response surface methodology (RSM) was used to design the experiment and analyze the data. RSM is a collection of mathematical and statistical techniques which is used to model and analyze problems in which a response of interest is influenced by several factors [25-27]. In this study, SPSS software (Version 25, IBM Corp [28]) was used to conduct the experimental design and statistical analysis. There were 29 testing combinations designed by using a Box-Behnken design model of RSM. The number of experiments is determined according to Eq. (2.2).

\[ N = 2k(k - 1) + cp \]  \hspace{1cm} (2.2)

where, \( k \) and \( cp \) are the number of factors and the number of the central point, respectively [29]. Each testing combination was replicated three times, generating a total of 87 testing runs. The mean of three replicates was used in the statistical analysis.
After completing all the tests, the relationships of the response (i.e., efficiency of moisture vapor removal) with the four factors were displayed in the form of a response surface plot based on the calculated results using a regression model. Meanwhile, the analysis of variance (ANOVA) was conducted using the mean of three replicates for each testing combination.

2.3.4.3 Experiment of verification of the regression model

To verify the regression model for the prediction of the efficiency of moisture vapor removal, a verification experiment was conducted at a temperature of 30°C, initial RH% of 70%, air flow rate of 700 cm³/min, and vacuum pressure of 74.5 kPa. These parameters were randomly selected within the range of each variable listed in Table 2.1, but they were different from the values used for developing the regression model. The test was replicated three times. The mean value of three replicates was compared with the result predicted by the regression model.

2.4 Results and Discussion

2.4.1 The Reduction of RH with Time

The experimental results show that all the curves share the same trend so that only representative curves with testing conditions labeled are plotted in Figure 2.6. It shows that the RH of the dehumidified air at the outlet 2 dropped quickly at the beginning (less than 5 mins into the run) after the membrane system started working and then reached a steady-state to maintain a constant RH during the remaining testing period. Since the RH at outlet 2 could reach a constant in such a short time, the testing period was set in 20 minutes. The durability and lifetime of the membrane system were not addressed in this study.
2.4.2 Effects of Test Variables on the Efficiency of Moisture Vapor Removal

2.4.2.1 Main Effects of Test Variables

The main effects of four factors are shown in Figure 2.7. The main effect of a specific factor was plotted as the other three factors were fixed at the medium level, as listed in Table 2.1. The results reveal that the efficiency of moisture vapor removal increased by approximately 75% with the increase of temperature from 25°C to 45°C and vacuum pressure from 68 kPa to 88 kPa, respectively. On the contrary, it decreased by approximately 25% with an increase in air flow rate from 600 cm³/min to 1000 cm³/min. Increasing the initial RH from 65% to 85% had little effect on the efficiency of moisture vapor removal.
Figure 2.7: Main effects of the four factors on the efficiency of moisture vapor removal. (The other three factors fixed at the medium level)

The influence of temperature on the moisture vapor removal may be explained by the difference in the kinetic energy of gas molecules at different temperatures. The kinetic energy of gas molecules at a high temperature is larger than that at a low temperature. Higher the temperature, the higher can be the mobility of moisture vapor molecules, increasing the number of such molecules absorbed at the surface of the membrane. The impact of temperature on the moisture vapor permeance has not been widely investigated in studies regarding PDMS membranes but in studies of other types of polymer-based membranes. Park et al. [30] revealed that the moisture vapor permeance of polyethyleneimine (PEI)/Polyether-block amide (PEBAX) composite hollow
fiber membrane increased with temperature from 50°C, 70°C, and 90°C. Metz [19] examined the influence of temperature on the permeability and selectivity of water vapor for poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) block co-polymers. They concluded that the permeability and selectivity for these block copolymers are temperature and structure dependent. However, because of the limitation of material supply, the permeability and selectivity of PDMS used in this study were not measured at different temperatures. They will be addressed in future work. The high vacuum pressure, in turn, generates a large difference in pressure between the two sides of the membrane, driving the moisture vapor molecules to diffuse from the high to the low concentration side. Regarding the air flow rate, the negative impact caused by increasing its value is due to a reduced residence time of the water vapor molecules when traveling on the tube side of the membrane module. Therefore, less water vapor molecules were absorbed by the membrane. Our results about the influence of vacuum pressure, air flow rate, and initial RH are in line with the water vapor removal results obtained from a polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) hollow fiber membrane system [7]. In their study, the water vapor permeability of a thin PDMS layer (about 3.61µm) was 13,335 Barrer. The efficiency of moisture vapor removal was approximately 50% as the initial RH was in the range of 60% to 90%, and the vacuum pressure was about 98 kPa. The 80% of moisture vapor was removed from the moist air as the feed flow rate was low to 400 cm³/min, while only 50% of moisture vapor was separated as the feed flow rate was high to 1000 cm³/min. The impact of temperature was not addressed in their study. The results presented in this study and literature indicate that to achieve a better performance of moisture removal, the desired operating settings of the membrane system are high temperature, high vacuum pressure, and low air flow rate.
2.4.2.2 Interaction Effects of Test Variables

The interaction effects of two of four factors on the efficiency of moisture vapor removal are plotted in terms of a response surface contour plot, as seen in Figure 2.8 (a-f). In each plot, the contour curves show the efficiency of water vapor removal at various levels of temperature, vacuum pressure, RH, and air flow rate predicted by a simplified regression model (adj. $R^2=0.947$), which will be discussed in the subsection of analysis of ANOVA. Each of these plots presents the effect of two factors on the efficiency. The remaining two factors were kept constant at their medium level (see Table 2.1).

The contour plot in Figure 2.8 (a) provides information about the trend of the efficiency of water vapor removal as a function of temperature and vacuum pressure. The constant initial RH and air flow rate were 75% and 800 cm$^3$/min, respectively. It reveals, for instance, that the increase in temperature from 25°C to 45°C led to an increase in efficiency from approximately 30% to 50% at a low vacuum pressure level of 68 kPa. At 45°C, if the vacuum pressure decreases from 88 to 68 kPa, the efficiency decreases from approximately 82% to 50%. The interaction of temperature and vacuum pressure can be beneficial in the membrane system design by using a vacuum pump with a variable speed drive to reduce the noticeable energy consumption of continuously running the pump. For example, during the drying process, the water vapor release rate, defined as the mass of water vapor per hour, decreases as the moisture content of lumber is below the fiber saturation point of lumber, which takes place at the last few steps of drying schedule. In this situation, the membrane system can be operated at a relatively low vacuum pressure but maintain an acceptable efficiency of water vapor removal.

Figure 2.8 (b) shows the contour plot of efficiency as a function of temperature and air flow rate at a constant vacuum pressure of 78 kPa and initial RH of 75%. The plot shows a decrease in the
efficiency of moisture vapor removal from approximately 44% to 35% as a consequence of an increase of flow rate from 600 cm$^3$/min to 1000 cm$^3$/min at a constant temperature level of 25°C. At the high temperature of 45°C, increasing the air flow rate from 600 cm$^3$/min to 1000 cm$^3$/min results in a decrease in the efficiency of moisture vapor removal from approximately 76% to 58%. This indicates that the temperature influences the mobility of gas molecules at any level of air flow rate.

Figure 2.8 (c) shows the contour plot of efficiency as a function of pressure and air flow rate at a constant temperature of 35°C and initial RH of 75%. The plot shows a decrease in the efficiency of moisture vapor removal from approximately 45% to 30% as a result of an increase of flow rate from 600 cm$^3$/min to 1000 cm$^3$/min at a constant vacuum pressure of 68kPa. As a result of high vacuum pressure at 88 kPa, a decrease in the efficiency of moisture vapor removal from approximately 70% to 58% is observed.

The contour plot in Figure 2.8 (d) provides information about the trend of the efficiency of moisture vapor removal as a function of temperature and initial RH when the vacuum pressure and air flow rate are set at 78 kPa and 800 cm$^3$/min, respectively. It can be observed that altering the initial RH does not significantly affect the efficiency of moisture removal at any temperature level. For instance, the differential in the efficiency of moisture vapor removal is approximately 4% as increasing RH from 65% to 85% at a temperature level of 35°C. This similar trend is observed in Figure 2.8 (e) and (f), which show the interaction effects of pressure and initial RH and air flow rate and initial RH on the efficiency of moisture vapor removal.
Figure 2.8: Effects of the interactions between two factors on the efficiency of moisture vapor removal. (The other two factors fixed at the medium level)
2.4.3 Analysis of Variance (ANOVA) and a Regression Model of Efficiency of Moisture Vapor Removal

The analysis of variance (ANOVA), which is based on the mean values of 29 testing runs with three repetitions for each run, is illustrated in Table 2.2. The statistical significance of each factor and their interactions is denoted by the p-value, the significance of which is 0.05. As shown in Table 2.2, the significant factors (p-value< 0.0001) include temperature, vacuum pressure, and air flow rate. However, initial RH (p-value=0.89) is not statistically significant for the efficiency of moisture vapor removal. In addition, the interaction of the temperature and vacuum pressure (p-value = 0.0273) is statistically significant for the efficiency of moisture vapor removal.

Table 2.2: Analysis of variance of test variables and their interactions

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Prob &gt; F</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>5297.53</td>
<td>14</td>
<td>378.40</td>
<td>28.41</td>
<td>&lt; 0.0001</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>2424.05</td>
<td>1</td>
<td>2424.05</td>
<td>182.01</td>
<td>&lt; 0.0001</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>1962.48</td>
<td>1</td>
<td>1962.48</td>
<td>147.35</td>
<td>&lt; 0.0001</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>RH</td>
<td>0.27</td>
<td>1</td>
<td>0.27</td>
<td>0.020</td>
<td>0.8887</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FR</td>
<td>551.19</td>
<td>1</td>
<td>551.19</td>
<td>41.39</td>
<td>&lt; 0.0001</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>T*P</td>
<td>80.88</td>
<td>1</td>
<td>80.88</td>
<td>6.07</td>
<td>0.0273</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>T*RH</td>
<td>0.99</td>
<td>1</td>
<td>0.99</td>
<td>0.074</td>
<td>0.7891</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T*FR</td>
<td>18.53</td>
<td>1</td>
<td>18.53</td>
<td>1.39</td>
<td>0.2578</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P*RH</td>
<td>8.40</td>
<td>1</td>
<td>8.40</td>
<td>0.63</td>
<td>0.4402</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P*FR</td>
<td>9.01</td>
<td>1</td>
<td>9.01</td>
<td>0.68</td>
<td>0.4245</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH*FR</td>
<td>0.92</td>
<td>1</td>
<td>0.92</td>
<td>0.069</td>
<td>0.7965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T²</td>
<td>0.54</td>
<td>1</td>
<td>0.54</td>
<td>0.041</td>
<td>0.8432</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P²</td>
<td>40.28</td>
<td>1</td>
<td>40.28</td>
<td>3.02</td>
<td>0.1040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH²</td>
<td>207.93</td>
<td>1</td>
<td>207.93</td>
<td>15.61</td>
<td>0.0014</td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>FR²</td>
<td>2.00</td>
<td>1</td>
<td>2.00</td>
<td>0.15</td>
<td>0.7040</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
According to the ANOVA analysis, a quadratic regression model was developed. The regression model shown in Eq. (2.3) is a simplified model by removing the items that have a p-value > 0.05 in Table 2.2. The adjusted $R^2$ value is 0.947. This regression model could be used to predict the efficiency of moisture vapor removal as the four factors are in the range defined in this study.

$$Efficiency, \% = -50.236 - 2.086 \times T + 2.324 \times P - 0.034 \times FR + 0.045 \times T \times P - 0.017 \times P^2 - 4.346^{-5} \times RH^2$$ \hspace{1cm} (adj. $R^2 = 0.947) \hspace{1cm} (2.3)$$

where,

$T =$ temperature, ranging from 20°C to 45°C;

$P =$ vacuum pressure, ranging from 68 kPa to 88 kPa;

$RH =$ initial RH, ranging from 65% to 85%; and

$FR =$ air flow rate, ranging from 600 cm$^3$/min to 1000 cm$^3$/min.
The plots of the distribution of residuals in Figure 2.9 are used to assess the goodness-of-fit in regression. The scatter plot of predicted values versus actual response values (Figure 2.9 a) shows that the data scattered symmetrically are close to the regressed 45° diagonal line, which indicates a good agreement between the predicted results and experimental ones. On the other hand, the normal probability plot of residuals (Figure 2.9 b) is approximately linear, which proves that the error terms are normally distributed. In addition, the plot of internally studentized residuals versus run numbers...
predicted (Figure 2.9 c) shows that the variation around the estimated regression line is uniform and there is no unusual data exceeding the upper and lower limits. As for the plot of internally studentized residuals versus run numbers (Figure 2.9 d), it also proves enough accuracy of the regression model because of the random dispersion of the residues and a good distribution of experimental results [31].

2.4.4 Verification of the Regression Model

The verification test was repeated three times. The mean ± standard deviation of the experimental result was 46.92±2.75%, while the value calculated by Eq. (2.3) is 43.69%. The experimental result is about 6.88% larger than the predicted one. It reveals that the regression model can be used to estimate the efficiency of the moisture vapor removal of the membrane system in the specified ranges of four factors.

2.5 Conclusions

In this study, a mini-scale PDMS membrane-based dehumidification system was constructed. The main effects and interactions effects of temperature, air flow rate, initial RH, and vacuum pressure on the efficiency of moisture vapor removal were investigated through experiments and statistical analysis. The major findings are outlined below:

1) Increasing the temperature and vacuum pressure could cause a significant increase in the efficiency of moisture vapor removal;

2) The initial RH had little influence on the efficiency of moisture vapor removal;

3) Increasing the air flow rate had a negative impact on the efficiency of moisture vapor removal; and

4) The simplified regression model could be used to predict the efficiency of moisture vapor removal.
The membrane-based dehumidification system demonstrates great potential to be used in the wood drying process and elsewhere that moisture management is a big concern, for instance, relatively humid indoor environment in the Southern U.S. The results found in this study indicate the PDMS membrane is only suitable for the low temperature drying process. This membrane system could be used in a dehumidification kiln drying process or as a pre-drying process before doing the conventional steam kiln drying. The future work of this study will address the limitations of low temperature tolerance of PDMS membrane to expand its application in the medium or high temperature drying process. One attempt will be adding cellulose nanocrystalline (CNC) into PDMS to increase the diffusion coefficient of the PDMS membrane and resistance to thermal degradation. The energy saving when applying the membrane dehumidification system will be discussed and compared with a heat pump dehumidification system in the following studies.
2.6 References


28. IBM SPSS statistics for Windows, version 25.0 I Spss - New York: IBM Corp, 2019


3 NUMERICAL SIMULATION OF THE WATER VAPOR SEPARATION OF A MOISTURE-SELECTIVE HOLLOW-FIBER MEMBRANE FOR THE APPLICATION IN WOOD DRYING PROCESSES

3.1 Chapter Summary

In this study, a simplified two-dimensional axisymmetric finite element analysis (FEA) model was developed, using COMSOL Multiphysics® software, to simulate the water vapor separation in a moisture-selective hollow-fiber membrane for the application of air dehumidification in wood drying processes. The membrane material was dense polydimethylsiloxane (PDMS). A single hollow fiber membrane was modelled. The mass and momentum transfer equations were simultaneously solved to compute the water vapor concentration profile in the membrane. A water vapor removal experiment was conducted by using a lab-scale PDMS hollow fiber membrane module operated at constant temperature of 35 °C. Three operation parameters of air flow rate, vacuum pressure, and initial relative humidity (RH) were set at different levels. The final RH of dehydrated air was collected and converted to water vapor concentration to validate simulated results. The simulated results were fairly consistent with the experimental data. Both experimental and simulated results revealed that the water vapor removal efficiency of the membrane system was affected by air velocity and vacuum pressure. A high water vapor removal performance was achieved at a slow air velocity and high vacuum pressure. Subsequently, the correlation of Sherwood (Sh)–Reynolds (Re)–Schmidt (Sc) numbers was established using the validated model, which is applicable at a constant temperature of 35 °C and vacuum pressure of 77.9 kPa. This study delivers an insight into the mass transport in the moisture-selective dense PDMS hollow fiber membrane-based air dehumidification process, with the aims of providing a useful reference to the scale-up design, process optimization using hollow fiber membrane materials.
3.2 Introduction

Fast developing and cutting-edge membrane separation technology has been widely used in environmental remediation, food, chemical, and pharmaceutical industries. The membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes that involve a phase change process, such as distillation, sublimation, or crystallization. Among a broad range of applications, dense membranes for vapor/gas separation (also called moisture-selective dense membranes) became popular in industrial separation applications since the serial production of commercial polymeric membranes was implemented in the 1980s [1]. Literature review reveals that many polymer-based membrane materials, such as polydimethylsiloxane (PDMS), poly ether-block-amide (PEBAX), sulfonated poly(ether ether ketone) (SPEEK), can be used for the removal of water vapor (dehumidification) from air or gas streams and therefore have been applied in certain air conditioning units to improve the energy saving of building systems [2–4]. The advantages of moisture-selective membrane technology include less energy consumption due to no phase change of water involved, simplicity in maintenance and operation, high selectivity, ease of scale up, and low initial cost [5,6].

In our previous study, we explored the potential application of moisture-selective polydimethylsiloxane (PDMS) membrane in the steam-kiln wood drying process since a considerable amount of water vapor and thermal energy is stored in exhaust air [7]. Recycling and reusing such waste thermal energy would improve the energy efficiency of the kiln-drying process. One solution was to dehydrate the water vapor in the hot and humid exhaust air and redirect the dehydrated hot air into the kiln to transport water vapor evaporated from the wood. In the lab-scale experiment, a hollow-fiber membrane-based air dehumidification system was set up and tested.
Compared with a plate-frame membrane module, the hollow-fiber membrane module was chosen due to its compact size and the extremely large surface area per unit volume of the membrane module [2,8]. A brief description of the system and its performance is described in the section of Materials and Methods. This study aims to investigate the mass transfer in the hollow-fiber membrane using a numerical simulation method and establish the correlation of Sherwood number (Sh), Reynolds number (Re) and Schmidt number (Sc). This correlation is key information to assist engineers in designing the proper size of the hollow-fiber module and suitable operation parameters for different capacities of wood drying kilns in order to achieve the fast removal of water vapor from humid air [9–13]. Ideally, this can be accomplished with mathematical models established based on mass transfer to simulate the operating conditions at industrial scale coupled with a combination of well-designed lab-scale experiments that target a similar performance at industrial scale as observed at lab-scale. Nowadays, mathematical models can be solved using a numerical analysis technique/software, such as COMSOL Multiphysics® software. The finite element analysis (FEA) based software has been widely used to create multiple physics-based models to simulate the movement of various entities, such as mass, momentum, or energy through a medium, fluid, or solid. The simulation of membrane separation processes (such as gas–gas, gas–liquid, liquid–solid, etc.) has been carried out by many researchers using the function of computational fluid dynamics (CFD) models [11,14–17]. However, only a couple of studies focused on the water vapor separation of polymeric-based hollow fiber membranes. One relevant study compared the water vapor concentration within a hollow fiber membrane modeled using a CFD model and a random walk approach [16]. In addition, the workload needed to drive the feed flow to estimate the energy consumption was calculated and discussed. The random walk approach showed results that were in good agreement.
with commercial CFD software and experimental data. The simulation outcome can be used to find the optimum working conditions for a hollow fiber membrane module. Another study employed a CFD model to simulate the pressure-driven water vapor separation in different hollow fiber composite membrane for air dehumidification [17]. The ultra-thin moisture selective dense layer of the composite membrane was modeled as a permeable barrier and its permeation was defined by the boundary conditions of the membrane domain. The velocity, pressure, and water vapor concentration profiles and mass transfer process in one single hollow fiber membrane were solved, verified, and analyzed.

As an effective technique, we also used the FEA method to study the mass transfer in the moisture selective dense PDMS hollow fiber membrane for air dehumidification in the process of energy saving in wood drying. An air dehumidification experiment was conducted to collect data of water vapor removal from the feed air stream, which was used for model validation. A two-dimensional axisymmetric FEA model was developed to simulate the mass transfer in one single hollow-fiber membrane. Then the modeling results of water vapor concentration at different feed air velocities were used to establish the correlation of Sh–Re–Sc. This correlation could be used for optimization and design of the hollow fiber membrane and to facilitate the industrial-scale application of PDMS hollow fiber membrane modules.

3.3 Materials and Methods

3.3.1 Materials

A polydimethylsiloxane (PDMS) membrane material was selected, which had a high water vapor permeability of 36,000 Barrer and an acceptable H₂O/N₂ selectivity of 129 [7,18]. A small hollow fiber PDMS membrane module with bundles of hollow fibers was purchased from PermSelect-MedArray Inc. Table 3.1 lists the geometric information of the membrane module and single
hollow fiber and the physical properties of PDMS membrane material, which were used as inputs in the FEA model.

Table 3.1: Geometric information of the hollow fiber membrane module and single hollow fiber and physical properties of PDMS membrane material.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total surface area [19]</td>
<td>1 m$^2$</td>
</tr>
<tr>
<td>Number of hollow fibers, n</td>
<td>12,600</td>
</tr>
<tr>
<td>Volume fraction, φ</td>
<td>0.887</td>
</tr>
<tr>
<td>Fiber inner radius, $r_1$ [19]</td>
<td>95 µm</td>
</tr>
<tr>
<td>Fiber outer radius, $r_2$ [19]</td>
<td>150 µm</td>
</tr>
<tr>
<td>Fiber wall thickness, T [19]</td>
<td>55 µm</td>
</tr>
<tr>
<td>Fiber length, L [19]</td>
<td>0.1 m</td>
</tr>
<tr>
<td>Diffusion coefficient of water vapor in PDMS membrane at 35 °C, $D_{w,m}$ [20,21]</td>
<td>$1.70 \cdot 10^{-8}$ m$^2$/s</td>
</tr>
<tr>
<td>Diffusion coefficient of water vapor in air at 35 °C, $D_{w,a}$ [22]</td>
<td>$2.67 \cdot 10^{-5}$ m$^2$/s</td>
</tr>
<tr>
<td>Solubility of water vapor in air at 35 °C, $S_{w,a}$ [23]</td>
<td>0.036 g/g$_{air}$</td>
</tr>
<tr>
<td>Solubility of water vapor in PDMS membrane at 35 °C, $S_{w,PDMS}$ [24]</td>
<td>$3.00 \cdot 10^{-4}$ g/g$_{polymer}$</td>
</tr>
</tbody>
</table>

3.3.2 Methods

3.3.2.1 Experimental Setup and Testing Procedure

As shown in Figure 3.1, the lab-scale membrane system was placed in a temperature- and RH-controlled environmental chamber. The humid air entered the membrane module through inlet 1. The air flow rate was controlled by an air blower and monitored by a mass/volume flow meter. The humid air passed through the lumen of hollow fibers and the dehydrated air came out of outlet 2, which was collected for the measurement of RH. The temperature and RH of both humid air and dehydrated air were monitored and recorded with time at an interval of 10 s by temperature and humidity sensors and a data logging system. The water vapor that permeated through the wall of hollow fibers came out of outlet 3 and outlet 4 and was expelled to the outside of the environmental chamber through a vacuum pump. The vacuum pump was equipped with a vacuum regulator and water vapor trap. Port 5 was blocked during the whole testing process. The RH values measured were then converted to water vapor concentrations in air.
Figure 3.1: Schematic of a lab-scale membrane air dehumidification system. Reproduced with permission from Reference [7].

Table 3.2: Experimental design of operating hollow-fiber membrane air dehumidification system.

<table>
<thead>
<tr>
<th>ID</th>
<th>Air Velocity, m/s</th>
<th>Vacuum Pressure, kPa</th>
<th>Initial RH</th>
<th>Initial Concentration of Water Vapor, $C_{w,in}$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.028</td>
<td>67.7</td>
<td>75%</td>
<td>1.72</td>
</tr>
<tr>
<td>2</td>
<td>0.037</td>
<td>67.7</td>
<td>65%</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>0.0465</td>
<td>67.7</td>
<td>75%</td>
<td>1.72</td>
</tr>
<tr>
<td>4</td>
<td>0.028</td>
<td>77.9</td>
<td>65%</td>
<td>1.48</td>
</tr>
<tr>
<td>5</td>
<td>0.037</td>
<td>77.9</td>
<td>75%</td>
<td>1.72</td>
</tr>
<tr>
<td>6</td>
<td>0.0465</td>
<td>77.9</td>
<td>85%</td>
<td>1.96</td>
</tr>
<tr>
<td>7</td>
<td>0.028</td>
<td>88.0</td>
<td>75%</td>
<td>1.72</td>
</tr>
<tr>
<td>8</td>
<td>0.037</td>
<td>88.0</td>
<td>65%</td>
<td>1.48</td>
</tr>
<tr>
<td>9</td>
<td>0.0465</td>
<td>88.0</td>
<td>75%</td>
<td>1.72</td>
</tr>
</tbody>
</table>

The hollow fiber membrane system was operated at a constant temperature of 35 °C. The variable operation parameters are air flow rate, vacuum pressure, and initial RH. A total of nine (9) combinations were designed, which are listed in Table 3.2. Each combination was repeated three (3) times. The air flow rate and initial RH were converted to air velocity and concentration of water vapor, which are the required inputs in the FEA model.
The efficiency of water vapor removal of the air dehumidification membrane was calculated from Eq. (3.1), which is used to compare the experimental results and modeling results [7].

Efficiency(%) = \( \frac{(C_{w,\text{in}} - C_{w,\text{out}})}{C_{w,\text{in}}} \times 100 \)  

(3.1)

where, \( C_{w,\text{in}} \) (mol/m\(^3\)) and \( C_{w,\text{out}} \) (mol/m\(^3\)) are the initial and final concentrations of water vapor in air, respectively.

### 3.3.3 Finite Element Analysis Modeling

#### 3.3.3.1 Physical Model of the Hollow Fiber Membrane

Figure 3.2 illustrates a schematic of a hollow fiber membrane module for air dehumidification and the three domains of tube, membrane, and shell, which are divided into one single hollow fiber membrane. In general, the air dehumidification process is accomplished by both convective and diffusive mass transfer, which is regarded as an isothermal process. Water vapor and air are regarded as ideal gases. As the humid air flows inside the tube (i.e., lumen) of the fiber, the air transports along the length of the fiber at a constant flow rate. Gas species diffuse in the tube along the fiber direction and in the membrane across the wall thickness of the fiber [25]. Diffusion in the membrane follows Fick’s first law. A well-known solution-diffusion mechanism is used to describe gas/vapor separation in dense membrane [1]. Gas molecules are first adsorbed to the surface of the inner wall of the membrane and then they diffuse in the membrane and migrate to the surface of the outer wall of the membrane. On the shell domain, the gas molecules are desorbed from the outer wall of the membrane by applying a vacuum pressure. The mass transport process is convection dominated in the tube and shell domains, and diffusion dominated in the membrane. The latter is not affected by the bulk flow of the air stream. Because of the higher solubility and diffusivity of water vapor molecules (H\(_2\)O) in the membrane, H\(_2\)O in humid air can transport across the membrane layer to the shell domain more quickly and easily than nitrogen (N\(_2\)) and oxygen.
(O₂) molecules at the same condition. Hence, a majority of N₂ and O₂ are retained in the tube domain to achieve the goal of air dehumidification.

Based on the assumption of the homogenous geometry and material of all hollow fiber membranes and a uniform distribution in the module, the simulation of water vapor transfer is simplified to model a single hollow fiber. A cylindrical coordinate system is used in the FEA model: z-axis is along the length direction of the fiber and r-axis is along the radius direction of the hollow fiber.

3.3.3.2 Governing Equations of Mass Transfer

The convection mass transfer in a hollow fiber membrane can be described using a general continuity equation that complies with the law of mass conservation [16,26,27], in Eq. (3.2).

\[
\frac{\partial C_i}{\partial t} = - (\nabla C_i V) - (\nabla J_i) + R_i
\] (3.2)

where, \(C_i\) (mol/m³), \(J_i\) (mol/(m²·s)), \(V\) (m/s) and \(t\) (s) are concentration, diffusive flux, velocity and time, respectively. \(i\) denotes the gas species in air. \(R_i\) is the reaction rate of species \(i\), which is zero because no chemical reaction is involved in the air dehumidification process [15,23,24].

In this study, water vapor is the target gas species, i.e., \(i = w\) is used in the following discussion.

Under the steady-state mass transfer, i.e., Fick’s first law, Eq. (3.3) can be simplified as follows:
\[ V_z \frac{\partial c_w}{\partial z} = D_{w,j} \left[ \frac{1}{r} \frac{\partial c_w}{\partial r} + \frac{\partial^2 c_w}{\partial r^2} + \frac{\partial^2 c_w}{\partial z^2} \right] \]  

where, \( V_z \) (m/s) is the velocity of air in z direction. \( c_w \) (mol/m\(^3\)) is the concentration of water vapor. \( D_{w,j} \) is the diffusion coefficient of water vapor in a substrate (\( j = a \) as in air; \( m \) as in membrane). \( r \) and \( z \) refer to the radial and axial coordinates, respectively, as shown in Figure 3.2.

The velocity distributions in the tube and shell domains are obtained by solving Navier–Stokes equation [25], Eq. (3.4):

\[ \rho \frac{\partial \vec{V}}{\partial t} = -\nabla P + \mu \nabla^2 \vec{V} + \rho g \]  

where, \( \rho \) (kg/m\(^3\)) is the density of air. \( V \) (m/s) is the velocity of air. \( P \) (kPa) is pressure. \( \mu \) (kg/(m·s)) is the viscosity of air. \( g \) (m/s\(^2\)) is the standard acceleration due to gravity.

Specially, the velocity distribution of air in the tube domain is regarded to follow the Newtonian laminar flow because the Re number calculated using the experimental data ranges from 0.32 to 0.53 (\( \leq 2300 \)).

In the membrane domain, only water vapor diffusion governs the vapor transfer. Therefore, the velocity in the membrane domain is zero.

The boundary conditions applied in the hollow fiber system are described below:

**Tube side/domain:**

At \( z = L \), \( c_w = c_{w,\text{in}} \)  

Henry’s Law is applied to the interface of air (in the tube) and the inner wall surface of membrane [25], [26], [28]:

At \( r = r_1 \), \( c_{w,m} = K \times c_{w,t} \)  

(No slip condition)

where, \( K \) is a partition coefficient of water vapor in two phases of gas (i.e., air) and solid (i.e., membrane), which is determined by the solubility of water vapor in the gas and solid phases [29]–[33], Eq. (3.7).
\[
\log K = \log S_{w,PDMS} - \log S_{w,air} \tag{3.7}
\]

where, \( S_{w,a} \) is the solubility of water vapor in air and \( S_{w,PDMS} \) is the solubility of water vapor in the PDMS membrane material used in this study.

At \( r = 0 \), \( \frac{dC_{w,t}}{dr} = 0 \) (Symmetry) \( \tag{3.8} \)

**Membrane domain:**

At \( r = r_2 \), \( C_{w,m} = C_{w,s} \) (No slip condition) \( \tag{3.9} \)

**Shell domain:**

At \( z = 0 \), \( V_z = 0 \), \( C_{w,s} = 0 \) \( \tag{3.10} \)

At \( z = L \), \( P = P_{\text{Vacuum}} \) \( \tag{3.11} \)

At \( r = r_3 \), \( \frac{dC_{w,s}}{dr} = 0 \) (Symmetry boundary; No slip condition) \( \tag{3.12} \)

### 3.3.3.3 Geometry and Mesh Generation of FEA Model and Numerical Solution

An FEA model was developed via COMSOL software with a Computational Fluid Dynamics (CFD) module (COMSOL Multiphysics Version 5.4). As shown in Figure 3.3, a 2D-axisymmetric geometry was built to model the three domains of tube, membrane, and shell. The inner radius \( r_1 \) and outer radius \( r_2 \) of the tube are 95 µm and 150 µm, respectively. The radius of the shell domain \( r_3 \) is 350 µm, which was calculated using Happel’s free surface model, Eq. (3.13) [25]. The total length \( L \) modeled is 0.1 m. The inlet of the tube domain for the humid air was set at \( z = L \) (i.e., \( C_w = C_{w,\text{in}} \)), while the outlet of the tube domain for dehydrated air was set at \( z = 0 \). On the shell domain, the constant vacuum pressure was set at \( z = L \) (i.e., \( P = P_{\text{Vacuum}} \)). A fine mesh size was chosen after doing a mesh convergence analysis and a total of about 70,000 mesh elements was created in the FEA model. Figure 3.3 shows a segment of the meshed geometry due to the extremely large length to radius ratio.
\[ r_3 = r_2 \times \left( \frac{1}{1 - \varphi} \right)^{1/2} \]  

(3.13)

where, \( \varphi \) is the volume fraction of the voids in the hollow fiber membrane module.

The simulation domains were solved by setting two physical modes in COMSOL software, namely, the laminar flow mode and the transport of vapor/gas species mode. The velocity field and the concentration field applied to the three domains were coupled and solved simultaneously. The static finite element analysis combined with error control was conducted with the PARDISO solver, which is a linear direct numerical solver. The convergence criteria were set to \( 10^{-8} \). As a result of simulation calculation, the concentration distribution of water vapor in the three domains was obtained.

![Figure 3.3: Schematic of a segment of the half longitudinal section of a single fiber mesh distribution.](image)

3.3.4 Correlation of Sh–Re–Sc

The correlation relationship of Sh–Re–Sc numbers is established in the form of an exponential mathematical model [34], Eq. (3.14).

\[ \text{Sh} = A \text{Re}^B \text{Sc}^C \]  

(3.14)

where, A, B, and C are constants. Sh, Re and Sc numbers are calculated in Eq. (3.15)–(3.17) [8,35].

\[ \text{Sh} = \frac{k_1 D}{D_{w,a}} \]  

(3.15)
\[ \text{Re} = \frac{\rho V D}{\mu} \]  
\[ \text{Sc} = \frac{\mu}{\rho D} \]  

The performance of a segment of the membrane for each condition can be used to obtain the overall mass transfer coefficient \( (k_o) \) given in Eq. (3.18) and derived in the Appendix A [8,25,36]. If the diffusion through the membrane is put in terms of a mass transfer coefficient of the membrane \( (k_m) \) as in Eq. (3.19), \( k_o \) is a sum of resistances given in Appendix A. The shell side coefficient \( (k_s) \) is found to be small compared to the others. Therefore, the overall and membrane coefficient \( (k_o \text{ and } k_m) \) can be used to calculate the tube side mass transfer coefficient \( (k_t) \) for the particulate conditions in the FEA given in Eq. (3.20).

\[ k_o = \frac{D V z}{4 L} \ln \frac{C_{w,\text{out}}}{C_{w,\text{in}}} \]  
\[ k_m = \frac{D_{w,m}}{T} \]  
\[ k_t = \frac{k_o \times k_m}{k_m - k_o} \]

where, \( D \) (m) is the diameter of one fiber.

### 3.4 Results and Discussion

#### 3.4.1 Experimental Results

The PDMS membrane system could quickly remove the water vapor from the air. It was observed that a significant drop of RH occurred in the first five minutes and then the RH remained constant at a lower value. The duration of each run was 30 min. The averaged RH value of dehydrated air calculated using the data collected in the last ten minutes was converted to the concentration of water vapor and used in the following discussion. A summary of the final concentrations of water vapor in dehydrated air (mean and standard derivation (SD) values) is provided in Table 3.3.
Table 3.3: Summary of experimental and modeling results.

<table>
<thead>
<tr>
<th>ID</th>
<th>Air Velocity, m/s</th>
<th>Vacuum Pressure, kPa</th>
<th>Initial Concentration of Water Vapor, C_{w,in} (mol/m³)</th>
<th>Final Concentration C_{w,out} (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental Results</td>
</tr>
<tr>
<td>1</td>
<td>0.028</td>
<td>67.7</td>
<td>1.72</td>
<td>0.88 ± 0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.037</td>
<td>67.7</td>
<td>1.48</td>
<td>1.12 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.0465</td>
<td>67.7</td>
<td>1.72</td>
<td>1.19 ± 0.01</td>
</tr>
<tr>
<td>4</td>
<td>0.028</td>
<td>77.9</td>
<td>1.48</td>
<td>0.64 ± 0.01</td>
</tr>
<tr>
<td>5</td>
<td>0.037</td>
<td>77.9</td>
<td>1.72</td>
<td>0.91 ± 0.02</td>
</tr>
<tr>
<td>6</td>
<td>0.0465</td>
<td>77.9</td>
<td>1.96</td>
<td>0.98 ± 0.02</td>
</tr>
<tr>
<td>7</td>
<td>0.028</td>
<td>88.0</td>
<td>1.72</td>
<td>0.52 ± 0.03</td>
</tr>
<tr>
<td>8</td>
<td>0.037</td>
<td>88.0</td>
<td>1.48</td>
<td>0.73 ± 0.03</td>
</tr>
<tr>
<td>9</td>
<td>0.0465</td>
<td>88.0</td>
<td>1.72</td>
<td>0.78 ± 0.04</td>
</tr>
</tbody>
</table>

3.4.2 FEA Modeling Results

Water Vapor Concentration Profile in Three Domains

Figure 3.4 illustrates the concentration distribution of water vapor in a hollow fiber membrane under the operation condition No. 5 in Table 3.3. It is pointed out that, for demonstration only, the direction of fiber length was scaled down by 200X due to an extremely large ratio of a single fiber length and radius. In the tube domain, the humid air with an initial water vapor concentration of 1.72 mol/m³ flows from the top edge of the tube domain (at z = L), while dehydrated air with a final water vapor concentration of 0.79 mol/m³ flows out from the bottom edge of the tube domain (at z = 0). The decrease of water vapor concentration along the fiber length is plotted in Figure 3.5, which data was extracted by averaging the results of water vapor concentration at the same height of the fiber length direction in the tube domain. It reveals that the drop of water vapor concentration with the fiber length follows an exponentially decreasing trend. In the membrane domain, the concentration of water vapor varies from 0 to 0.016 mol/m³. Across the thickness of the membrane, the decrease in the concentration of water vapor is clearly observed. In the shell domain, the water
vapor concentration is approximately zero, denoted by the scale bar in Figure 3.4. The water vapor concentration distribution is in line with the results discussed in other studies related to membrane separation [16,25].

Figure 3.4: Distribution of concentration of water vapor in three domains of a hollow fiber membrane (air velocity = 0.037 m/s, initial concentration of water vapor = 1.72 mol/m³, and vacuum pressure = 77.9 kPa).

Figure 3.5: Axial concentration distribution of water vapor in the tube domain of hollow fiber membrane (air velocity = 0.028 m/s, initial concentration of water vapor = 1.72 mol/m³, and vacuum pressure = 67.7 kPa).
3.4.3 Model Validation

To validate the modeling results, the water vapor concentration of the dehydrated air was obtained by using an averaged value of water vapor concentration distributed along the bottom edge (at $z = 0$) of the tube domain. The average results are listed in Table 3.3. The data in Table 3.3 were used to calculate the efficiency of water vapor removal. Both the simulated and experimental results are plotted in Figure 3.6. Overall, the experimental results are lower than the modeling simulated results to different degrees. It is noticeable that the difference between the experimental results and simulated results is reduced with the increase of air velocity, regardless of vacuum pressure and initial water vapor concentration. This is acceptable since the FEA model was developed based on assumptions made for ideal situations and some parameters in the model were from reference articles. Meanwhile, slight fluctuations of temperature and RH were observed during the testing. Both the experimental results and simulated results show the same trend of the influence of two operation parameters, air velocity and vacuum pressure, in the water vapor removal efficiency. The best performance of water vapor removal efficiency was achieved at the lowest air velocity (i.e., 0.028 m/s) and highest vacuum pressure (i.e., 88 kPa) applied. Increasing air velocity from 0.028 m/s to 0.0465 m/s resulted in a slight decrease by approximately 25% in the efficiency at the lowest vacuum pressure of 67.7 kPa. As increasing the vacuum pressure to 88 kPa, the decrease in efficiency due to the increase of air velocity was reduced to about 15%. A detailed discussion on the influence of operation parameters on the efficiency was given in our previous study [7]. The FEA model developed in this study is in good agreement with the experimental values for different values of air velocity and vacuum pressures.
3.4.4 Correlation Relationship of Sh–Re–Sc Numbers

The verified FEA model was further used to assist in establishing a correlation relationship of Sh–Re–Sc numbers at a constant initial water vapor concentration of water vapor (i.e., 1.72 mol/m$^3$), temperature (35 °C) and vacuum pressure (77.9 kPa) that is applied at the shell domain of the membrane system. These parameters were set as constant because the initial water vapor had little influence in the water vapor removal efficiency of the membrane and the temperature and vacuum pressure represented the medium level of operation conditions [7]. Only the inlet air velocity was set in a broad range of 0.019 m/s to 0.075 m/s at an interval of 0.009 m/s. The final water vapor concentration of dehydrated air was calculated using the FEA model. Eq. (3.14)–(3.20) were used to establish the correlation of Sh–Re–Sc in Figure 3.7. Among three constants of A, B, and C in Eq. (3.14), A and B were obtained by doing a regression analysis. Constant C, the power of Sc number, was set as 0.33, which was determined based on literature that studied similar hollow fiber membrane modules [8,35,37].

Figure 3.7 illustrates the correlations of Sh–Re–Sc in other studies [8,35,37]. The two studies regarding the hollow-fiber membrane module system developed a 2-D FEA model to simulate the fluid flow and mass transfer in hollow fiber membrane systems [8,35]. The FEA modeling was
used in the analysis of the correlation of Sh–Re–Sc. Another study regarding oxygen-liquid water separation of hollow fiber membrane module system discussed the mass transfer and the correlation of Sh–Re–Sc in terms of an experimental approach [37]. Although the FEA model developed in this study is a simplified model (one hollow fiber model), the simulated results are fairly acceptable, and the model can be used for membrane material screening and geometry optimization analysis. The correlation of Sh–Re–Sc numbers using the data set calculated by FEA model is presented in Eq. (3.21). It can be seen in Figure 3.7 that the correlation obtained from the FEA model, is compatible with the correlations obtained from previous studies.

\[
\text{Sh} = 1.45 \text{Re}^{0.34} \text{Sc}^{0.33}
\]  

(3.21)

Figure 3.7: Correlation among Re, Sc and Sh numbers, based on both of the modeling results and experimental results of this study and the results of previous studies.

3.5 Conclusions

In this study, a simplified two-dimensional axisymmetric finite element analysis model was developed, using COMSOL Multiphysics® software, to investigate the water vapor separation of a dense PDMS hollow fiber membrane module system for air dehumidification with potential applications in wood drying processes. In the FEA model, one single hollow-fiber was modelled. The convection mass transfer was calculated using a continuity equation and a momentum
equation accompanied by well-defined boundary conditions. The water vapor concentration of dehydrated air obtained by solving the coupled equations using the finite element analysis model agreed well with the experimental data with a difference of less than 20%. The validated model was then used to calculate the mass transfer coefficient of water vapor and Sherwood number. The water vapor removal efficiency of the membrane system was affected by air velocity and vacuum pressure. A high water vapor removal performance was achieved at a slow air velocity and high vacuum pressure. A correlation of Sh–Re–Sc was also established using modeling results. The FEA model and relevant findings could be used in the design, process optimization and module development using hollow fiber membrane.

Table 3.4: Abbreviation

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>constant parameter</td>
</tr>
<tr>
<td>B</td>
<td>constant parameter</td>
</tr>
<tr>
<td>C</td>
<td>constant parameter</td>
</tr>
<tr>
<td>$C_{w,\text{in}}$</td>
<td>concentration of water vapor in the inlet air</td>
</tr>
<tr>
<td>$C_{w,\text{out}}$</td>
<td>concentration of water vapor in the outlet air</td>
</tr>
<tr>
<td>$C_{w,j}$ (mol/m$^3$)</td>
<td>concentration of water vapor in tube</td>
</tr>
<tr>
<td>$C_{w,a}$ (mol/m$^3$)</td>
<td>concentration of water vapor in air</td>
</tr>
<tr>
<td>$C_{w,s}$ (mol/m$^3$)</td>
<td>concentration of water vapor in shell</td>
</tr>
<tr>
<td>$C_{w,m}$ (mol/m$^3$)</td>
<td>concentration of water vapor in membrane</td>
</tr>
<tr>
<td>$C_{i}$ (mol/m$^3$)</td>
<td>concentration of $i$ species</td>
</tr>
<tr>
<td>$C_{w}$ (mol/m$^3$)</td>
<td>concentration of water vapor</td>
</tr>
<tr>
<td>D (m)</td>
<td>diameter of one fiber</td>
</tr>
<tr>
<td>$D_{w,j}$</td>
<td>diffusion coefficient of water vapor in a substrate</td>
</tr>
<tr>
<td>$D_{w,a}$ (m$^2$/s)</td>
<td>diffusion coefficient of water vapor in air</td>
</tr>
<tr>
<td>$D_{w,m}$ (m$^2$/s)</td>
<td>diffusion coefficient of water vapor in membrane</td>
</tr>
<tr>
<td>g (m/s$^2$)</td>
<td>standard acceleration due to gravity</td>
</tr>
<tr>
<td>i</td>
<td>denotes the gas species in air</td>
</tr>
<tr>
<td>$J_{i}$ (mol/m$^2$s)</td>
<td>diffusive flux</td>
</tr>
<tr>
<td>k</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>K</td>
<td>partition coefficient of water vapor in two phases</td>
</tr>
<tr>
<td>$k_{m}$ (m/s)</td>
<td>membrane side mass transfer coefficient</td>
</tr>
<tr>
<td>$k_{o}$ (m/s)</td>
<td>overall mass transfer coefficient</td>
</tr>
<tr>
<td>$k_{s}$ (m/s)</td>
<td>shell side mass transfer coefficient</td>
</tr>
<tr>
<td>$k_{t}$ (m/s)</td>
<td>tube side mass transfer coefficient</td>
</tr>
<tr>
<td>L (m)</td>
<td>fiber length</td>
</tr>
<tr>
<td>n</td>
<td>number of hollow fibers</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>P (kPa)</td>
<td>pressure</td>
</tr>
<tr>
<td>(P_{\text{vacuum}}) (kPa)</td>
<td>vacuum pressure</td>
</tr>
<tr>
<td>R</td>
<td>radial direction</td>
</tr>
<tr>
<td>(r_1) (µm)</td>
<td>inner radius of the fiber</td>
</tr>
<tr>
<td>(r_2) (µm)</td>
<td>outer radius of the fiber</td>
</tr>
<tr>
<td>(r_3) (µm)</td>
<td>radius of the shell</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>(R_i)</td>
<td>reaction rate of species i</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>(S_{\text{w,air}})</td>
<td>solubility of water vapor in air</td>
</tr>
<tr>
<td>(S_{\text{w,PDMS}})</td>
<td>solubility of water vapor in PDMS</td>
</tr>
<tr>
<td>T (µm)</td>
<td>thickness of the membrane</td>
</tr>
<tr>
<td>t (s)</td>
<td>Time</td>
</tr>
<tr>
<td>(\bar{V})</td>
<td>average velocity of the fluid inside the tube</td>
</tr>
<tr>
<td>V (m/s)</td>
<td>velocity</td>
</tr>
<tr>
<td>(V_z) (m/s)</td>
<td>velocity of air in z direction</td>
</tr>
<tr>
<td>(V_{z,\text{shell}}) (m/s)</td>
<td>velocity of air in the shell in z direction</td>
</tr>
<tr>
<td>(V_{z,\text{tube}}) (m/s)</td>
<td>velocity of air in the tube in z direction</td>
</tr>
<tr>
<td>w</td>
<td>water vapor</td>
</tr>
<tr>
<td>Z</td>
<td>axial direction</td>
</tr>
<tr>
<td>Greek:</td>
<td></td>
</tr>
<tr>
<td>(\rho) (kg/m³)</td>
<td>density of air</td>
</tr>
<tr>
<td>(\mu) (kg/(m.s))</td>
<td>viscosity of air</td>
</tr>
<tr>
<td>(\varphi)</td>
<td>volume fraction</td>
</tr>
</tbody>
</table>
3.6 References


34. Cabe, W.L.M.; Smith, J.C.; Harriott, P.; University, N.C.S.U.C. Unit Operation of Chemical Engineering. **2018**.


4 INFLUENCE OF CELLULOSE NANOCRYSTAL (CNC) IN POLYDIMETHYLSILOXANE (PDMS) MEMBRANES FOR WATER VAPOR/AIR SEPARATION AT ELEVATED TEMPERATURES

4.1 Chapter Summary

This research study aimed to develop a type of dense composite membrane made of cellulose nanocrystals (CNCs) and polydimethylsiloxane (PDMS) to efficiently separate water vapor from exhaust moist warm air at elevated temperatures up to 80 °C such that the air recovers its drying capability and can be recirculated as the working medium. The study synthesized CNC/PDMS membranes using a CNCs suspension, PDMS prepolymer, and curing agent; 2) optimized the concentration of CNC in the membranes to achieve the best performance of water vapor separation at different temperatures, 3) characterized the PDMS and newly synthesized CNC/PDMS membranes using AFM, FTIR, TMA, and SEM, and 4) measured the CTE of the prepared samples to study the dimensional stability as a function of temperature change. First, an appropriate amount of the CNCs suspension was added to a mixture of the PDMS prepolymer and curing agent at a weight concentration of 0%, 2%, 4%, and 6%. A casting method was used to fabricate membrane samples. The water vapor permeability of the membrane samples was measured with a Payne diffusion cell (dry cup method) coupled with a Dynamic Vapor Sorption (DVS) instrument, while the nitrogen gas permeability was measured with a gas permeation cell. The results showed that the optimal addition of 2% CNCs to the PDMS increased both water vapor and nitrogen gas permeability of the membrane over three different temperatures, but the selectivity was not significantly improved. FTIR spectra, SEM, and AFM images showed the existence and morphology of CNC in PDMS. TMA results proved that the addition of 2% CNC reduced the coefficient of thermal expansion (CTE) of PDMS by about 9%. 

69
4.2 Introduction

Recently, membrane separation technology for air dehumidification has become an interesting topic for researchers and industry. Water vapor is separated from the air through a dense membrane without any phase change or temperature change, so this process is also known as an isothermal membrane-based air dehumidification (IMAD) process [1]. IMAD has been applied in many industries, in which require moisture control during the manufacturing process, such as a drying step in food industries, chemical industries, pharmaceuticals and more [2], [3]. Moreover, when it is combined with other units, such as heating, ventilation, and air conditioning (HVAC) units in building systems, pre-air dehumidification could achieve cooling energy saving [4]. Similarly, it could be a potential energy-saving technology in wood drying processes [5]. Wood drying is an energy-demanding process that requires heat to warm up the air which circulates through a stack of lumber to remove its moisture [6]. After absorbing the moisture, the air in dry kilns is saturated and should be vented as exhaust. Fresh and cold air is introduced to the kiln; however, it once again needs extra energy to be heated [7], [8]. In contrast, if applying an air dehumidification membrane system to a dry kiln, it could remove the moisture from saturated air without any phase change, thereby allowing the warm air to be recycled into the system, retaining heat. The dehumidified air, which is still at a high temperature, can return to the drying system to run another cycle of drying [5].

Many polymer-based membrane materials, such as polydimethylsiloxane (PDMS), Polyether-block-amide (PEBAX), and Sulfonated poly(ether ether ketone) (SPEEK), can be used to make a dense membrane for air dehumidification [4]. Among these materials, PDMS is commercially used in IMAD systems because of its low cost, chemical stability, nontoxicity, and good processability. When it is fabricated as a hollow-fiber form, PDMS tubular membranes have a high ratio of surface
area to volume and are ease of scale-up [5], [9]. However, most polymeric materials, including PDMS, are avoided in the working environment with a temperature greater than 50°C. For instance, in the study of flue gas dehydration using PEBAX®1074 and sulfonated SPEEK membrane materials, field tests were carried out when the temperature of flue gas was cooled below 50°C [10]. In another study, feed gas streams are cooled solely to accommodate a membrane gas separation process, and then they are heated back up [11]. Reducing the gas temperature and then heating it up add extra cost and energy to the process [11], [12].

In most softwood drying processes, the temperature of the air increases up to about 82°C [6]. Therefore, when testing the suitability of membranes for dehumidifying the exhaust air, it is important to address the influence of temperature on membrane’s performance (permeability and selectivity) instead of solely focusing on thermal stability/degradation analysis [13]. The performance of polymeric membrane materials can be improved by adding nanomaterials [12], ZnO [14], TiO₂ [15], SiO₂ [16], titanate nanotubes (TNTs) [17], Zeolite [18], [19] and more. However, most of these nanoparticles are non-sustainable and in some cases are petroleum based.

Cellulose nanocrystals (CNCs), a class of nanomaterials with dimensions of 100-300 nm long and 5-70 nm in diameter derived from sustainable and renewable lignocellulosic biomass, can solve environmental problems related to other inorganic nanoparticles by serving as nature's storage for carbon dioxide. It has many attractive features, such as large specific surface area, high tensile strength and stiffness, abundance of surface hydroxyl groups, extremely low coefficient of thermal expansion (CTE), and more [20]-[23]. So, it has been used to substitute for inorganic nanoparticles (such as TiO₂, Al₂O₃) in film-type composites as reinforcement fillers to improve the strength, thermal expansion stability, optical property, etc. of the composites [24].
When the solution-diffusion mechanism governs gas diffusion in the dense polymeric membranes, the gas molecules dissolve into a membrane, diffuse across the membrane thickness, and then desorb from the other side of the membrane [5]. This study aimed to develop a high-performance composite membrane for air dehumidification at elevated temperatures for wood drying applications. CNCs were chosen as an additive to PDMS because of two hypotheses: 1) the surface hydroxyl groups of CNCs could increase the moisture adsorption sites in the PDMS membrane to improve the solubility of water vapor on the membrane surface and create a large water vapor concentration difference for a fast diffusion and 2) CNC's low thermal expansion attribute could restrain the PDMS thermal expansion at elevated temperatures if CNCs disperse in PDMS uniformly.

To achieve the goal, four objectives of this study were to 1) synthesize CNC/PDMS membranes using CNC suspension with four concentrations (0%, 2%, 4%, and 6%); 2) measure the water vapor permeability, nitrogen gas permeability, their selectivity, and coefficient of thermal expansion of the membrane samples at three different temperatures (25°C, 50°C, and 80°C); 3) characterize the morphology of the membrane samples, and 4) determine the optimal CNC concentration for making a high-performance CNC/PDMS composite membrane.

4.3 Materials and Methods

4.3.1 Materials

PDMS prepolymer and curing agent kits (Dow SYLGARDTM 184 Silicone Elastomer kit) were purchased from Dow Inc. (MI, USA). A CNC suspension at 11.8% solids was purchased from the USDA Forest Products Laboratory, distributed by the Process Development Center of the University of Maine (ME, USA). CNCs were subjected to comprehensive characterization in a previous study [25]. The results of the study revealed that the CNC particles had an average length
of 134 ± 52 nm and a width of 7 ± 2 nm. The aspect ratio of the particles was determined to be 19. Additionally, the study reported a sulfate half-ester (-OSO$_3$-) content of 335 mmol kg$^{-1}$ for the CNCs.

4.3.2 Methods

4.3.2.1 Synthesis of membranes

The PDMS prepolymer and curing agent at the ratio of 10:1 by weight (e.g., 10 grams of PDMS prepolymer and 1 gram of curing agent) was mixed mechanically for 5 minutes at room temperature. The solution was degassed for 45 seconds with a planetary centrifugal bubble free mixer (THINKY ARE-310, Tokyo, Japan). Then the solution was cast on a Teflon plate using a casting knife. The wet film had a nominal thickness of 150 μm. The wet film was cured in an oven at 50°C for 24 h. The pure PDMS was used as control group (i.e., 0% CNC).

For making CNC/PDMS membranes, ten (10) grams of the PDMS prepolymer and 1 gram of the curing agent were mixed mechanically for 5 minutes at room temperature. Appropriate amount of CNC suspension was added to the 11-gram solutions to achieve the CNC solid concentrations of 2%, 4%, and 6% in total solids, respectively. The mixture was then mechanically mixed for 1 hour, a fine mixture obtained at this point, degassed for 45 seconds, and cast on a Teflon plate using a casting knife to obtain a wet membrane with a nominal thickness of 130 and 150 μm for Pure PDMS and CNC/PDMS films, respectively [26], [27]. The wet membranes were first dried at room temperature in a vacuum desiccator with a vacuum pressure of 88 kPa for 1 hour, intended to remove any remaining air bubbles in the wet membranes. After that, the semi-cured membranes were transferred to an oven and cured at 50 °C for 24 h [26]. The thickness of dry film samples was measured using a digital micrometer (Mitutoyo, IL, USA) with an accuracy of 0.001 mm. Multiple measurements were performed to determine the average thickness of the film samples.
4.3.2.2  
**Scanning electron microscopic (SEM) analysis**

The morphology of the CNC/PDMS membrane samples was observed using a scanning electron microscope (SEM) (NVision 40, Zeiss, Germany). The sample was placed on a specimen mount using carbon tape and then was coated with conductive silver. The regions of interest of the sample were sputter coated with gold (23 nm) using a Cressington 108 auto sputter coater (Ted Pella Inc., Redding, CA, USA). The images were taken at an accelerating voltage of 3 kV.

4.3.2.3  
**Atomic Force Microscopy (AFM) analysis**

The PDMS and CNC/PDMS samples were cut into 5 mm x 5 mm areas for observation on an AFM (MFP-3D, Oxford Instruments Oxon, UK). Images were collected with an AC200TS-R3 probes with 9 ± 6 (nN/nm) spring constants. Alternating current mode produced images with a set point of (0.4 V) and constant free air amplitude of (1 V).

4.3.2.4  
**ATR-FTIR analysis**

The ATR-FTIR analysis was performed using a PerkinElmer Spectrum Two™ FTIR spectrometer (Shelton, CT, USA) to evaluate the nature of the interaction between the CNCs and PDMS in the membranes. Each sample was measured at a resolution of 4 cm⁻¹. The data were obtained under an accumulation of 16 scans in the range of 450-4000 cm⁻¹.

4.3.2.5  
**Measurement of water vapor permeability of membranes**

The water vapor transmission rate (WVTR) was measured using a dynamic vapor sorption (DVS) instrument (Model: DVS Advance; Surface Measurement Systems, London, UK) as shown in Figure 4.1. The sample was placed to seal a Payne cell. Silicone gel beads were placed in the cell to absorb water vapor that entered the cell to maintain a 0% RH in the headspace. The surrounding environment of the Payne cell was controlled by DVS to desired testing conditions. For each sample type, nine (9) replicates cut from three same membranes were tested. The thickness of each
sample was measured using a digital micrometer. Each sample was tested at 25°C, 50°C, and 80°C and a constant RH of 60%. The increase of mass of the Payne cell assembly with time was recorded simultaneously. The tests followed the ASTM E96 Standard test method for water vapor transmission of materials (ASTM 2016). The H₂O permeability (\(P_{H₂O}\)) was calculated using Eq. (4.1):

\[
P_{H₂O} = \frac{WVTR \times T_{mem}}{\Delta \text{Vapor pressure}} = \frac{(\Delta m/\Delta t) \times T_m}{A \times \Delta p \times 18} \left( \frac{mol}{m \cdot s \cdot Pa} \right)
\]

(4.1)

Where, \(\Delta m/\Delta t\) is the slope of a linear section of the mass versus time, g/s; \(T_m\) is the thickness of the sample membrane, m; \(A\) is the open area of the Payne cell, \(1.18 \times 10^{-4} \text{ m}^2\); \(\Delta p\) is the partial pressure difference of water vapor, \(\Delta p = \frac{\Delta RH}{100} \times \text{Saturated water pressure}\) at 25°C, 50°C, and 80°C, Pa (Saturated water vapor pressure at 25°C= 3171 Pa, 50°C= 12351 Pa, 80°C= 47415 Pa); 18 g/mol is the molecular weight of H₂O.

4.3.2.6 Measurement of nitrogen gas permeability of membranes

The pure nitrogen gas transmission rate (NGTR) was measured using a single gas transmission cell (Custom Scientific Instruments Inc, PA, USA) as shown in Figure 4.2, following the ASTM D1423-82(2015) Standard test method for determining gas permeability characteristics of plastic
film and sheeting (ASTM 2015). Samples were cut into circles with a diameter of 0.12 meter and thickness was recorded. One sample was mounted to separate the cell into the upper and lower chambers. Compressed nitrogen gas flowed into the lower chamber, diffused through the sample, and entered the upper chamber. The volume expansion of the upper chamber was measured by recording the movement of a liquid color slug in the capillary tube. Nine (9) replicates for each sample type were tested. The transmission cell was placed in a water bath to maintain the desired temperatures of 25°C, 50°C, and 80°C. The pressure difference between the lower chamber and upper chamber was measured by a pressure gauge. The N₂ gas permeability was calculated using Eq. (4.2):

\[
P_{N_2} = \frac{N G T R \times T_m}{\Delta p} = \frac{P_0 \times S \times \pi D^2 \times T_m}{\Delta p \times 4 A R T} \left( \frac{\text{mol}}{\text{m} \cdot \text{s} \cdot \text{Pa}} \right)
\]  

(4.2)

Figure 4.2: Schematic of a single gas transmission cell

Where \( P_0 \) is the ambient pressure, 101325 Pa, \( S \) is the rate of rising of the capillary slug (m/s); \( D \) is the capillary tube’s inner diameter, \( 0.4957 \times 10^{-3} \) m; \( A \) is the open area of the cell, \( 0.6655 \times 10^{-2} \) m²; \( T_m \) is the thickness of the sample membrane, m; \( \Delta p \) is the pressure difference between the
lower and upper chamber, i.e., gauge pressure, Pa; \( T \) is the temperature of gas, K; \( R \) is the gas constant (8.3143 \( \text{m}^3 \cdot \text{Pa}/(\text{mol} \cdot \text{K}) \)).

4.3.2.7 Calculation of Selectivity of water vapor and nitrogen

The selectivity (\( \alpha \)) was obtained from the ratio of \( \text{H}_2\text{O} \) to \( \text{N}_2 \) permeability, Eq. (4.3).

\[
\alpha = \frac{P_{\text{H}_2\text{O}}}{P_{\text{N}_2}}
\]  
(4.3)

4.3.2.8 Measurement of coefficient of thermal expansion (CTE)

The in-plane coefficient of thermal expansion (CTE) of the PDMS and CNC/PDMS membrane samples were measured using a thermomechanical instrument (Q400 TMA, TA Instrument). Samples were cut into 5 mm \( \times \) 5 mm areas and one sample at a time was sandwiched between two crystal wafers to ensure force dispersion. An expansion probe rested on the surface of the samples with a 0.02 N preload. As the temperature was raised from 25 °C to 100 °C a heating rate of 5 °C/min, the change in thickness of the sample was recorded, allowing the calculation of CTE from the slope of the resulting expansion temperature plots. CTE is calculated using Eq. (4.4) [23].

\[
\text{CTE} = \frac{\Delta L}{L_0 \times \Delta t}
\]  
(4.4)

Where \( L_0 \) is the initial length of the sample (\( \mu \text{m} \)); \( \Delta t \) is the temperature change (° C), and \( \Delta L \) is the thermal expansion (or contraction) of the sample after the temperature change.

For each concentration, three samples were prepared and tested, where performed in triplicate. Therefore, the average of Nine (9) replicates for each sample type were measured and reported.

4.3.2.9 Statistical analysis

Two-way analysis of variance (ANOVA) was performed for two independent variables (CNC concentration and temperature) to understand the main effects and interaction effects of them on the water vapor and nitrogen gas permeability, and selectivity of the membrane samples. One-way ANOVA was conducted for the effect of the independent variable (CNC concentration) on CTE,
followed by Tukey’s multiple comparisons test, Significance was set at $P < 0.05$. All statistical analyses were run in OriginPro software version 2022b [28].

4.4 Results

4.4.1 Appearance and Morphology of CNC/PDMS Membrane Samples

The appearance of four types of membrane samples is provided in Figure 4.3. The Pure PDMS has the highest transparency, and the transparency of the film is decreased with increasing the CNC concentration. The SEM images (Figure 4.4) show the top surface morphology of four membrane samples. The dispersion of CNC in PDMS is dependent on the concentration of CNC added. CNC particles are relatively small and distributed randomly in PDMS when 2% of CNC was added. In contrast, when the concentration of CNC was increased to 4% and 6%, the CNC aggregation became more significantly distinctive. In addition, these SEM images show the PDMS and CNC/PDMS membranes are dense membranes, and no pores or defects are observed at this level of magnification. AFM images (Figure 4.5) were used to estimate the 3D shape and dimensions of CNC nanoparticles agglomerations. Most of the CNC particles have a height in the range of 10 nm to 100 nm. The maximum height of agglomerated CNC particles could reach over 100 nm. More high peaks are observed with the increase in CNC concentration.

![Figure 4.3: Appearance of the membrane Samples](image_url)

<table>
<thead>
<tr>
<th>Pure PDMS (0% CNC)</th>
<th>2% CNC/PDMS</th>
<th>4% CNC/PDMS</th>
<th>6% CNC/PDMS</th>
</tr>
</thead>
</table>


Figure 4.4: SEM images of composite membrane materials of CNC/PDMS: (a) 0%, (b) 2%, (c) 4%, and (d) 6%.
Figure 4.5: 3D images of AFM results of composite membrane materials (a) Pure PDMS, (b) 2% CNC/PDMS, (c) 4% CNC/PDMS, and (d) 6% CNC/PDMS.

4.4.2 ATR - FTIR Analysis

Figure 4.6 shows the FTIR spectra of an air-dried CNC film (Control-1), pure PDMS sample (Control-2), and CNC/PDMS samples with CNC concentrations of 2%, 4%, and 6%. For Control-1 CNC film, a strong O-H stretching vibration at 3332 cm\(^{-1}\) and bending band of H-O-H bond at 1638 cm\(^{-1}\) are observed [29], [30]. For Control-2 PDMS membrane, the featured peaks of PDMS include 2960 cm\(^{-1}\) for CH\(_3\) group vibration, 1257 cm\(^{-1}\) for the symmetric deformation of the CH\(_3\) group, 887 cm\(^{-1}\) for Si-C vibration, and 790 cm\(^{-1}\) for Si-O vibration [31]. When low concentrations of CNCs were blended in PDMS, the spectra of CNC/PDMS samples show that peaks at 3332 cm\(^{-1}\) and 1638 cm\(^{-1}\) almost disappeared but the peak at 1057 cm\(^{-1}\) representing the stretching vibrations of C-O in CNC became slightly distinctive [30]. The results reveal that the addition of CNC from 2% to 6% did not change the general spectra pattern of CNC/PDMS samples. Therefore, the performance of CNC/PDMS membrane is mainly governed by the PDMS.
Figure 4.6: FTIR spectra of all membrane samples and control groups

Figure 4.7: Water vapor permeability at elevated temperatures and a humidity differential of 60%
4.4.3 Permeability of Water Vapor

The values of water vapor permeability (Figure 4.7) increased with the CNC concentration from 0% (pure PDMS) to 2% and then decreased. The mean±SD values of water vapor permeability at 25°C for Pure PDM, 2% CNC/PDMS, 4% CNC/PDMS, and 6% CNC/PDMS were 30,683.6±615.9, 38,295.6±1,070.9, 35,883.6±1,248.8, and 35,846.1±1,338.3 Barrer, respectively. The addition of 2% CNC resulted in an increase of 24.8%, 30.9%, and 11.2% at 25°C, 50°C, and 80°C, respectively. Higher concentrations of CNC (4% and 6%) show a slightly decreasing trend for water vapor permeability, while the permeability values remained higher than those for pure PDMS membranes. This trend is the same in all three temperatures except for 80°C. When the temperature increased from 25°C to 80°C, the permeability of water vapor decreased dramatically. Two-way ANOVA results reveal that the effects of CNC concentration, temperature and their interaction on water permeability were statistically significant (Table B.1 Supplementary document). Furthermore, the comparison between different CNC concentrations shows that the 2% CNC/PDMS is significantly different from other samples, but there is not any significant difference between pure PDMS (0% CNC), 4% CNC/PDMS, and 6% CNC/PDMS samples (Table B.2). Therefore, 2% CNC is the optimal concentration in terms of water vapor permeability.

4.4.4 Permeability of Nitrogen Gas

The values of Nitrogen gas permeability (Figure 4.8) increased with the CNC concentration from 0% (pure PDMS) to 2% and then slightly decreased. The reduction in permeability at higher concentrations might be because of the added strength provided by CNCs and limiting the polymer chains [12]. The mean±SD values of Nitrogen gas permeability at 25°C for Pure PDM, 2% CNC/PDMS, 4% CNC/PDMS, and 6% CNC/PDMS were 263.7±4.6, 324.9±18.7, 310.0±8.4, and 310.3±7.3 Barrer, respectively.
The nitrogen gas permeability (Figure 4.8) was increased by 23.2%, 27.8%, and 16.0% at three temperatures when adding 2% CNC to the PDMS membrane. Similarly, higher concentrations of CNC (4% and 6%) show a slightly decreasing trend for nitrogen permeability compared with 2% CNC which again could be due to the added strength of the polymer chains [12]. The nitrogen permeability increased as the temperature was elevated from 25 °C to 80 °C.

Two-way ANOVA results show the effect of CNC concentration on nitrogen permeability was not statistically significant but the effect of temperature on permeability was statistically significant (Table B3). The interaction between temperature and concentration was not statistically significant either. Furthermore, the comparison between different CNC concentrations reveals that there was not a statistically significant difference between 2%, 4%, and 6% CNC/PDMS membranes but all the CNC/PDMS were significantly different from the Pure PDMS (Table B.4). Therefore, 2% CNC is the optimal concentration in terms of nitrogen gas permeability.
4.4.5 Selectivity of Water Vapor and Nitrogen

The selectivity of water vapor over nitrogen (Figure 4.9) at 25 °C of pure PDMS, 2%CNC/PDMS, 4%CNC/PDMS, and 6%CNC/PDMS were 116.3, 117.9, 115.7, and 115.5, respectively. Two-way ANOVA results (Table B.5) show that the effect of CNC concentration on selectivity was not statistically significant but the effect of temperature on selectivity was statistically significant. The interaction between temperature and concentration was not statistically significant for selectivity.

![Figure 4.9: Selectivity of H2O/N2 at elevated temperatures](image)

4.4.6 Coefficient of Thermal Expansion (CTE) of Membranes

The dimensional stability of CNC/PDMS membranes influences how well the membrane operates at elevated temperatures. It was evaluated in terms of the coefficients of thermal expansion (CTE) of pure PDMS and CNC/PDMS membranes (Figure 4.10). The mean±SD of CTE for pure PDMS, from room temperature up to 100°C, was 301.1±12.6 µm/m.°C. This measured value is in good agreement with the published values for CTE of PDMS which is 309 ppm/°C [32]. After adding
2% CNC, the mean±SD of CTE was reduced to 274.4±8.5 μm/m.°C, which is about 12% lower than that of pure PDMS. This decrease in CTE was expected because CNC has a very low CTE of 9 μm/m.°C [33] and it helps to restrain the expansion of PDMS at elevated temperatures when CNCs are dispersed in PDMS [23]. However, the mean±SD of CTE of 4% CNC/PDMS and 6% CNC/PDMS was 269.5±13.2 and 264.3±8.6, respectively. Increasing the CNC concentration to 4% and 6% did not further decrease the CTE greatly. One-way ANOVA results (Table B.6) show that the decrease in the CTE between pure PDMS sample and 2% CNC/PDMS sample was statistically significant. Also, the comparison between different CNC concentrations (Table B.7) shows that there is not a significant difference between 2%, 4% and 6% CNC/PDMS samples and all these samples are significantly different from Pure PDMS. Once again, 2% CNC is the optimal concentration in terms of CTE.

Figure 4.10: The CTE values for different samples

4.5 Discussion

4.5.1 Influence of CNC Agglomeration on Membrane Appearance and Properties

When CNC suspension was mechanically mixed with the PDMS prepolymer and curing agent solution and then dried until fully cured, CNC agglomeration occurred because of the poor
compatibility of hydrophilic CNC and hydrophobic PDMS. When more agglomerated CNC particles were formed as the increase of CNC concentration, the membrane transparency decreased ascribed to the mismatch of refractive indexes between CNC and PDMS. Combined SEM and AFM images, the CNC particles are present on the membrane surface with needle-like shapes. The water vapor and nitrogen gas permeability, and CTE results of CNC/PDMS membrane samples show that 2% CNC was the optimal concentration. Increasing the CNC concentration did not further enhance the membrane performance. The reason is also explained by the poor compatibility. The compatibility of CNC and PDMS might be improved by modifying the CNC, such as the silylation of CNC [26], [27].

4.5.2 Effects of Temperature on Permeability of Water Vapor and Nitrogen Gas

Gas transport through dense polymeric membranes is governed by the solution-diffusion mechanism. Therefore, the effects of temperature on both solution and diffusion processes should be considered. The influence of temperature on solubility has been well addressed in terms of the van't Hoff relationship. Gas solubility correlates with its condensability. For less condensable gases (e.g., N₂ and O₂) that often have lower critical temperatures (Table 4.1), the change in the enthalpy of mixing is positive (ΔHs > 0), resulting in an increase in the gas solubility with an increase in the temperature. However, for condensable gases and vapors (e.g., water vapor) that have higher critical temperatures, the enthalpy change is negative (ΔHs < 0), thereby showing a decrease in solubility with increasing temperature [11], [34]. The diffusion of gas molecules in a dense membrane is a thermally activated process and increases as the temperature increases, which is well described by the Arrhenius equation [34]. However, the sensitivity of this correlation depends on the size of the penetrants (i.e., vapor/gas species) and the type of polymer, both of which influence the value of activation energy [11].
Consequently, for water vapor, with an increase in temperature, there is an increase in diffusivity along with a decrease in solubility. However, for water vapor permeability, sorption is the preponderant factor [35]. Which means the magnitude of solubility change is greater than that of diffusivity change (because of high condensability which correlates with the high critical temperature as shown in Table 4.1), thereby resulting in a decrease in permeability. However, for the N₂ and O₂ molecules which are larger in kinetic diameter and less condensable, while increasing the temperature, there is increase in both the diffusivity and the solubility. This leads to an increase in permeability [11].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinetic diameter (pm)</th>
<th>Critical temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor</td>
<td>250</td>
<td>647</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>364</td>
<td>126</td>
</tr>
<tr>
<td>Oxygen</td>
<td>346</td>
<td>154</td>
</tr>
</tbody>
</table>

**Table 4.1: Kinetic diameter and critical temperature of molecules[9], [36]**

4.5.3 **Effectiveness of CNC as a Nanofiller on Water Vapor and Nitrogen Gas Permeability**

In this study, a bio-based material CNC was used as a nano filler in the PDMS matrix to improve the PDMS membrane performance for air dehydration, to the best of our knowledge, which is the first time to report this type of application of CNC. CNC’s renewable and sustainable features make it possible as alternatives to non-renewable nanofillers, like zeolites (ZIF), silicon dioxide (SiO₂), and titanate nanotubes (TNTs), reported in the previous studies [16]-[19]. While in most of the other studies regarding mixed matrix membranes, the nano filler they used in PDMS is not bio based and not renewable. The CNC used in this study is renewable and can be produced from sustainable sources, two features that make it superior to other nano particles such as zeolites (ZIF). On the other hand, to the best of our knowledge, this is the first time to make a mixed matrix membrane with PDMS for improving water vapor permeability of PDMS. Our study revealed that
the water vapor permeability and nitrogen permeability of PDMS membrane at room temperature were found to be 3,683 Barrer and 263 Barrer, respectively, consistent with previous studies [37], [38]. After adding the optimal concentration of 2% CNC, the water vapor and nitrogen gas permeability at room temperature were increased by 24.8% and 23.5 %, respectively. In the study conducted by Mao et al., the addition of approximately 30 wt.% of ZIF-L to PDMS led to a significant 8.0% increase in water vapor permeability at 40°C [18]. Similarly, Sahin et al. conducted another study where they added 20 wt.% of ZIF-71 to PDMS and observed a significant enhancement of around 34% in the permeability of nitrogen gas at 35°C [19]. CNCs have demonstrated several benefits in comparison to ZIF nanoparticles. For instance, they require a significantly lower weight ratio to achieve a similar improvement in water vapor and nitrogen gas permeability.

Typically, the addition of nanoparticles to rubbery polymers like PDMS does not result in a significant increase in free volume, owing to the polymer's rubbery nature, which allows it to flexibly incorporate the nanoparticles within its flexible chain [16]. However, Beltran et al. reported an increase in the gas permeability of PDMS after adding modified SiO$_2$, due to the increase in the free volume of the membrane [16]. Such an increase in free volume led to an increase in the diffusion coefficient. These findings suggested that PDMS, a rubbery polymer, may exhibit an increase in free volume upon the incorporation of nonporous fillers of SiO$_2$ [16]. Li et al. found that adding TNTs into the PDMS matrix resulted in a significant enlargement of the fractional free volume (FFV) [17]. The enlargement of the FFV created more diffusion paths for small penetrants, and consequently, increased the gas permeability of the nanocomposite membranes. In our study, the effectiveness of CNC on the enhancement of water vapor and nitrogen gas permeability could be also explained by the modified FFV.
4.6 Conclusions

In this study, CNC/PDMS membranes with the CNC weight concentrations of 0%, 2%, 4%, and 6% were successfully synthesized. The samples were defect-free and contained no observable pores under microscopic imaging because of the degassing step during preparation. The SEM images and AFM results revealed the CNC nanoparticles were dispersed in the PDMS matrix either randomly or in small agglomerations depending on CNC concentrations. The FTIR spectra confirmed the existence of CNCs in the CNC/PDMS samples. The addition of CNC alters the permeability and selectivity of the membranes. The optimal CNC concentration was 2% with enhanced water vapor permeability at all temperatures up to 24.8% while increasing the selectivity slightly up to 3.1%. In addition, the 2% CNC/PDMS samples showed an 8.9% lower value for CTE which results in higher thermal dimensional stability of the sample. The future work would be the modification of CNCs, e.g., silylation, to increase the compatibility between CNCs and PDMS polymer and increase the dispersion of CNCs in the PDMS matrix.
4.7 References


5 SYLALATED CNC/PDMS COMPOSITE MEMBRANES WITH IMPROVED SELECTIVITY FOR H₂O/AIR SEPARATION

5.1 Chapter Summary

Cellulose nanocrystals (CNCs) are purported as a potential nano-reinforcement in polymer composites, however, the hydrophilic surface nature of CNCs limits their usage in composites if the polymers are hydrophobic, which results in poor compatibility. In this research, renewable biobased CNCs were modified using silylation, which is based on introducing a siloxane group to increase the compatibility between CNCs and polydimethylsiloxane (PDMS) polymer. A silylated CNC/PDMS composite membrane was manufactured, which has applications in air dehydration. For this purpose, CNC was obtained from a hydrolysis process using sulfuric acid, and the CNC suspension in water was then dried using a spray drying technique. The dried CNC powder was dispersed in a solvent and the surface modification of CNCs was carried out through the reaction between hydroxyl groups of the CNCs and the silylation agent. Finally, the silylated CNCs (SCNCs) were added to the PDMS solution to make SCNC/PDMS membrane samples with an SCNC weight concentration of 2%. Pure PDMS and CNC/PDMS membrane samples were made as controls. Characterization analyses of FTIR and XRD of SCNCs confirmed the effectiveness of the silylation. SEM, AFM, and polarized light microscopy analyses indicated the improved dispersion of SCNCs in the polymer matrix compared to the not-modified CNC. The SCNC/PDMS membrane exhibited a 23% increase in water vapor permeability and a 79.6% increase in selectivity for water vapor over nitrogen gas at 25°C, compared to the pure PDMS membrane. Furthermore, Thermo-mechanical Analysis (TMA) technique provided evidence that the addition of both CNC and SCNC resulted in a decrease in the Coefficient of Thermal Expansion (CTE) of
the PDMS membrane. These findings contribute to the development of cellulose-based materials with improved performance for their potential applications in various fields.

5.2 Introduction

Water vapor is commonly present in various gas streams, including air, flue gas, and natural gas. To meet different industrial demands, it is crucial to remove water vapor from these gas streams [1]. Membrane separation is a promising technology for water vapor removal from the air or gas attributed to its advantages over traditional methods (such as, absorption, adsorption, condensation, etc.), such as simplified operation, energy efficiency, and low capital investment [2], [3]. The target application in this study focuses on water vapor/air separation. This technology involves the separation of water vapor from air via a dense membrane without any accompanying phase or temperature changes. As a result, this process is also referred to as isothermal membrane-based air dehumidification (IMAD) [4]. IMAD has been successfully implemented in numerous industries that require moisture control during manufacturing processes, including but not limited to food, chemical, and pharmaceutical industries.

The efficiency of water vapor/air separation technology largely depends on membrane materials used. Polymeric membranes, including glassy and rubbery polymers, are favored because of their excellent permeability and processibility. Glassy polymers, such as polysulfone and polyimide, usually have exceptional permeability but are limited by expensive raw materials, harsh synthetic conditions, and low chemical stability [2]. Among rubbery polymers, polydimethylsiloxane (PDMS) is recognized as one of the most permeable rubbery polymers because of its flexible siloxane linkages and a satisfactory $\text{H}_2\text{O}/\text{N}_2$ selectivity (around 140, for instance) [1], [2], [5], [6]. Polymer membranes, despite being a promising technology for various separation processes, often encounter a trade-off between permeability and selectivity, referred to as Robeson's upper bound
The demand for novel membrane materials has become essential for improving the efficiency of separation technologies [7]. The focus of current membrane separation research is on developing materials that exhibit high permeability, selectivity, and tunable interactions with target penetrants, while also being robust against thermal and mechanical stresses [8]. Mixed matrix membranes (MMMs) have emerged as an effective approach for enhancing the performance of polymeric membranes by combining the polymer with nanofillers [8]. Performance improvement of MMMs for separation applications depends on several key factors, including the intrinsic properties of the dispersed phase (such as size, shape, and porosity) and the interface compatibility between the polymer and nanofiller [9].

There have been many nanoparticles such as TiO$_2$ [10], ZnO [11], SiO$_2$ [12], Zeolite [13] and more for reinforcing PDMS. However, the majority of these nanoparticles are considered unsustainable and, in certain instances, are derived from petroleum-based sources.

Cellulose nanocrystals (CNCs) are derived from renewable biomass resources, such as wood pulp, exhibiting a high aspect ratio, large surface area, unique surface chemistry, and easy chemical modification. These characteristics make CNCs appealing as nanofillers to enhance the mechanical and physical properties of various materials, including polymers [14], [15]. In addition, CNCs offer exceptional benefits such as remarkable mechanical properties, low coefficient of thermal expansion and hydrophilic nature. These exceptional properties besides being biodegradable, nontoxic, and biocompatible, provide an eco-friendly alternative to conventional nanofillers associated with environmental and health risks [16].

Therefore, in light of the growing concerns regarding environmental sustainability, the development of polymeric materials reinforced with CNCs has been studied for decades [15], [16]. Visakh et al. demonstrated that incorporating 2.5 and 5 w.t.% concentrations of CNCs extracted
from bamboo pulp enhances the thermal and mechanical stability of natural rubber [17]. In another study, Siqueira et al. found that after the addition of CNC suspension to natural rubber, dynamic mechanical analysis showed improved stiffness for the resulting nanocomposites [18]. However, these studies primarily focused on the mechanical and thermal properties of composites, lacking investigations into the gas permeability of the CNC/polymer composite films. Consequently, there exists a research gap in exploring the potential of CNCs as nanofillers in PDMS to enhance water vapor/air separation, an aspect that remains unexplored by other researchers.

Therefore, in chapter 4, the incorporation of CNC in the PDMS was studied, and it was revealed that the addition of 2 wt. % CNC to PDMS increased the water vapor permeability of the PDMS by 24.8 % at room temperature, decreased the coefficient of thermal expansion by 9% and the selectivity was retained. However, in that study, a CNC suspension in water was used, and the agglomeration of CNCs in PDMS occurred due to water evaporation during drying and the hydrophilic nature of CNCs, which limits their compatibility with hydrophobic polymers [16]. After this challenge was found in our last study, this motivated our research group to solve this challenge by using CNC powder and chemical modification. Therefore spray-dried CNCs were used, a cost-effective drying method that offers scalability, easy dispersion as particle reinforcement, and consistent particle sizes [19].

The hydrophilic properties of CNCs, characterized by the abundance of hydroxyl groups, result in inadequate compatibility with hydrophobic polymer matrices [15], [16]. To overcome this challenge, several techniques have been explored, including graft polymerization with hydrophobic polymers, low molecular weight esters, and silane coupling agents [16]. These techniques result in modified CNCs with improved hydrophobicity and desirable compatibility with hydrophobic polymer matrices [16].
As for PDMS, some studies tried to modify CNCs to increase the compatibility with PDMS. In one study, Yang et al. reported an experiment of adding modified CNCs to silicone rubber and observed an increase in the tensile strength as the concentration of modified CNCs increased from 0 to 3 w.t.% [20]. In another study, with the addition of 4 wt.% silylated CNC to PDMS, the storage modulus was improved [21]. However, these studies did not study the effect of modified CNCs as a nanofiller in PDMS to improve water vapor/air separation, and there is a knowledge gap.

The goal of this study is to employ the silylation technique to modify the surface of spray-dried CNCs (SCNCs) and effectively disperse the SCNCs in a PDMS matrix, resulting in SCNC/PDMS nanocomposites. In addition, the other objectives were to characterize the prepared SCNC/PDMS and study the dispersion of the SCNCs within the PDMS with different characterization methods. Then, the water vapor permeability, nitrogen permeability and selectivity of the prepared membranes as well as the mechanical and thermal stability were studied.

5.3 Materials and Methods

5.3.1 Materials

A CNC suspension at 11.8 wt.% solids was purchased from the USDA Forest Products Laboratory and distributed by the Process Development Center of the University of Maine (ME, USA). Then, a dry CNC powder was prepared at the Advanced Structures and Composites Center (ASCC) of the University of Maine (Orono, Maine, U.S). To enable the subsequent silylation step in an organic solvent system, the CNC suspension was dried using a mini spray dryer (Buchi B-290 laboratory mini-spray dryer, New Castle, DE, USA).

PDMS prepolymer and curing agent kits (Dow SYLGARDTM 184 Silicone Elastomer kit) were purchased from Dow Inc. (MI, USA). Trimethoxymethylsilane (MTMS), the silylating agent, was obtained from sigma-aldrich.com, U.S. n-Hexane was be obtained from Thermo Fisher Scientific.

5.3.2 Methods

5.3.2.1 Silylation of CNC

The obtained CNC powder was further dried in an oven at 60°C overnight to eliminate residual water. First 0.4 grams of the dried CNC powder was dispersed in 20 ml of n-hexane and was mechanically mixed for one hour. The pH of the suspension was adjusted to 4.0 using glacial acetic acid. Then 10 ml of MTMS (silylation agent) was added to the suspension. And then continued mechanical mixing for 3 hours to complete the silylation reaction between hydroxyl groups of the CNCs and the silylation agent and the SCNC suspension was prepared [15], [16].

5.3.2.2 Preparation of SCNC/PDMS membranes

To prepare the SCNC/PDMS membranes, a mixture of PDMS prepolymer and curing agent in a weight ratio of 10:1 was mechanically mixed for 5 minutes. Subsequently, an appropriate amount of the SCNC suspension was added to the PDMS/curing agent mixture to achieve a concentration of 2 weight percent (w.t.%) of SCNCs in PDMS. The mixture was mechanically stirred for one hour and was then degassed for 45 seconds to eliminate any air bubbles using a centrifugal bubble-free mixer (THINKY ARE-310, Tokyo, Japan). The degassed mixture was then cast onto Petri dishes. A schematic of this preparation method and the corresponding chemical reactions are illustrated in Figure 5.1.a and b. In the next step, to ensure the removal of any remaining air bubbles in the wet membranes, they were initially placed in a vacuum desiccator with a vacuum pressure of 88 kPa for 1 hour at room temperature [22]. Following this, the membranes were dried for 24 hours at room temperature and were carefully removed from the Petri dishes, resulting in the SCNC/PDMS membranes with thicknesses ranging from approximately 150 µm to 300 µm.
5.3.2.3 **Synthesis of other membranes**

The synthesis methods of PDMS and CNC/PDMS membranes were explained in chapter 4. They were used as a control in this chapter.

![Diagram of the fabrication method of SCNC/PDMS membrane](image)

**Figure 5.1:** a) diagram of the fabrication method of SCNC/PDMS membrane, b) chemical formula of silylated CNCs and SCNC/PDMS membrane

5.3.2.4 **Membrane characterization and performance tests**

The methods of characterization including scanning electron microscopic (SEM) analysis, atomic force microscopy (AFM) analysis, Fourier transform infrared spectrometer (ATR-FTIR) analysis, and coefficient of thermal expansion (CTE) measurement were the same as those explained in
chapter 4. Three replicates were performed for each type of sample. Just for CTE measurement, nine replicates were conducted for each sample type. Furthermore, the methods for the measurement of water vapor permeability of membranes, measurement of nitrogen gas permeability of membranes, and calculation of selectivity of water vapor and nitrogen were the same as the methods explained in Chapter 4. A total of nine replicates were conducted for each result. For more information, please refer to the methods section of Chapter 4.

5.3.2.5 X-ray diffraction (XRD)

The XRD patterns of powder CNCs and SCNCs in the scattering angle (2θ) range from 10° to 50° were analyzed using a Siemens D500 diffractometer at the Frontier Institute for Research in Sensor Technologies (FIRST) of the University of Maine, at a scanning speed of 1° 2θ/min. For each sample type, three replicates were conducted.

5.3.2.6 Polarized light microscopy (PLM)

Imaging was performed using an AmScope polarized light microscope (Model ME520TA, Irvine, CA, USA). The microscope was equipped with an AmScope MU900 digital camera featuring a pixel size of 1.67 µm by 1.67 µm and a 12-bit parallel analog-to-digital converter, which converts the 8-bit RGB data to a digital format for computer analysis. During the observations, samples were placed between the crossed polarizers and a lambda (red, first order or full wave) retardation filter. The lambda filter, known for its frequent application in the examination of birefringent materials, aids in measuring thickness, improving contrast in weakly birefringent samples, and identifying birefringence in crystalline and polymeric materials [23].
In the absence of a birefringent sample, the lambda filter alters the background of the polarized light microscope (PLM) images from dark field to a vivid pinkish-red hue. A halogen bulb was utilized as the light source. A total of three replicates were performed for each type of sample.

5.3.2.7 Statistical analysis

Two-way analysis of variance (ANOVA) was performed for two independent variables (Type of membrane and temperature) to understand the main effects and interaction effects of them on the water vapor and nitrogen gas permeability, and selectivity of the membrane samples. One-way ANOVA was conducted for the effect of the independent variable (Type of membrane) on CTE, followed by Tukey's multiple comparisons test, Significance was set at P < 0.05. All statistical analyses were run in OriginPro software version 2022b [24].

5.4 Results

5.4.1 Morphology of CNCs and SCNCs

The morphology of the CNCs, and CNCs after silylation with MTMS were analyzed with SEM. As shown in Figure 5.2 the unmodified spray-dried CNCs have spherical shape. Individual CNC is not seen. This figure also shows that the CNCs after silylation maintain the round shape and the morphology of the CNCs after silylation (i.e., SCNCs) does not change significantly. Because the SCNCs were dried into film to be presented in the SEM, they look to be agglomerated. However, in the process of making composite SCNC/PDMS membranes, there is no step of drying of SCNCs and therefore this agglomeration does not happen.

The SEM-EDS results (Figure 5.2 c and d) show that the silicon (Si) element is uniformly detected all over the SCNCs, but this Si element was not detected in the CNCs. This confirms successful and uniform silylation of CNC.
5.4.2 ATR - FTIR Analysis

FT-IR (Figure 5.3) was used to verify the silylation of CNCs. The SCNC spectrum revealed multiple additional absorption peaks. The new bands appearing at 1272, 898, and 782 cm\(^{-1}\) represent the bending of the C-H bonds in the methyl group, the stretching of the Si-OH bond, and the Si–C or Si–O bonds, respectively. The existence of these peaks proves the successful silylation of CNCs. In addition, a reduction of the O–H absorption peak intensity at 3340 cm\(^{-1}\) was observed, which shows most of the O-H groups on the surface of CNCs had been replaced with new functional groups [21], [25].
5.4.3 X-ray Diffraction (XRD)

Figure 5.4 shows the XRD diffraction patterns for the spray-dried CNCs and the air-dried SCNCs. Both samples show peaks at 20 of 14.86°, 15.97°, 22.39°, and 34.45° which are characteristic peaks of cellulose I [15], [25], [26]. In addition, the preservation of typical crystalline characteristics associated with cellulose I, indicates that the surface modification did not damage the nanocrystals' crystalline integrity [21]. A new peak was observed in 20 of 10.92° corresponding to the silylation agent (MTMS) [27].

Figure 5.3: FT-IR spectra of CNC powder and SCNC powder

Figure 5.4: XRD patterns of CNC powder and SCNC powder
5.4.4 Morphological Analysis and Polarized Light Spectroscopy

Figure 5.5 shows the morphology of CNC/PDMS and SCNC/PDMS membranes as observed with FE-SEM. Figure 5.5.a shows the SEM image of pure PDMS with no particles on the surface. Figure 5.5.b is the SEM image from the surface of the CNC/PDMS membrane. Particles appearing on the surface of the CNC/PDMS membrane are mostly larger than 1 µm, indicating an agglomeration of the CNCs. Figure 5.5.C is an image of SCNC/PDMS membrane. In contrast, after introducing SCNCs into the PDMS, sub-micron sized particles are observed, reflecting a better dispersion of particles in the PDMS matrix than those seen in the unmodified CNCs in PDMS. Moreover, examination of the SEM images revealed that both the PDMS, CNC/PDMS, SCNC/PDMS membranes exhibit a dense structure, devoid of any observable pores or defects at the current magnification level.

In addition, polarized light spectroscopy was further used to analyze the dispersion of nanoparticles within the membranes. CNCs exhibit birefringence. When looking at a film under the polarized light microscope, the light passing through the film can reveal the size and distribution of CNC particles inside the film as well as on the surface. The red, blue, and green spots in the images as shown in Figure 5.5 e and f represent CNCs or SCNCs particles distributed in the polymer. Different colors are seen depending on the different orientations of CNCs inside the polymer. The magenta color represents the transparent area of the PDMS phase, as displayed in Figure 5.5.d except for some contaminants on the surface. Figure 5.5 e and f display colorful spots overlapping on the magenta background, but the spots in Figure 5.5.f are smaller and denser, indicating the SCNCs had a better dispersion inside the PDMS than the unmodified CNCs. This is because there is better compatibility between the PDMS and silylated CNCs.
The SCNC loses some of the OH functional groups as proved by the FTIR results; therefore, it has less tendency to bond with itself and is less likely to agglomerate. In comparison, the SEM images only show the dispersion of the nano particles on the surface of the membranes, while the polarized light spectroscopy shows the nano particles on the surface as well as inside the membrane.

![SEM images of composite membrane materials of CNC/PDMS](image)

*Figure 5.5: SEM images of composite membrane materials of CNC/PDMS: (a) Pure PDMS, (b) 2% CNC/PDMS, (c) 2% SCNC/PDMS. Polarized light results of composite membrane materials of CNC/PDMS: (d) Pure PDMS, (e) 2% CNC/PDMS, (f) 2% SCNC/PDMS.*

### 5.4.5 Appearance and Morphology of SCNC/PDMS Membrane Samples

The appearance of PDMS, CNC/PDMS, and SCNC/PDMS films is depicted in Figure 5.6. Pure PDMS exhibits transparency, while the CNC/PDMS film displays translucence which could be attributed to nanocrystal agglomeration. Conversely, the SCNC/PDMS film exhibits improved clarity compared to the CNC/PDMS film due to the superior dispersion of silylated CNCs within the PDMS matrix. Although membrane clarity is not a critical issue, it is an indicator of the quality of nanocrystal dispersion within the PDMS matrix.
5.4.6 Atomic Force Microscopy (AFM)

The study utilized AFM images, presented in Figure 5.7, to assess the dispersion and dimensions of CNC nanoparticles in PDMS. Figure 5.7.b, which is for CNC/PDMS, shows that the agglomerated nanocrystals are smaller than 2 microns and have the highest peak of approximately 250 nm, suggesting that the CNC nanoparticles are relatively large and not well dispersed in the PDMS matrix. In contrast, Figure 5.7.c demonstrates that SCNCs are distributed in smaller sizes and in a more random manner throughout the polymer matrix. The highest peak of the SCNCs is about 50 nm, which is significantly smaller than that of the CNC nanoparticles in Figure 5.7.b. The decrease in the highest peak is attributed to the improved compatibility between the SCNCs and PDMS matrix after the silylation process. Furthermore, the AFM images reveal that the
SCNC/PDMS sample has a smoother surface compared to the CNC/PDMS sample, indicating better nanoparticle dispersion in the polymer matrix.

As a baseline, pure PDMS was also examined and shown in Figure 5.7.a, and no nanoparticles were observed. The highest peak on the AFM image of pure PDMS was approximately 3 nm, which is significantly smaller than the highest peaks observed in the AFM images of the CNC and SCNC nanoparticles in PDMS. This confirms that the observed peaks in the AFM images of the CNC/PDMS and SCNC/PDMS samples were indeed attributed to the presence of the nanoparticles and not artifacts of the AFM imaging process.

Additionally, valuable insights into surface roughness were obtained through AFM analysis. The surface of pure PDMS displayed the lowest roughness, while the SCNC/PDMS membrane exhibited a smoother surface than the CNC/PDMS membrane. The improved distribution of SCNCs within the PDMS matrix may be the reason for this observation. The greater compatibility of SCNCs with PDMS and the uniform distribution of nanoparticles decrease the chain mobility of PDMS and therefore reduces the variation in the density. Consequently, the incorporation of SCNCs in PDMS results in a smoother surface in comparison to CNC/PDMS, thus enhancing the dimensional stability of the PDMS network chain structure. In a separate study, Gwon et al. reported a smoother surface in modified CNC-reinforced poly(lactic) acid (PLA) polymer, likely because of the improved compatibility between the modified CNC and PLA and reduced density differences [14].
5.4.7 Permeability and Selectivity of Membranes

Figure 5.8: Water vapor permeability of the membrane samples

Figure 5.8 shows the water vapor permeability of pure PDMS, 2 w.t.% CNC/PDMS, and 2 w.t.% SCNC/PDMS membrane samples. The addition of both the SCNCs and CNCs increased the water vapor permeability at all three temperatures. The water vapor permeability values of SCNC/PDMS were comparable to those of the CNC/PDMS, both of which were higher than those of the pure PDMS. The values for the SCNC/PDMS membrane were smaller than the ones for the CNC/PDMS. The lower values could be attributed to the modification of the CNC which makes it more compatible with PDMS and reduction of free volume compared to the CNC/PDMS. The same phenomena were observed in a different study in which they used two kinds of surface-modified SiO$_2$ nanoparticles. The nanoparticles that had better compatibility and a higher degree of interaction with PDMS, resulted in lower free volume formation and consequently, reduced the gas permeability compared to the nanoparticles that had lower compatibility with PDMS [28].

Two-way ANOVA results reveal that the effect of the type of membrane, temperature, and their interaction on water permeability were statistically significant (Table C.1). Furthermore, the
comparison between membranes (Table C.2), shows that the PDMS, 2% CNC/PDMS, and 2% SCNC/PDMS are significantly different from each other.

Furthermore, the effect of the temperatures on the water vapor permeability of the membranes was studied. The results showed that by increasing the temperature from 25 °C to 80 °C, the water vapor permeability is decreased. The reason is that with increasing temperature, the diffusivity of water vapor increases, and the solubility decreases, but the effect of solubility is dominant. The permeability decreases since it is the result of normalizing the water vapor transmission rate with water vapor pressure, which increases substantially with temperature. It is typically that the water vapor transmission rate increases with increasing temperature under the same humidity difference across the sample. This phenomenon was explained in more detail in Chapter 4.

Figure 5.9: Nitrogen gas permeability of the membrane samples

Figure 5.9 shows the nitrogen gas permeability of the membranes. The values for the pure PDMS are in agreement with a previous study [29]. The addition of the CNC to the PDMS has increased the nitrogen gas permeability by 23.2% at 25 °C. While the addition of SCNC to the PDMS has decreased this value by 31.5% compared to the pure PDMS at the same temperature. The reason
could be because, after silylation of the CNCs, the SCNCs become more compatible with the PDMS polymer, and a more uniform and improved dispersion of the SCNCs within the PDMS matrix takes place as observed in the PLM, AFM, and SEM results. The improved dispersion of the nano fillers within a polymer matrix results in the reduction of polymer chain mobility [14] and this results in the reduction of film permeability. This effect is more significant for low-sorbing gases such as $N_2$ and $O_2$. So, this could be the reason for the reduction of $N_2$ permeability through the SCNC/PDMS membrane [12].

As illustrated in Figure 5.10, the pure PDMS membrane has a polymer structure. After adding the CNCs into the PDMS, because of the low compatibility between the CNCs and PDMS, agglomeration of the CNCs within the PDMS structure is observed, and attributed to this agglomeration, the surface has higher roughness and, in some areas, more nanoparticles agglomerate and, in some sections, fewer particles exist. This results in a difference in the density of the membrane in different sections and this causes increased free volume [12]. However, after adding the SCNCs, attributed to the improved compatibility between the SCNC and PDMS, there is a better dispersion and more uniform structure, which causes a reduction of the polymer chain mobility. Thus, the gas permeability decreases. However, this effect is more pronounced for low-
sorbing gases like N₂ and O₂ rather than water vapor, which is condensable and non-low-sorbing gas. More details about the condensability of the N₂, O₂, and water vapor were explained in Chapter 4.

The effect of temperature on the nitrogen gas permeability of the membranes is also studied. As the temperature increased from 25 °C to 85 °C, the N₂ permeability increased. This is because both the diffusivity and solubility of N₂ increase with increasing of temperature. More details were explained in chapter 4.

In addition, two-way ANOVA results show the effect of type of membrane, temperature and their interaction on nitrogen permeability were significant (Table C.3). Furthermore, the comparison between different membranes (Table C.4), reveals that PDMS, 2% CNC/PDMS and 2% SCNC/PDMS membranes are significantly different.

The nitrogen gas permeability values of SCNC/PDMS were much lower than the CNC/PDMS and pure PDMS. The nitrogen gas permeability decreased by about 31.6 % at 25°C, 43.1 % at 50°C, and 45.9 % at 80°C compared with the pure PDMS, and by about 44.5 at 25°C, 55.5 % at 50°C, and 53.4% at 80°C in comparison to the CNC/PDMS.

Figure 5.11: Selectivity of the membrane samples
Because of this reduction in the N\textsubscript{2} permeability of the SCNC/PDMS membrane, there was an increase in the selectivity of the membrane for water vapor/N\textsubscript{2} as observed in Figure 5.11. The selectivity of H\textsubscript{2}O/N\textsubscript{2} of the SCNC/PDMS was higher than that of the pure PDMS and the CNC/PDMS: about 79.6 \% and 75.9 \% at 25\textdegree C, 116.1\% and 110.2 \% at 50\textdegree C, and 119.0 \% and 108.1 \% at 80\textdegree C, respectively.

Two-way ANOVA results (Table C.5) show that the effect of the type of membrane, temperature, and their interaction is significant on selectivity. In addition, the comparison between different membranes (Table C.6), reveals that 2\% SCNC/PDMS membrane is significantly different from other samples, while PDMS and 2\% CNC/PDMS are not significantly different.

5.4.8 Coefficient of Thermal Expansion (CTE) of Membranes

Figure 5.12 illustrates the coefficient of thermal expansion (CTE) of the membranes, which reflects their dimensional stability with temperature variations. The average value ± standard deviation (SD) of CTE for pure PDMS, ranging from room temperature to 100\textdegree C, was measured as 301.1 ± 12.6 \(\mu\text{m/m.}^{\circ}\text{C}\). This measured value aligns well with the published CTE value for PDMS, which is 309 ppm/\textdegree C [30]. Upon incorporating 2\% CNC, the mean ± SD of CTE decreased to 274.4 ± 8.5 \(\mu\text{m/m.}^{\circ}\text{C}\), representing a reduction of approximately 11\% compared to pure PDMS. This decline in CTE was expected since CNC exhibits an exceptionally low CTE of 9 \(\mu\text{m/m.}^{\circ}\text{C}\) and aids in limiting PDMS expansion at elevated temperatures when dispersed within the PDMS matrix [31]. However, the mean±SD of CTE of SCNC/PDMS was 267.2±9.5 \(\mu\text{m/m.}^{\circ}\text{C}\), which is 14\% lower than pure PDMS and it shows improvement in the dimensional stability of the membrane.
One-way ANOVA results (Table C.7) show that the effect of the type of membrane is significant. In addition, the comparison among different membranes (Table C.8) shows that PDMS is different from 2% CNC/PDMS and 2% SCNC/PDMS. However, there is no statistical significance observed between the 2% CNC/PDMS and 2% SCNC/PDMS membranes. These results show that both the CNC and SCNC were able to reduce the CTE of PDMS by some levels.

### 5.5 Conclusions

The study has developed cellulose nanocrystal (CNC)-reinforced polydimethylsiloxane (PDMS) membranes for water vapor/air separation. Spray-dried CNCs derived from renewable biomass resources were modified through silylation to enhance their hydrophobicity and compatibility with PDMS. The resulting SCNCs and SCNC/PDMS nanocomposites were characterized and evaluated with a suite of analytical tools. The spray drying process generated micron sized cellulose beads. The successful surface silylation of CNCs with MTMS in an acidified organic solvent was confirmed through SEM-EDS, FTIR, and XRD analyses. The morphology of the SCNCs remained intact, indicating that the silylation occurred primarily on the surface. The SEM-EDS mapping image indicates that the silicon element was distributed evenly on the surface of the SCNC. The

---

Figure 5.12: The CTE values for different samples
FT-IR analysis revealed additional peaks and peak intensity changes corresponding to the result of the silylation, and X-ray diffraction confirmed the preservation of the crystalline integrity of the nanocrystals.

The SCNCs exhibited improved dispersion within the PDMS matrix compared to unmodified CNCs, resulting in a smoother surface, and enhanced dimensional stability. The water vapor permeability increased with the addition of both CNCs and SCNCs, while SCNCs showed slightly lower permeability due to better compatibility. The nitrogen gas permeability was significantly reduced in SCNC/PDMS membranes compared to unmodified CNCs and pure PDMS, resulting in increased selectivity for water vapor/N2. Overall, the surface silylation improved the properties of the SCNC/PDMS membranes, making them the potential for various applications, including air dehydration membrane technology.
5.6 References


18. Siqueira, G., Tapin-Lingua, S., Bras, J., da Silva Perez, D. & Dufresne, A. Mechanical properties of natural rubber nanocomposites reinforced with cellulosic nanoparticles obtained
from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers. 


22. Planes, M., Brand, J. & Lewandowski, S. Improvement of the thermal and optical performances of protective polydimethylsiloxane space coatings with cellulose nanocrystal additives. *Applied Materials and Interfaces* (2016)


6 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions
Throughout this dissertation, comprehensive investigations have been conducted to advance the development and characterization of CNC-PDMS membranes for moisture management and air dehumidification applications. The research comprised four key parts: the performance evaluation of a constructed mini-scale PDMS membrane-based dehumidification system, the development of a two-dimensional axisymmetric finite element analysis (FEA) model for water vapor separation in a PDMS hollow fiber membrane module system, the synthesis and characterization of CNC/PDMS membranes, and the surface silylation of CNCs to enhance their compatibility with PDMS.

From the results and discussions presented in the previous chapters of this dissertation the following conclusions could be drawn:

1. The constructed PDMS membrane-based dehumidification system exhibited promising efficiency in moisture vapor removal, with temperature and vacuum pressure playing crucial roles in enhancing the process. The initial RH had minimal influence on the process while increasing the air flow rate decreased the efficiency. Additionally, a simplified regression model was developed, which has the potential to predict the efficiency of moisture vapor removal. The membrane-based dehumidification system exhibited great potential for moisture management, particularly in wood drying processes and humid indoor environments.
The two-dimensional axisymmetric FEA model accurately simulated the water vapor transfer phenomenon in a dense PDMS hollow fiber membrane. The model simulated the mass transfer combined by the continuity and momentum equations with appropriate boundary conditions. The calculated water vapor concentration of the dehydrated air exhibited excellent agreement with experimental data, validating the FEA model. Furthermore, the FEA model was employed to calculate the mass transfer coefficient of water vapor and Sherwood number, revealing that the water vapor removal efficiency of the membrane system was influenced by air velocity and vacuum pressure. A correlation between the Sherwood number, Reynolds number, and Schmidt number was established based on the modeling results. The FEA model, along with its comprehensive findings, offers valuable insights for the design, process optimization, and module development of hollow fiber membrane systems.

CNC/PDMS membranes with varying CNC weight concentrations were successfully synthesized and characterized. The successful synthesis yielded defect-free membranes, and microscopic imaging confirmed the absence of observable pores. SEM and AFM analyses showed that the distribution of CNC nanoparticles within the PDMS matrix varied depending on the CNC concentration, with random dispersion or small agglomerations observed. FTIR spectroscopy confirmed the presence of CNCs in the CNC/PDMS samples. Notably, the optimal CNC concentration of 2% demonstrated enhanced water vapor permeability across all temperatures. Additionally, selectivity slightly increased and the coefficient of thermal expansion (CTE), exhibited about 9% reduction, indicating improved thermal dimensional stability.
IV. Spray-dried CNCs were successfully silylated using a silylation agent and the silylation process primarily occurred on the CNCs' surface, preserving their cellulose nanostructure. The silylation of CNCs resulted in improved dispersion within the PDMS matrix. The SCNC/PDMS showed enhanced dimensional stability, and slightly lower water vapor permeability compared to unmodified CNC/PDMS, due to better compatibility with PDMS. Moreover, the SCNC/PDMS membranes demonstrated significantly reduced nitrogen gas permeability compared to unmodified CNC/PDMS and pure PDMS. This enhanced selectivity for water vapor over nitrogen, making the membranes promising for water vapor separation applications. Overall, the surface silylation process improved the properties of the SCNC/PDMS membranes, providing potential opportunities for their utilization in various fields, such as air dehydration membrane technology.

In conclusion, this dissertation has significantly contributed to the understanding and advancement of cellulose nanocrystal/PDMS membranes for moisture management and air dehumidification. The findings provide valuable insights into the optimization and application potential of these membranes, opening avenues for further research and development in this field. Overall, this research contributes to the broader goal of sustainable and efficient separation technologies, with potential applications in various industries requiring moisture management and air dehumidification.
6.2 Future work

✓ The application of a PDMS membrane module for air dehydration in a lab scale module was studied and the permeability and selectivity of CNC/PDMS and SCNC/PDMS membranes were tested. However, in future work, a membrane module using SCNC/PDMS could be built, and the efficiency of the membrane module could be studied.

✓ In this study the effect of temperature on the permeability and selectivity of the membrane and the coefficient of thermal expansion of the membranes were studied. Nonetheless, as a future undertaking, it would be valuable to investigate the long-term durability of the membranes at elevated temperatures, which is a crucial aspect of their application in high-temperature separation technologies.

✓ The FEA model could be modified to simulate a three-dimensional membrane module. In addition, in this research, only the mass transfer was simulated using the FEA model, a subsequent study could incorporate heat transfer to analyze the influence of temperature on membrane performance.

✓ The permeability of membranes for single gases of water vapor and nitrogen gas has been investigated, However, as part of future research, it would be valuable to explore the permeability of gas mixtures to examine the interaction of gases.
6.3 References


42. IBM SPSS statistics for Windows, version 25.0 I Spss - New York: IBM Corp, 2019


129


82. Planes, M., Brand, J. & Lewandowski, S. Improvement of the thermal and optical performances of protective polydimethylsiloxane space coatings with cellulose nanocrystal additives. *Applied Materials and Interfaces* (2016).


134


In this section, a mass balance equation is described to calculate the overall mass transfer coefficient, $k_o$, and the mass transfer coefficients in tube ($k_t$), membrane ($k_m$), and shell ($k_s$) domains.

Taking a full-length hollow fiber membrane as a model, a differential equation of mass balance in terms of water vapor concentration and average air velocity is established in Eq. (A.1). The membrane is also divided into three domains: tube, membrane, and shell domains. A cylindrical ordination system is used in Figure A.1.

Figure A.1: Schematic of a single hollow fiber.

\[
C_{w,t}|_{z} V_z \frac{\pi D^2}{4} - C_{w,t}|_{z+\Delta z} V_z \frac{\pi D^2}{4} - k_o (C_{w,t}|_{z} - C_{w,s}) \pi D \Delta z = 0
\]  
(A.1)

where, $C_{w,t}$ (mol/m$^3$) is concentration of water vapor at a differential length, $\Delta z$, in the tube domain. $C_{w,s}$ (mol/m$^3$) is the concentration of water vapor in the tube domain. $V_z$ (m/s) is the velocity of humid air following into the tube domain. $D$ (m) is the diameter of a single hollow fiber. $k_o$ (m/s) is the overall mass transfer coefficient of water vapor.

It is assumed that mass transfer in r direction is constant. In our study, $C_{w,s}$ was unneglectable because the water vapor molecules migrated to the shell domain were immediately removed by a vacuum pump applied. In Eq. (A.1), it is treated as zero, then Eq. (A.1) can be further rewritten as Eq. (A.2):
\[ k_0 = \frac{D V_{z2}}{4 L} \ln \frac{c_{w,\text{out}}}{c_{w,\text{in}}} \]  \hspace{1cm} (A.2)

\( k_0 \) comprises three components: \( k_t, k_m, k_s [1],[2] \). The relationship among them is given in Eq. (A.3):

\[ \frac{1}{k_0} = \frac{1}{k_t} + \frac{1}{k_m} + \frac{1}{k_s} \]  \hspace{1cm} (A.3)

\( k_m \), is given in Equation (A.4) [8]:

\[ k_m = \frac{D_{w,m}}{T} \]  \hspace{1cm} (A.4)

where, \( D_{w,m} (m^2/s) \) is the diffusion coefficient of water vapor in the membrane, \( T (\mu m) \) is the thickness of the membrane.

The water vapor molecules migrated to the shell domain were removed rapidly by a vacuum pump. Therefore, \( k_s \) is redeemed as infinity, i.e., \( k_s = \infty \). Correspondingly, the resistance of the shell domain is neglectable.

Combining Equations (A.3) and (A.4), \( k_t \) is obtained by using Equation (A.5):

\[ k_t = \frac{k_0 \times k_m}{k_m - k_0} \]  \hspace{1cm} (A.5)

**APPENDIX B**

*Table B.1: Overall 2-way ANOVA results for the effect of concentration and temperature on water vapor permeability*

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>3</td>
<td>1.40E+08</td>
<td>4.67E+07</td>
<td>11.26</td>
<td>0.00</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>2.80E+09</td>
<td>1.40E+09</td>
<td>337.69</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>6</td>
<td>7.71E+07</td>
<td>1.28E+07</td>
<td>3.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Model</td>
<td>11</td>
<td>3.02E+09</td>
<td>2.74E+08</td>
<td>66.16</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>9.95E+07</td>
<td>4.14E+06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>35</td>
<td>3.12E+09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.2: Concentrations means comparison for the water vapor permeability results

<table>
<thead>
<tr>
<th></th>
<th>MeanDiff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC/PDMS</td>
<td>5096.40</td>
<td>959.72</td>
<td>7.51</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>2449</td>
<td>7743.8</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td>-3439.00</td>
<td>959.72</td>
<td>5.06</td>
<td>0.01</td>
<td>0.05</td>
<td>1</td>
<td>-6087</td>
<td>-791.7</td>
</tr>
<tr>
<td>4% CNC/PDMS</td>
<td>-4499.00</td>
<td>959.72</td>
<td>6.63</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>-7147</td>
<td>-1852.0</td>
</tr>
<tr>
<td>2% CNC/PDMS</td>
<td>1657.20</td>
<td>959.72</td>
<td>2.44</td>
<td>0.33</td>
<td>0.05</td>
<td>0</td>
<td>-990</td>
<td>4304.7</td>
</tr>
<tr>
<td>2% CNC/PDMS</td>
<td>597.06</td>
<td>959.72</td>
<td>0.88</td>
<td>0.92</td>
<td>0.05</td>
<td>0</td>
<td>-2050</td>
<td>3244.5</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td>-1060.00</td>
<td>959.72</td>
<td>1.56</td>
<td>0.69</td>
<td>0.05</td>
<td>0</td>
<td>-3708</td>
<td>1587.3</td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level

Table B.3: Overall 2-way ANOVA results for the effect of concentration and temperature on Nitrogen gas permeability

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>3</td>
<td>32004.90</td>
<td>10668.30</td>
<td>32.97</td>
<td>0.00</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>336814.00</td>
<td>168407.00</td>
<td>520.46</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>6</td>
<td>1882.98</td>
<td>313.83</td>
<td>0.96</td>
<td>0.46</td>
</tr>
<tr>
<td>Model</td>
<td>11</td>
<td>370702.00</td>
<td>33700.20</td>
<td>104.15</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>7765.74</td>
<td>323.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>35</td>
<td>378467.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.4: Concentrations means comparison for the Nitrogen gas permeability results

<table>
<thead>
<tr>
<th></th>
<th>Mean Diff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC/PDMS Pure PDMS</td>
<td>80.28</td>
<td>8.48</td>
<td>13.39</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>56.88</td>
<td>103.67</td>
</tr>
<tr>
<td>4% CNC/PDMS Pure PDMS</td>
<td>58.43</td>
<td>8.48</td>
<td>9.75</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>35.04</td>
<td>81.82</td>
</tr>
<tr>
<td>6% CNC/PDMS Pure PDMS</td>
<td>58.37</td>
<td>8.48</td>
<td>9.74</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>34.98</td>
<td>81.76</td>
</tr>
<tr>
<td>4% CNC/PDMS 2% CNC/PDMS</td>
<td>-21.84</td>
<td>8.48</td>
<td>3.64</td>
<td>0.07</td>
<td>0.05</td>
<td>0</td>
<td>-45.23</td>
<td>1.54</td>
</tr>
<tr>
<td>6% CNC/PDMS 2% CNC/PDMS</td>
<td>-21.90</td>
<td>8.48</td>
<td>3.66</td>
<td>0.07</td>
<td>0.05</td>
<td>0</td>
<td>-45.29</td>
<td>1.48</td>
</tr>
<tr>
<td>6% CNC/PDMS 4% CNC/PDMS</td>
<td>-0.06</td>
<td>8.48</td>
<td>0.01</td>
<td>1</td>
<td>0.05</td>
<td>0</td>
<td>-23.45</td>
<td>23.33</td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level

Table B.5: Overall 2-way ANOVA results for the effect of concentration and temperature on selectivity

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>3</td>
<td>316.96</td>
<td>105.65</td>
<td>2.51</td>
<td>0.08</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>52997.22</td>
<td>26498.61</td>
<td>629.94</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>6</td>
<td>152.36</td>
<td>25.39</td>
<td>0.60</td>
<td>0.72</td>
</tr>
<tr>
<td>Model</td>
<td>11</td>
<td>53466.54</td>
<td>4860.59</td>
<td>115.54</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>1009.56</td>
<td>42.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>35</td>
<td>54476.11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.6: Overall one-way ANOVA results for the effect of concentration on CTE

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>3</td>
<td>3020.41</td>
<td>1006.80</td>
<td>10.48</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>768.04</td>
<td>96.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>3788.45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.7: Concentrations means comparison for the CTE results

<table>
<thead>
<tr>
<th></th>
<th>MeanDiff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC-PDMS</td>
<td>-30.73</td>
<td>8.00</td>
<td>5.43</td>
<td>0.02</td>
<td>0.05</td>
<td>1</td>
<td>-56.35</td>
<td>-5.11</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% CNC-PDMS</td>
<td>-35.63</td>
<td>8.00</td>
<td>6.29</td>
<td>0.01</td>
<td>0.05</td>
<td>1</td>
<td>-61.25</td>
<td>-10.01</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% CNC-PDMS</td>
<td>-40.76</td>
<td>8.00</td>
<td>7.20</td>
<td>0.00</td>
<td>0.05</td>
<td>1</td>
<td>-66.38</td>
<td>-15.14</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% CNC-PDMS</td>
<td>-4.90</td>
<td>8.00</td>
<td>0.86</td>
<td>0.92</td>
<td>0.05</td>
<td>0</td>
<td>-30.51</td>
<td>20.71</td>
</tr>
<tr>
<td>2% CNC-PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% CNC-PDMS</td>
<td>-10.03</td>
<td>8.00</td>
<td>1.77</td>
<td>0.61</td>
<td>0.05</td>
<td>0</td>
<td>-35.65</td>
<td>15.58</td>
</tr>
<tr>
<td>2% CNC-PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% CNC-PDMS</td>
<td>-5.13</td>
<td>8.00</td>
<td>0.90</td>
<td>0.91</td>
<td>0.05</td>
<td>0</td>
<td>-30.75</td>
<td>20.48</td>
</tr>
<tr>
<td>4% CNC-PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level.

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level.

APPENDIX C

Table C.1: Overall 2-way ANOVA results for the effect of type of membrane and temperature on water vapor permeability

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of membrane</td>
<td>2</td>
<td>1.51E+08</td>
<td>7.53E+07</td>
<td>149.6</td>
<td>0.00</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>1.84E+09</td>
<td>9.18E+08</td>
<td>1823.6</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>4</td>
<td>1.98E+07</td>
<td>4.94E+06</td>
<td>9.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Model</td>
<td>8</td>
<td>2.01E+09</td>
<td>2.51E+08</td>
<td>498.2</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>9.07E+06</td>
<td>0.50E+06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>26</td>
<td>2.02E+09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the 0.05 level, the population means of **Type of membrane** are significantly different.

At the 0.05 level, the population means of **Temperature** are significantly different.

At the 0.05 level, the interaction between **Type of membrane** and **Temperature** is significant.
Table C.2: Type of membrane means comparison for the water vapor permeability results

<table>
<thead>
<tr>
<th></th>
<th>Mean Diff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC-PDMS Pure PDMS</td>
<td>5466.5</td>
<td>334.5</td>
<td>23.1</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>4612.7</td>
<td>6320.3</td>
</tr>
<tr>
<td>2% SCNC-PDMS Pure PDMS</td>
<td>4377.5</td>
<td>334.5</td>
<td>18.5</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>3523.7</td>
<td>5231.3</td>
</tr>
<tr>
<td>2% SCNC-PDMS 2% CNC-PDMS</td>
<td>-1088.9</td>
<td>334.5</td>
<td>4.6</td>
<td>0.01</td>
<td>0.05</td>
<td>1</td>
<td>-1942.8</td>
<td>-235.1</td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level

Table C.3: Overall 2-way ANOVA results for the effect of type of membrane and temperature on nitrogen gas permeability

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of membrane</td>
<td>2</td>
<td>257102.4</td>
<td>128551.2</td>
<td>679.1</td>
<td>0.00</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>147501.8</td>
<td>73750.9</td>
<td>389.6</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>4</td>
<td>23763.0</td>
<td>5940.7</td>
<td>31.3</td>
<td>0.00</td>
</tr>
<tr>
<td>Model</td>
<td>8</td>
<td>428367.3</td>
<td>53545.9</td>
<td>282.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>3407.0</td>
<td>189.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>26</td>
<td>431774.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the 0.05 level, the population means of **Type of membrane** are significantly different

At the 0.05 level, the population means of **Temperature** are significantly different

At the 0.05 level, the interaction between **Type of membrane** and **Temperature** is significant
Table C.4: Type of membrane means comparison for the nitrogen gas permeability results

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Mean Diff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC-PDMS Pure PDMS</td>
<td>80.2</td>
<td>6.4</td>
<td>17.5</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>63.7</td>
<td>96.8</td>
</tr>
<tr>
<td>2% SCNC-PDMS Pure PDMS</td>
<td>-154.8</td>
<td>6.4</td>
<td>33.7</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>-171.3</td>
<td>-138.2</td>
</tr>
<tr>
<td>2% SCNC-PDMS 2% CNC-PDMS</td>
<td>-235.1</td>
<td>6.4</td>
<td>51.2</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>-251.6</td>
<td>-218.5</td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level

Table C.5: Overall 2-way ANOVA results for the effect of type of membrane and temperature on selectivity

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of membrane</td>
<td>2</td>
<td>21552.11</td>
<td>10776.06</td>
<td>247.22</td>
<td>0.00</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>54381.41</td>
<td>27190.70</td>
<td>623.80</td>
<td>0.00</td>
</tr>
<tr>
<td>Interaction</td>
<td>4</td>
<td>2988.21</td>
<td>747.05</td>
<td>17.13</td>
<td>0.00</td>
</tr>
<tr>
<td>Model</td>
<td>8</td>
<td>78921.75</td>
<td>9865.21</td>
<td>226.32</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>784.59</td>
<td>43.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected Total</td>
<td>26</td>
<td>79706.34</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the 0.05 level, the population means of **Type of membrane** are significantly different

At the 0.05 level, the population means of **Temperature** are significantly different

At the 0.05 level, the interaction between **Type of membrane** and **Temperature** is significant

Table C.6: Type of membrane means comparison for the selectivity results

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Mean Diff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC-PDMS Pure PDMS</td>
<td>1.7</td>
<td>3.1</td>
<td>0.7</td>
<td>0.8</td>
<td>0.05</td>
<td>0</td>
<td>-6.2</td>
<td>9.6</td>
</tr>
<tr>
<td>2% SCNC-PDMS Pure PDMS</td>
<td>60.7</td>
<td>3.1</td>
<td>27.6</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>52.8</td>
<td>68.7</td>
</tr>
<tr>
<td>2% SCNC-PDMS 2% CNC-PDMS</td>
<td>59.0</td>
<td>3.1</td>
<td>26.8</td>
<td>0</td>
<td>0.05</td>
<td>1</td>
<td>51.1</td>
<td>67.0</td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level
Table C.7: Overall ANOVA results for the effect of type of membrane on CTE

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>2</td>
<td>2427.50</td>
<td>1213.75</td>
<td>13.31</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>6</td>
<td>546.90</td>
<td>91.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>2974.40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the 0.05 level, the population means are significantly different

Table C.8: Type of membrane means comparison for the CTE results

<table>
<thead>
<tr>
<th></th>
<th>Mean Diff</th>
<th>SEM</th>
<th>q Value</th>
<th>Prob</th>
<th>Alpha</th>
<th>Sig</th>
<th>LCL</th>
<th>UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CNC-PDMS</td>
<td>-30.70</td>
<td>7.70</td>
<td>5.5</td>
<td>0.0</td>
<td>0.05</td>
<td>1</td>
<td>-54.6</td>
<td>-6.8</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% SCNC-PDMS</td>
<td>-37.84</td>
<td>7.70</td>
<td>6.8</td>
<td>0.0</td>
<td>0.05</td>
<td>1</td>
<td>-61.7</td>
<td>-13.9</td>
</tr>
<tr>
<td>Pure PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% SCNC-PDMS</td>
<td>-7.10</td>
<td>7.70</td>
<td>1.2</td>
<td>0.6</td>
<td>0.05</td>
<td>0</td>
<td>-31.0</td>
<td>16.8</td>
</tr>
<tr>
<td>2% CNC-PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sig equals to 1 indicates that the difference of the means is significant at the 0.05 level

Sig equals to 0 indicates that the difference of the means is not significant at the 0.05 level

C.1 Unsuccessful trials when synthesizing the membranes

CNC/PDMS membranes

The CNC/PDMS membranes were synthesized employing varying CNC concentrations: 0%, 2%, 4%, and 6%. However, CNC concentrations of greater magnitudes, specifically 8% and 10%, were subjected to examination. Nonetheless, within these elevated concentrations, the resultant CNC/PDMS solution exhibited excessive viscosity, rendering it impractical for degassing and subsequent casting onto a Teflon mold. Consequently, the CNC concentration was constrained to a maximum of 6%, representing the threshold at which successful film synthesis could be accomplished, yielding a finalized homogeneous membrane structure.
**SCNC/PDMS membranes**

For the preparation of the SCNC/PDMS membrane, the initial phase involved utilizing a CNC suspension in water. Yet, during this process, the introduction of silylated CNC suspension into the PDMS solution resulted in a biphasic solution. This phenomenon could be attributed to the inherent incompatibility between water, silylated CNC, and PDMS. The silylation of surface hydroxyl groups on CNC was achieved through the incorporation of MTMS into a 1 w.t.% CNC suspension, a procedure conducted over a span of 4 hours at room temperature. Moreover, ethanol was used as a solvent in the silylation process. However, this caused an issue where it wasn't compatible, resulting in the formation of a solution with multiple distinct phases after being added to PDMS.

Consequently, a subsequent endeavor encompassed the solvent exchange of the CNC suspension from water to an alternate solvent to obviate the water-based system. Nonetheless, the quest for a suitable non-polar organic solvent proved to be challenging. In one trial, CNC was exchanged into Dimethyl sulfoxide (DMSO). Nevertheless, the resultant solution containing DMSO also exhibited incompatibility with PDMS, yielding a biphasic outcome. In light of these challenges, a decision was reached to employ dried CNC powder, particularly Spray dried CNC.

**C.2 Spray-drying CNC manufacturing process information**

Cellulose nanocrystals (CNC) were obtained through a hydrolysis process using 65% sulfuric acid. To enable the subsequent silylation step in an anhydrous system, the CNC suspension in water was dried using a spray drying technique. The drying process was conducted using a mini spray dryer (BUCHI B-290), available at the Advanced Structures and Composites Center of the University of Maine (Orono, Maine, U.S.), by the research group led by and Dr. Gardner, Sugjun Huwang. Figure C.1 presents a schematic depicting the spray drying process used to produce CNC powder.
A Mastersizer 2000 analyzer (Malvern Instruments, Worcestershire, United Kingdom) was used to analyze the particle size distribution of the spray dried CNCs. The amount of the powders analyzed was 1 g, and the particle refractive index was 1.54 [4].

The surface area \([D_{3,2}]\) (Surface weighted mean) values were considered as the average particle size of SDCNFs powders in this study. The result of particle size distribution is presented in Figure C.2.
The particle shapes and size distributions were measured via a Morphologi-G3-ID morphologically directed Raman system (Malvern Instruments, Worcestershire, United Kingdom). The following two equations are HS Circularity (a) and aspect ratio (b) in the Morphologi-G3: [5]:

\[ \text{(a) HSCircularity} = \frac{4\pi \text{Area}}{\text{Perimeter}^2} \quad \text{(b) AspectRatio} = \frac{\text{Width}}{\text{Length}} \]

The aspect ratio and HS Circularity values lying between 0 to 1 indicate particles' shapes in the Morphologi-G3. For example, the closer their value to 1 indicates, the closer the shape of the circle, while the closer it is to 0 indicates a more prolonged rod shape [5]. The results are provided in Figure C.3.

![Figure C.3: Particle shapes and size distributions of the spray dried CNCs](image)

**C.3 Dynamic Mechanical Analysis (DMA)**

Dynamic mechanical analysis (DMA) was conducted using a Q850 dynamic mechanical analyzer (TA Instruments) in tension mode. The experiments were performed at a fixed frequency of 1.0 Hz an initial force of 0.02 N, and a strain of 0.05%. The temperature varied from -80 to 100 °C at a heating rate of 5 °C/min, and a strain of 0.05% was applied. The experiments were done in the air. For each sample type, three replicates were conducted.
Figures C.4a and b illustrate the impact of the CNCs and SCNCs on the storage modulus (E') and loss factor (tan δ) of the membranes, respectively. The tan δ results indicated that the introduction of the CNCs and SCNCs has a weak effect on the glass transition temperature (Tg) of the membranes. Typically, the glass transition temperature of PDMS membranes ranges from -45 °C to -50 °C, which is a characteristic of the PDMS component [6].

Despite the low loading level of the SCNCs, the storage modulus (E') of the SCNC/PDMS composite exhibited improvement at low (-50 °C), room (30 °C), and elevated (80 °C) temperatures compared to the neat PDMS and CNC/PDMS composite membranes. This enhancement in the storage modulus demonstrates the significant impact of SCNCs on the mechanical properties of PDMS.

It is worth noting that cellulose nanocrystals possess high mechanical modulus, ranging from 100 to 200 GPa depending on their sources, in contrast to the low modulus of 2-3 MPa exhibited by the soft PDMS matrix at room temperature [6]. Specifically, in this study, the addition of only 2 w.t. % of SCNC to the PDMS resulted in an increased storage modulus (E') of 2.28 MPa at 25 °C, whereas the values for CNC/PDMS and PDMS membranes were 1.91 MPa and 1.74 MPa, respectively. This result highlights the beneficial effect of incorporating SCNC into the PDMS matrix.

In the case of CNC/PDMS, the improvement in the storage modulus is not significant, possibly due to low compatibility between CNC and the hydrophobic PDMS matrix. However, after silylation of the CNC surface, the increase in storage modulus can be attributed to improved adhesion at the filler/matrix interface, resulting from enhanced compatibility between SCNC and PDMS [7].
References


BIOGRAPHY OF THE AUTHOR

Nasim Alikhani was born in Tehran, Iran on August 28, 1989. She graduated from Farzanegan High School administered under the National Organization for Development of Exceptional Talents (NODET) in 2007. She attended Iran University of Science and Technology and graduated in 2011 with bachelor’s degree in Chemical Engineering. She was admitted to the master’s degree at the Isfahan University and graduated with master’s degree in Chemical Engineering with a concentration in Environment in Oct 2017. She started her PhD at University of Maine in Summer 2019 at the School of Forest Resources working on application of Cellulose nano crystals in membrane technology for energy saving in wood drying. At the University of Maine Nasim has been a research assistant. She has been selected as the student of the year for the Blumenstock Family Forest Products Student of the Year award and she was the annual award winner, the 2nd place wood award from the Forest Products Society in 2022. Nasim is a candidate for the Doctor of Philosophy degree in Forestry from the University of Maine in August 2023.