

SURFACE ENGINEERING OF WOOD FIBER/FILLER NETWORKS

by

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Abstract

The hydrophilic property of cellulose substrates and their sensitivity to moisture limits their use in certain applications. The aim of this study is to enhance the barrier properties of cellulosic and lignocellulosic paper by utilizing environmentally benign techniques. Chemical Vapor Deposition (CVD), Plasma Enhanced Chemical Vapor Deposition (PECVD), and Atomic Layer Deposition (ALD) techniques were employed to deposit Dichlorodimethylsilane (DCDMS), tetrafluoromethane (CF_4), and aluminum oxide (Al_2O_3) on cellulosic and lignocellulosic papers, respectively. A wide range of fiber sizes from unrefined, 927 μm , to highly refined, 177 μm , were employed to make handsheets and the effect of the chemicals and the deposition techniques, mentioned above, on wettability and gas permeability of the handsheets was investigated. In this regard, the contact angles on handsheets prepared with unrefined fibers are significantly higher (140° - 153°) than those of the refined ones (95° - 120°) due to their higher surface roughness. However, on handsheets formed with refined fibers, although the treatments resulted in a hydrophobic surface, the water droplets absorb to the handsheets over time. It is also shown that at certain fiber size (561 μm) the water vapor transmission rate (WVTR) reaches its minimum value and further decrease of the fiber size does not significantly affect the WVTR. In terms of wettability, the cellulosic and lignocellulosic substrates coated by deposition of CF_4 resulted in the highest contact angles (120° - 153°). However, regarding moisture barrier properties, the Al_2O_3 deposited substrates resulted in the lowest WVTRs ($2.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$). Moreover, the impact of fabrication method was studied and the fiber drying mechanism during sheet formation was also elucidated. It was found that casting of a Micro Fiber (MF) suspension on hydrophobic substrates results in formation of optically translucent films with mechanical and barrier properties similar to

micro and nano fibrillated cellulose films. The manufacturing of the latter is energy intensive and hence the new method has potential advantage. Finally, Janus (hydrophilic-hydrophobic) fillers were fabricated and the effect of filler's dual functionality on barrier properties of handsheets loaded with Janus fillers was investigated. Silanization of handsheets substrates in conjunction with dual functionality of fillers results in formation of a superhydrophobic handsheet.

Lay Summary

Advances in our understanding of the properties of cellulosic wood fibers in experimental techniques and a demand for sustainable industrial and consumer products has created a unique opportunity to engineer wood fibers towards a number of applications ranging from food packaging to microelectronics and biomaterials. However, the main drawbacks of cellulosic substrates, namely, poor barrier property and high sensitivity to moisture limits its use in these applications. This thesis introduces environmentally benign techniques to fabricate water repellent cellulosic and lignocellulosic papers with low gas permeability, suitable in paper electronic and packaging applications. Additionally, the effects of fiber size and drying mechanism on barrier, optical, and mechanical properties of cellulose paper are investigated.

Preface

This thesis entitled “Surface Engineering of Wood Fiber/Filler Networks” presents the research the author performed during her PhD study under the supervision of Professor Peter Englezos and Proferssor Savvas G. Hatzikiriakos. Several techniques have been introduced and compared for controlling the barrier properties of lignocellulosic paper.

The following journal papers and conference presentations have been published or prepared for publication from the research work presented in this dissertation:

Journal Papers

1. **Mirvakili, M.**, Hatzikiriakos, S. G., Englezos, P. (2016), “Effect of Fibre Size on Wettability and Barrier Performance of Hydrophobic Cellulosic Papers”, *The Journal of Science and Technology for Forest Products and Processes (J-FOR)*, 5,38-44. (This paper is based on the data presented in Chapter 2 of this thesis.)
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The Fifth journal paper is written mostly by Seyed Moahammad Mirvakili. All other manuscripts were written mostly by the author of this thesis and revised by the supervisor (Prof. Peter Englezos) and the other co-authors.

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List of Symbols

R_a	Average roughness
f_{SL}	Fraction of solid surface area wet by liquid
γ_{SL}	Solid-Liquid interfacial tension
γ_{SV}	Solid-Vapor interfacial tension
γ_{VL}	Vapor-Liquid interfacial tension
θ_{Adv}	Advancing contact angle
θ_{CB}	Cassei-Baxter contact angle
θ_{Rec}	Receding contact angle
θ_W	Wenzel contact angle
θ_Y	Young contact angle
r	Roughness
φ	Angle of gel foot

List of Abbreviations

AKD	Alkyl Ketene Dimer
ALD	Atomic Layer Deposition
APS	Aminopropyl Triethoxysilane
ASA	Alkenyl Succinic Anhydride
BPA	Poly-Butyl Acrylate
CF ₄	Tetrafluoromethane
CI	Crystallinity Index
CNC	Crystalline Nano-Cellulose
CVD	Chemical Vapor Deposition
DCDMS	Dichlorodimethyl Silane
DDAB	Didodecyl Dimethylammonium Bromide
FITC	Fluorescein Isothiocyanate isomer I Celite
FQA	Fiber Quality Analyzer
FTIR-ATR	Fourier Transform Infrared Spectra- Attenuated Total Reflectance
ICP	Inductively Coupled Plasma
KR	Kraft Refined
KU	Kraft Unrefined
LBL	Layer-by-Layer
MF	Micro-Fiber
MFC	Micro Fibrillated Cellulose
NFC	Nano Fibrillated Cellulose
OP	Opaque
OTR	Oxygen Transmission Rate

PCVD	Plasma Chemical Vapor Deposition
PECVD	Plasma Enhanced Chemical Vapor Deposition
RH	Relative Humidity
SEM	Scanning Electron Microscopy
SRE	Specific Refining Energy
STT	Surface Tension Torque
TL	Translucent
TMA	Trimethylaluminum
TMP	Thermo-Mechanical Pulp
TR	TMP Refined
TU	TMP Unrefined
WVP	Water Vapor Permeability
WVTR	Water Vapor Transmission Rate
XPS	X-ray Photoelectron Spectroscopy

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Dedication

In memory of my father

To my family

with love and eternal appreciation

Chapter 1: Introduction

Advances in our understanding of properties of cellulosic wood fibers and increasing environmental concerns over sustainability and end-of-life disposal challenges have created a new field of research to engineer cellulosic substrates as potential replacements for synthetic plastics and other opportunities. Development of the next generation of cellulosic based materials with new applications in diverse areas, ranging from food packaging to microelectronics and biomaterials, requires techniques that can modify the functionality of cellulose fibers while maintaining desired substrate characteristics. Cellulosic paper serves as a promising candidate for the development of versatile, lightweight and environmentally friendly composites. However, it is hydrophilic and hygroscopic, which makes it difficult to beat the success of synthetic plastic materials without further modification. In this regard, fabrication of superhydrophobic cellulose-based substrates can be challenging due to the complex structure and limited thermal and chemical resistance of cellulosic surfaces. The most common approaches to fabricate superhydrophobic coating on cellulosic paper are through wet chemical methods such as dip coating¹⁻³, spray coating⁴⁻⁶, and polymerization techniques^{7,8}. However, the slow processing time and loss of the coating over time are the main drawbacks of these methods. A wide range of studies have examined surface alteration and dry approaches to modify and tune barrier properties of cellulosic surfaces^{7,9-18}. These methods involve morphological and chemical modifications by plasma processing⁹⁻¹¹, deposition of organic and inorganic coatings¹²⁻¹⁶, chemical vapor deposition¹⁷, and polymerization techniques⁷. While these techniques offer superhydrophobic and superamphiphobic properties on cellulosic substrates, some may result in non-uniform coatings, surface damage of the cellulose substrate, and reduction in strength properties.

This thesis demonstrates fabrication of hydrophobic and superhydrophobic lignocellulosic papers with high moisture/gas barrier properties by using refined and unrefined fibers in conjunction with three types of vapor deposition techniques. The effect of fiber size and drying mechanism of cellulosic paper substrates on barrier properties is also studied. Additionally, dual functional (hydrophobic/hydrophilic) fillers are fabricated, and the inclusion of these fillers in cellulosic handsheet and their effect on barrier properties of cellulosic paper are investigated.

1.1 Background

1.1.1 Wettability, Contact Angle, and Surface Tension

The total wetting on a surface of a material occurs due to high affinity of water molecules to that surface and results in formation of a liquid film on the surface. In this case the contact angle, which is a quantitative measurement for surface wettability, approaches zero. In contrast, when the liquid forms a droplet on the solid surface partial wetting of the surface occurs due to the higher affinity of water molecules to themselves than that to the solid surface.

The contact angle is defined as the angle between the tangent lines to the solid-liquid and liquid-vapor interfaces at the triple contact line (contact line of the three phases)¹⁹. The general definition for a hydrophobic surface is the existence of water contact angle greater than 90°, while for a wetting state with contact angle less than 90° the surface is referred as a hydrophilic surface. The wettability depends on surface energy, an intrinsic property, and surface roughness. An equation describing the contact angle on an ideal (perfectly smooth) solid surface was first introduced by Thomas Young in early 1800s²⁰. According to Young's equation, the contact angle, θ_Y , on an ideal flat surface at equilibrium is defined by surface tension acting at the three-phase interface (Fig. 1.1a) and is given by equation 1.1:

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{VL}} \quad (1.1)$$

where γ_{SV} , γ_{SL} , and γ_{VL} are the surface interfacial tension between solid-vapor, solid-liquid, and vapor-liquid respectively ¹⁹.

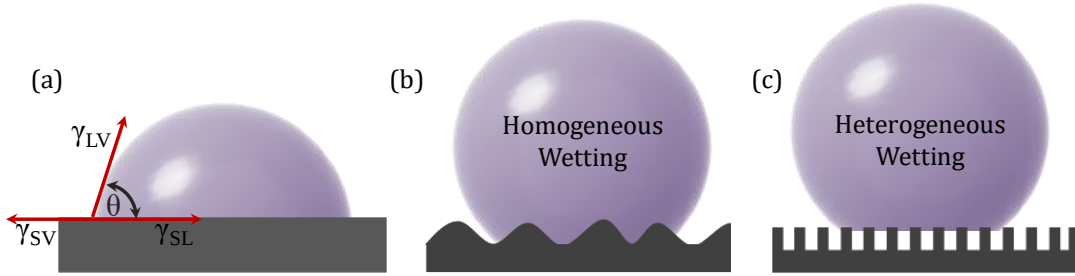


Figure 1.1. (a) The surface tension acting at three-phase interface on an ideal surface. (b) Homogeneous wetting regime. (c) Heterogeneous wetting regime

In principle, on a rough surface, the wettability of the surface may be associated with two different wetting states namely homogeneous and heterogeneous wetting ²¹ (Fig. 1.1b, and 1.1c). In the homogeneous wetting regime, the liquid fills the roughness grooves of the surface and wet the whole surface (Fig. 1.1b). However, on the heterogeneous wetting regime, air pockets form inside the roughness grooves under the liquid and results in a composite interface including vapor-solid, vapor-liquid, and liquid-solid ²¹. In this regard, the Young equation cannot be applied any longer for evaluation of the contact angle. In fact in the case of a rough surface the actual contact angle (with respect to the local orientation of the microgroove) and apparent contact angle (with respect to the horizontal line) on the surface can be formed (Fig. 1.2).

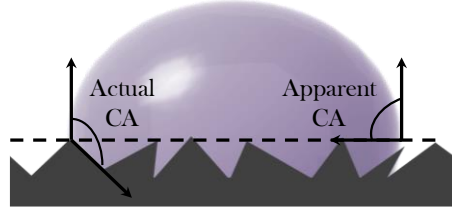


Figure 1.2. Actual and apparent contact angle

The actual or intrinsic contact angle is defined as the angle between the tangent lines of liquid-vapor and the real liquid-solid interface. The apparent contact angle is the angle between the tangent lines of the liquid-vapor and the nominal solid-liquid interfaces ¹⁹.

By multiplying a roughness factor to the Young's contact angle (θ_Y) relation Eq. 1.2 was obtained, by Wenzel in 1936 ²².

$$\cos \theta_W = r \cos \theta_Y \quad (1.2)$$

where θ_W is the Wenzel contact angle, and r is the roughness factor which is always greater than 1. It is defined as the ratio of actual surface area to the projected surface area (smooth surface). According to Wenzel relation, the roughness increases the contact angle of a hydrophobic surface and decreases the contact angle of a hydrophilic surface. The limitation for Wenzel relation is that for highly rough surfaces, the contact angle may fall into a nonphysical state in which the right-hand side of the equation is greater than one.

For a real surface with a non-uniform roughness and heterogeneous wetting there might exist ranges of apparent contact angles along the contact line (Wolansky, 1999). In 1944, Cassie and Baxter defined a relation for the contact angle ²³ (Eq. 1.3) on a composite surface or the heterogeneous wetting regime (Fig. 1.1c).

$$\cos \theta_{CB} = f_{SL} r \cos \theta_Y + f_{SL} - 1 \quad (1.3)$$

where f_{SL} is the fraction of the solid surface area wet by the liquid and r is the roughness ratio of the wetted area. Upon complete wetting of a solid surface f_{SL} is 1 and equation 1.2 is recovered.

1.1.2 Static vs. Dynamic Contact Angle

Static contact angles are measured when the contact area between liquid and solid surface is not changed during the measurement. In other words, when the droplet is standing on the surface and the triple line boundary is not moving the measured contact angle is called static contact angle²⁴. On the other hand, when the triple line boundary is moving, dynamic contact angles can be measured and referred to as advancing and receding contact angles. The measurement of a single static contact angle is not sufficient to characterize the wettability of a surface. The rough microstructures on the heterogeneous surfaces are barriers to the motion of the contact line. This results in an existence of a wide range of apparent contact angles on a surface¹⁹. This range lies between the advancing and receding contact angles²⁵. The advancing contact angle can be measured when the liquid droplet is spreading on the surface. On the other hand, when the droplet is contracted the receding contact angle can be measured. Fig. 1.3 shows the measurement process to obtain the advancing and receding contact angles of a droplet on a surface.

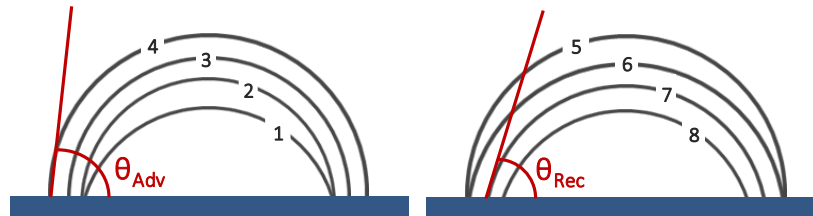


Figure 1.3. Advancing and receding contact angles

The difference between the advancing and receding contact angle is called contact angle hysteresis. A superhydrophobic surface is referred to a substrate with a high value of contact angle ($>150^\circ$) and low contact angle hysteresis ($<5^\circ$).

1.1.3 Water Vapor and Gas Permeability of Cellulosic and Lignocellulosic Substrates

The hydrophilic nature of paper and its permeability to gases limits its applications as a high-performance packaging material, display panels and electronic devices. Recently, the conversion of cellulosic material into a major fraction of individualized elementary fibrils, which is referred to as nanocellulose, offers a promising alternative to synthetic materials. Nanocellulose films exhibits good barrier and mechanical properties ²⁶. A formal naming convention for the nanocellulose material is under development and depending on the route utilized to produce it and the degree of fibrillation, different terminology has been used by researchers for this material ²⁷. Micro-fibrillated cellulose (MFC) and Nano-fibrillated cellulose (NFC) are the two common terms used to distinguish between the fibrillation methods. MFC, with the fibril diameter in the range of 10-50 nm, is produced by mechanical treatment of fibers. Microfibrils are the main component of the MFC suspension, but studies have shown that due to mechanical fibrillation, the MFC suspension may be inhomogeneous and contain fibers, fibrillar fines, fibers fragments, and nanofibrils²⁸. On the other hand, NFC, with a typical elementary fibril diameter in the range of 3-5 nm, is produced by chemical pretreatment followed by high pressure homogenization²⁷⁻²⁹. When MFC or NFC gels dried, films or aerogels can be obtained depending on the drying mechanism. The gas permeability of MFC and NFC films also depends on the source of the MFC raw material, the production treatment, and chemical modifications of MFC/NFC ²⁶. Syverud et al ³⁰ showed that the air permeability of paper, coated by 10% MFC was reduced significantly due to decrease of surface porosity. Pure MFC films showed water vapor transmission rate of $91 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ which is still a high value compared to those of polymer films ¹⁵.

1.1.4 Surface Modification of Cellulose Paper to Impart Hydrophobicity

Cellulose is an abundant biopolymer in nature, which is used in the paper making industry. Cellulose fiber has a large number of hydrophilic (hydroxyl) groups, which can easily form hydrogen bond with water molecules and facilitate absorption and spreading of water on the surface by capillary action. The other property of cellulose is its hygroscopic behavior which leads to high level of moisture absorption from the environment ¹³. The reported water contact angle for cellulosic paper is within a range of 17°- 47°. Controlling the wettability of the paper surface is crucial for certain applications. Due to the complex structure, limited thermal and chemical resistance of cellulosic surfaces, fabrication of hydrophobic/superhydrophobic cellulose-based substrates with low gas barrier properties can be challenging. Therefore, suitable methods for fabrication of such surfaces are limited. In the following sections, various approaches for fabrication of hydrophobic and superhydrophobic cellulose based surfaces are discussed.

1.1.4.1 Wet Chemical Methods

The most common approaches to fabricate hydrophobic coatings on cellulosic paper by wet chemical methods are dip coating ^{2,3,31,32}, spray coating ^{5,6,33}, and polymerization techniques⁸.

Dip Coating. This method involves dipping of the substrate in the coating slurry, drying, and curing. Usually the coating slurry consists of organic solvents, nano/micro particles for increasing the surface roughness, and binding components such as polymers.

Spray Coating. In this method, the liquid droplets of the coating slurry are sprayed on the surface. The steps that are involved in this method are spraying of the coating slurry, drying/ curing, and a possible treatment by a low surface energy material. In the novel approach of spray coating there is only one step of processing. In this method the coating is formed by a rapid physico-chemical

reaction and phase transition from liquid or gas to solid in the aerosol phase. Although the method is fast, the durability of the coating is not comparable to dip coating method.

Polymerization. This method involves closely controlled chemical reactions. The multi-step and the slow processing time are the main drawbacks of this method.

1.1.4.2 Dry Methods

The dry coating methods offer a simpler and straightforward process compared to wet chemical methods without requirements of additional drying and curing steps. Plasma processing and chemical vapor deposition (CVD) are the common dry methods ^{9,11}. In these methods the surface of lignocellulosic substrate can be tuned through a fine chemical and physical structure. This procedure usually requires two processing steps. These are the creation of nano-scale roughness on the surface by etching followed by the deposition of a low surface energy material on the surface.

The atmospheric non-thermal plasma processing provides some advantages over the typical surface modification methods. It is regarded as a green technology compared to the conventional wet-chemical methods. The waste and by products generation are very low with plasma processing. In addition, the energy intensive drying process is not required. Finally, plasma surface modification is an effective way of controlling the surface energy and chemical properties of substrates without affecting their bulk ones ³⁴. The main drawbacks of plasma and CVD processing is the cost of the equipment and for the case of plasma etching, the batch type and slow nature of the procedure is a disadvantage.

1.1.4.2.1 Plasma Enhanced Chemical Vapor Deposition

Plasma which is a state of ionized gas contains reactive components such as electrons, ions, photons, radicals, and variety of neutral species ^{9,34}. The plasma phenomenon was first observed by Irving Langmuir when he tried to strike an electrical discharge in a gas. He coined the term “plasma” ³⁵.

Generally, plasma processes apply radio frequency (RF) or microwave energy to gas molecules ³⁶. An electric discharge partially ionizes organic gases and creates highly activated species and radicals. Since this process can be performed at room temperature, it is considered as an advantage for the treatment of wood fibers due to decomposition of fibers at high temperatures.

Plasma treatments usually used for cleaning, etching or ablation, activating, and coating ³⁴. During plasma etching, the outermost layer of the surface is removed and depending on the processing time, energy, and substrate’s material, a degree of roughness is created on the surface. During plasma activation, the functional groups replaced with different atoms or ions to increase the surface energy of the non-reactive surfaces to enhance the adhesion properties. The deposition in the form of thin film occurs during plasma coating which is also called plasma polymerization or plasma enhanced chemical vapor deposition (PECVD) ³⁴. Hydrocarbons, organosilicons, halocarbons, and organometallics are the functional layers that can be deposited by PCVD ³⁴.

The advantage of plasma enhanced chemical vapor deposition is its operation at lower temperatures compared to CVD methods. During operation the substrate can be maintained at low temperature since the formation of the reactive species in the gas phase takes place by collision in the gas phase. Some of the desirable properties of PECVD films are good adhesion, low pinhole density, good coverage, and uniformity.

Plasma treatment on cellulosic substrates introduced in 1970s in which microwave plasma employed for modification of the bonding properties of cellulose ³⁷. Since then a variety of precursor gases such as: nitrogen, argon, oxygen, hydrogen, ammonia, sulfur dioxide, hydrocarbons, fluorocarbons, halogens, and organosilanes have been used for treatment of cellulose substrates ⁹. Among these precursors, hydrocarbon, organosilicon, and fluorocarbon have been employed by plasma processing to impart hydro/superhydrophobicity on cellulose papers ³⁴. One of the desired features of plasma deposition is the individual coverage of fibers by polymer thin film which does not block interfibre pores ⁹ and may affect the water vapor and gas diffusion through the paper.

1.1.4.2.2 Atomic Layer Deposition

Atomic layer deposition (ALD) is a chemically versatile, layer by layer thin film deposition process which has been widely employed to deposit thin films of various materials ^{16,38,39}. The advantages of ALD rely on the self-limiting chemical reactions of the precursors on the surface of the substrate, allowing for controlling film thickness at atomic level ³⁸. This method is proven to create densely packed and uniform films with low defect density, precise thickness, and low impurity contamination ³⁸⁻⁴¹. Studies have shown that ALD coatings are perfectly suited to produce high performance permeation barriers on polymeric and porous materials, such as poly(2, 6-ethylenenaphthalate), polylactide (PLA), polyimide, polyethylene films, coated boards, and etc. ^{40,42-46}. In this regard Al_2O_3 is one of the widely studied materials grown by ALD to improve oxygen and moisture barrier properties of synthetic and bio-based plastics, biopolymers, and fiber-based materials ^{43,46,47}. More specifically, the studies for Al_2O_3 films grown by ALD on paper-based products have been limited to the gas diffusion barrier performance of various (1) coated

paperboards ((board basis weights between 200-310 $\text{g}\cdot\text{m}^{-2}$) coated with polylactide, galactoclugomannan, and polyethylene (coating basis weight ranging from 15-35 $\text{g}\cdot\text{m}^{-2}$)), (2) pigment coated and calendared high gloss paper (60 $\text{g}\cdot\text{m}^{-2}$) (3) polyethylene coated paper (4) commercial uncoated copy paper (80 $\text{g}\cdot\text{m}^{-2}$) and (5) nanofibrillated cellulose (60 $\text{g}\cdot\text{m}^{-2}$)^{43,46,47}. It is shown that Al_2O_3 deposited films improved the oxygen and water vapor barrier performance^{43,46,47}. Accordingly, the lowest water vapor transmission rate (WVTR) for paperboards and paper samples are reported for polylactide-coated boards with 25 nm Al_2O_3 deposition with value of $1\pm0.2 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (at 23°C and 75% relative humidity (RH)) and for polyethylene (LDPF) coated papers with 50 nm Al_2O_3 deposition with value of $3.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (at 23°C and 75% RH) respectively^{43,46}. It is also reported that 25 nm coatings of Al_2O_3 on nano-fibrillated cellulose films decreased the WVTR from $\sim 615 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ to $\sim 400 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ⁴³.

In addition to the effect of Al_2O_3 ALD coatings on gas permeability, its effect on wetting properties has been investigated^{43,44,48-51}. On the hydrophilic PLA films, PLA-coated boards, and polyethyleneterephthalate films, the contact angles of water droplets decreased after Al_2O_3 ALD^{43,44,51}. While results on natural cotton cellulose fibers (cotton mats and cotton balls) show that there is transition in wetting properties from hydrophilic to hydrophobic after few cycles of ALD, and as the ALD coating cycles continue the fibers return to hydrophilic state due to the formation of hydroxylated aluminum oxide^{48,50}.

The effect of ALD coating on uncoated thin paper substrates free of hydrophobic binders, chemical modifiers, fillers and additives have not previously been studied. The highly porous structure of uncoated paper products has limited its use as a substrate of interest for applications where low wettability and gas permeability is required.

1.1.5 Hydrophobic Fillers Modification for Fabrication of Hydrophobic Paper

The traditional methods to control the wettability of paper are internal sizing and surface sizing. Internal sizing refers to the control of water penetration within the bulk. It can be obtained by adding the natural or synthetic sizing agents such as rosin, or alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) to the pulp suspension during stock preparation ⁵². Well-sized paper has a contact angle of 90°-100°. The disadvantage of the traditional internal sizing agent (AKD and ASA) are their poor recyclability due to a low melting point and the loss of sizing over time ⁵³. Surface sizing, is performed in the final stage of papermaking process by filling the pores using low surface energy waxes and chemicals. The mineral fillers can be used for surface filling and surface coating applications ⁵⁴. Mineral fillers are used in papermaking for enhancing the physical and optical properties of paper. By increasing the concentration of filler in a paper pulp suspension (furnish) the amount of sizing agents used should also increase in order to keep the desired hydrophobicity in the finished paper ^{55,56}. However, because of the disproportionate fraction of the sizing agent that is being absorbed on the high surface area of the fillers, the sizing agent may be lost from the furnish ⁵⁶. This will result in lower effectiveness of the sizing agent and increase of the papermaking cost. One method to eliminate the negative effect of high filler loading on sizing efficiency is the use of hydrophobic fillers. Many attempts have been devoted for the synthesis and fabrication of hydrophobic and superhydrophobic mineral fillers surfaces ^{5,57-59}. However, good dispersion of the fillers are always highly demanded and for hydrophobic fillers high shear is required for their dispersion.

1.1.6 Janus Particles

Janus particles are named after the Roman god Janus that is represented with two heads placed back to back. The term Janus is used to describe particles whose surfaces of both hemispheres are different ⁶⁰. For example, one side is hydrophilic, while the other is hydrophobic. This property can be used for assemblies like dual functional devices. By combining a hydrophilic hemisphere with a hydrophobic hemisphere, amphiphilic Janus particles can be formed, which is useful for the stabilization of water in oil or oil in water emulsions. Also, fabrication of amphiphilic Janus particles may result in a homogeneous dispersion of particles in the aqueous phase such as wood fibre suspension. Similarly, films with one surface hydrophilic and the other highly hydrophobic are called Janus films and have potential applications, where surfaces of dual function are required ⁶⁰. One of the approaches for synthesizing Janus colloidal particles is based on Pickering emulsion strategy. Consider droplets of oil and water in Fig. 1.4.

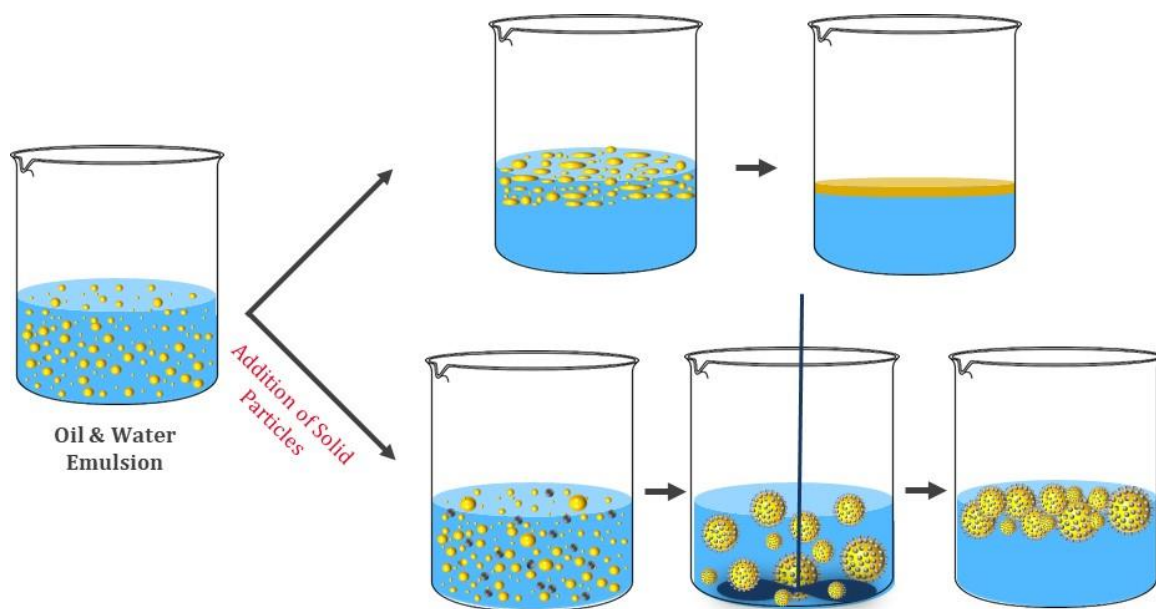


Figure 1.4. Formation of Pickering emulsion

If oil and water are mixed, oil droplets will form and disperse in water. Eventually these oil droplets will coalesce and form a thin film on water to decrease the amount of energy in the system. However, if solid particles are added to the oil in water emulsion, they will bind to the liquid/liquid interface and prevent the oil droplets from coalescing and thus stabilize the emulsion. This strategy was used in this study to form Janus filler particles.

1.2 Research Objectives

The main goal of this project is the use of cellulose paper in new higher value-added applications by improving its barrier properties through fabrication of (1) hydrophobic and superhydrophobic cellulosic and lignocellulosic papers/films with low gas permeability suitable for high performance packaging and paper electronics, and (2) Janus paper substrate by using functionalized fillers (Janus hydrophobic fillers). Therefore, the surface energy and/or structure of cellulosic paper will be adjusted to achieve different wettability (hydrophobicity and/or superhydrophobicity), low WVTR (water vapor transmission rate), and low OTR (oxygen transmission rate). The paper should have sufficient high tensile strength as well as low recycling cost. In addition, the hydrophobicity of paper needs to be assessed when it is in contact with water for a long period of time.

The first part of the research fully explores the effect of fiber size on the barrier properties of cellulosic and lignocellulosic papers/films in conjunction with three different chemical vapor deposition techniques, namely, CF_4 plasma enhanced chemical vapor deposition, chemical vapor deposition of silane, and Al_2O_3 atomic layer deposition. In addition, precursor type and deposition techniques were compared with respect to their effect on wettability and gas permeability of paper

substrates. The effect of cellulosic and lignocellulosic films' preparation technique and drying mechanism on its optical, physical and mechanical properties is also investigated.

The research aims to overcome the current limitations of the paper based electronic devices by designing and fabricating the paper through judicious control of the cellulose fiber size and fiber alignment to create hydrophobic paper with low gas permeability.

The second part of the study focuses on the modification of silica and titanium dioxide fillers in order to render them partially hydrophobic. The inclusion of these Janus hydrophobic/hydrophilic fillers in cellulosic handsheets and their effect on the barrier properties is investigated. The challenge is the partial hydrophobization of fillers without sacrificing their dispersability in the aqueous fiber suspension.

In summary, the objectives of the present thesis are:

1) To fabricate hydrophobic/superhydrophobic handsheets with low water vapor transmission rate by surface treatment of handsheets utilizing three different chemical vapor deposition techniques. The work will focus on:

- Studying the effect of fiber size on wettability, gas permeability, and water absorption of lignocellulosic papers/films, and identify optimum fiber size to be used in order to minimize water vapor transmission and air permeability.
- Studying the effect of precursor type and vapor phase deposition technique on barrier properties of papers/films.
- Studying the effect of film preparation's and drying method on its optical, physical and mechanical properties.

2) To fabricate dual functional (Janus) fillers, namely, SiO₂, and TiO₂.

3) To fabricate hydrophobic/superhydrophobic handsheets using dual functional fillers. The study is investigating:

- The effect of fillers dual functionality on wettability and water vapor transmission rate of handsheets.
- The effect of fillers dual functionality on their distribution and loading in handsheets.

1.3 Thesis Organization

The organization of this dissertation is as follows. A brief introduction to the fabrication of hydrophobic and superhydrophobic lignocellulosic paper via different techniques is presented in chapter 1. Literature review on experimental methods for surface coating of cellulose paper/films, modification of fillers, and characterizations of the barrier properties are also discussed in this chapter. The effect of fiber size on wettability and barrier performance of O₂/CF₄ plasma treated and vapor phase silanized lignocellulosic substrate are studied in Chapter 2. In this regard, refined and unrefined paper substrate from Kraft and thermo-mechanical fibers are compared. The effect of surface roughness on the wettability of the cellulosic and lignocellulosic papers/film is also discussed in this chapter. Chapter 3 reports the effect of atomic layer deposited Al₂O₃ thin film on barrier performance of unrefined and refined Kraft and TMP films. The effect of Al₂O₃ film's thickness and roughness on wettability is reported in this chapter. The long-term stability of contact angle is also investigated. In chapter 4 the drying mechanism of refined fibers on surfaces with different wettability is studied and its effect on optical, mechanical, and gas permeability is reported. The fabrication of dual functional paper substrate using Janus SiO₂ and TiO₂ fillers is

reported in chapter 5. The effect of filler dual functionally on wettability and water vapor permeability of Janus paper is given in this chapter.

Chapter 2: Effect of Fiber Size on Wettability and Barrier Performance of Hydrophobic Cellulosic Paper

This chapter presents a simple and rapid method to alter the surface chemistry of cellulosic and lignocellulosic papers using vapor phase organosilane deposition and plasma tetrafluoromethane deposition. A wide range of refined pulps, obtained at different specific refining energy (SRE), are used to prepare handsheets. The objective is to determine if the water vapor transmission rate of handsheets made with refined fibers in conjunction with hydrophobic treatment can be minimized. Moreover, the effect of fiber size on the wettability of handsheets after vapor phase silanization and O₂/CF₄ plasma treatment is determined.

2.1 EXPERIMENTAL METHODS

2.1.1 Pulp Refining

In this work, Bleached Softwood Kraft Pulps and Thermo-Mechanical Pulps (TMP) from pulp and paper mills in central British Columbia were used. The pulps were refined at the pilot plant of the Pulp and Paper Centre at The University of British Columbia (Vancouver, B.C. Canada) in two optimized stages. During the process, the pulp was refined between two parallel grooved plates, called rotor and stator (Fig. 1)⁶¹.

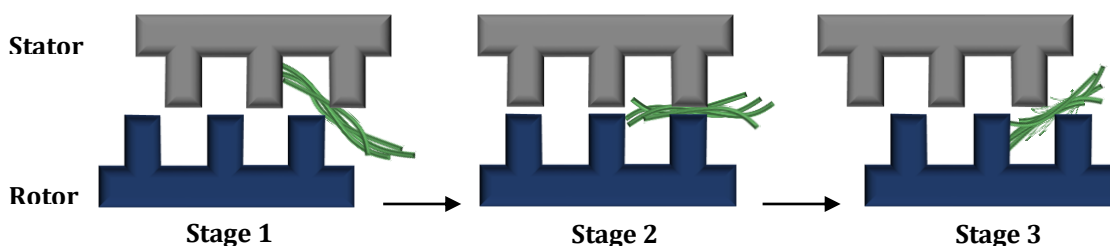


Figure 2.1. Primary steps of refining process

Generally, the refining process is performed in three main stages shown in Fig. 2.1. During the first stage, which is called fiber pick up stage, the fibers in the pulp slurry of consistency of 3.4%, (pulp consistency is defined as the $[\text{oven dried weight of pulp} / (\text{weight of pulp} + \text{water})] \times 100$), are collected and trapped between the edges of the plates' bars. In the second stage, the fibers are compressed by the surface of rotor and stator bars and most of the water is compressed out of the fibers. Finally, fibers are altered by shear forces resulting in delamination of the fiber cell wall ⁶¹. The amount of refining is described by evaluating the amount of energy given to the fiber by refiner and it is called specific refining energy (SRE, [kWh/t]). SRE can be calculated by dividing the net power by the fiber mass flow rate ⁶¹. In this study, different fiber sizes were obtained subjected to varying levels of specific refining energies. The results here, present testing of nine fibre sizes for softwood Kraft pulps and nine fibre sizes for thermo-mechanical pulps summarized in Table 2.1. For the ease of reference, the handsheets prepared with these pulps are addressed as Kraft Unrefined (KU), Kraft Refined 1 (KR₁) to Kraft Refined 8 (KR₈), TMP Unrefined (TU), and TMP Refined 1 (TR₁) to TMP Refined 8 (TR₈).

Table 2.1. Refined and unrefined pulp fiber sizes

Handsheet Type	Fiber size (μm)	Handsheet Type	Fiber Size (μm)
Kraft Unrefined (KU)	927	TMP Unrefined (TU)	520
Kraft Refined ₁ (KR ₁)	880	TMP Refined ₁ (TR ₁)	471
Kraft Refined ₂ (KR ₂)	561	TMP Refined ₂ (TR ₂)	406
Kraft Refined ₃ (KR ₃)	457	TMP Refined ₃ (TR ₃)	295
Kraft Refined ₄ (KR ₄)	392	TMP Refined ₄ (TR ₄)	261
Kraft Refined ₅ (KR ₅)	320	TMP Refined ₅ (TR ₅)	195
Kraft Refined ₆ (KR ₆)	300	TMP Refined ₆ (TR ₆)	158
Kraft Refined ₇ (KR ₇)	245	TMP Refined ₇ (TR ₇)	142
Kraft Refined ₈ (KR ₈)	177	TMP Refined ₈ (TR ₈)	139

The average fibre size distribution in a pulp suspension was measured by using the Scircoco 2000 Malvern Mastersizer (Malvern Instruments Inc., Malvern, UK). The device reports the fibre size as volume mean equivalent sphere diameter. The detection limit of the Mastersizer is within the range of 0.02-2000 μm . The error associated with fibre size measurements reported in Table 2.1 are within $\pm 4 \mu\text{m}$ to $\pm 10 \mu\text{m}$. It should be noted that the fibers' length was also measured with Fiber Quality Analyser (FQA). However reliable results were not obtained since 90% of the highly refined fibers were not detected by FQA for measurements.

2.1.2 Handsheet Preparation

The handsheets in this study consist of only softwood natural fibers, and are free of any chemical modifiers, fillers and additives. The handsheets with long fiber sizes (KU, KR₁, and TU) are prepared using a modified former on an applied vacuum ¹¹. For smaller fibre sizes (KR₂-KR₈ and TR₁-TR₈), due to the low retention of fibers in the former, the handsheets were prepared by casting and drying. In this method, the pulp suspension with consistency of 1% was stirred under vacuum for 15 min. The suspension was poured into a petri dish and shaken manually to remove any entrained air. The suspension was dried at 23° C and 50% relative humidity (referred as standard conditions) to form cellulosic and lignocellulosic handsheets. Five handsheets for each fiber size were prepared and all handsheets have basis weight of about 60 g·m⁻².

2.1.3 Handsheet Hydrophobization

In order to render the handsheets hydrophobic or superhydrophobic two distinct methods were employed. In the first method all handsheets mentioned in Table 2.1, were treated by vapor phase silanization using dimethyldichlorosilane ($\geq 99.5\%$ purchased from Sigma-Aldrich, bp of 70°C) as the silane agent. The reaction was performed in a vacuum oven at 75°C for 15 min (this time and

temperature are not optimized). Specifically, 1 mL of silane agent poured in a small vial and placed at the bottom of a glass container. The handsheets were placed on mesh that separates the glass container in two parts, the bottom part that contains the small vial of silane agent, and the top part that contains the handsheets. The glass container was covered in order to prevent deposition of the silane agent on the oven walls. In each set 9 handsheets were treated.

In the second method, the handsheets prepared with Kraft softwood pulps (KU, KR₁-KR₈) were rendered hydrophobic by using Plasma Enhanced Chemical Vapor Deposition (PECVD) method. CF₄ was used as a precursor. Prior to CF₄ deposition the surface of the handsheets were etched by O₂ plasma in order to create nano scale roughness on the surface of handsheets. The detailed procedure of the second method is described elsewhere ¹¹.

2.1.4 Handsheet Characterization

Contact Angles. The contact angles were obtained by dispensing 3 μ L distilled deionized water droplets on handsheets using a piston-driven air displacement pipet. The water droplet images on handsheets were captured by a high-resolution camera with macro lens (Nikon D90) and analyzed with FTA32 Version 2.0 software. The reported contact angles are average of 30 measurements.

Water Vapor Transmission Rates (WVTR). The WVTRs through the handsheets were measured at 23°C and 50% relative humidity (RH) by a cup method. In this method, 1.6 cm cut handsheet discs were sandwiched between two rubber washers (0.9 cm aperture) and mounted on small Erlenmeyer flasks filled with calcium chloride desiccant. To secure good sealing a screw-cap (11 mm aperture) tighten on the flasks. The weight of the whole set up increased as water vapour passed through the handsheets and absorbed by the desiccant. The weight of samples was tracked

for 10 days and the average values are reported. All handsheets preconditioned 48 hours prior to measurements.

Water Absorption. The TAPPI standard T835 om-94 was followed for water drop absorption measurements. Briefly, water droplet dispensed on the surface of the handsheets and the time (in seconds) it took for droplet to completely absorbed is determined.

Air Permeability. The TAPPI standard method of T460 om-02 was followed for air permeability measurements. The tests were performed at 23° C and 50% RH.

Roughness. The roughness of selected handsheets were obtained using Wyko NT110 optical profilometer. The average roughness values (R_a) were analyzed by Vision software.

Scanning Electron Microscope Imaging (SEM). The SEM images were obtained by Hitachi S-3000N-VP scanning electron microscope at operating voltage of 5-10 kV.

2.2 RESULTS AND DISCUSSION

2.2.1 Effect of Vapor Phase Treatments on Wettability

As expected, all handsheets were found to be hydrophilic prior to treatment. The vapor phase silanization and CF_4 plasma conferred high hydrophobicity to all handsheets as characterized by the contact angles shown in Fig. 2.2.

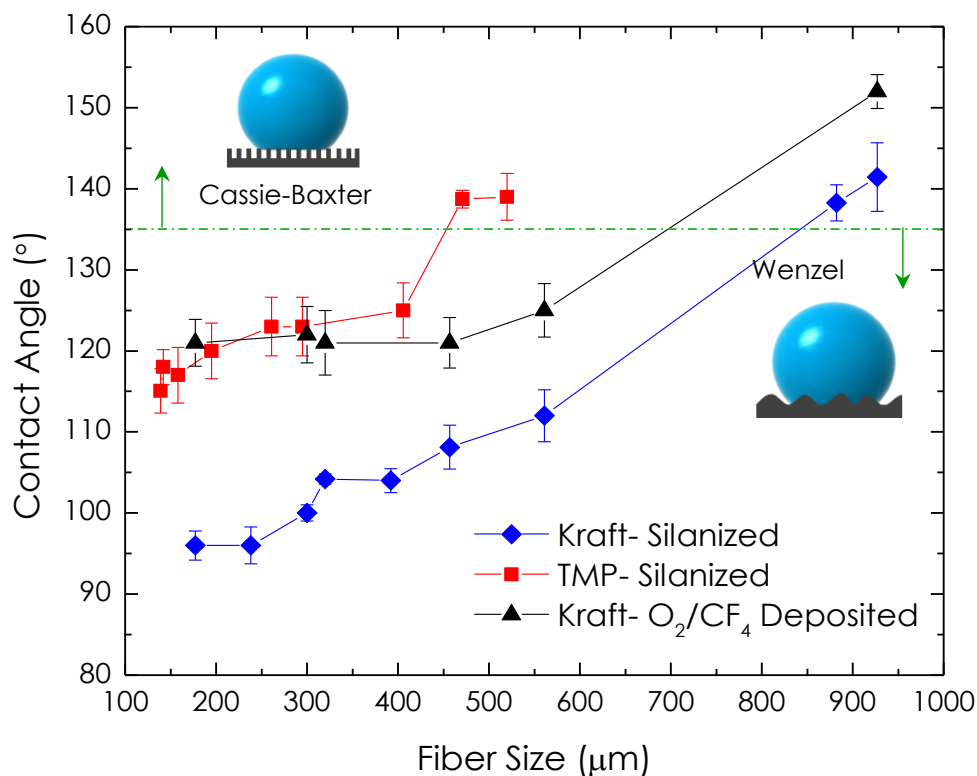


Figure 2.2. Contact Angles vs. Fiber Size on hydrophobic handsheets

As the results illustrate, the contact angles decreased with decrease of fibre size. The trend in contact angles is due to the combined effects of roughness and surface chemistry (i.e. presence of hydroxyl groups) of the handsheet. The roughness is discussed first. Since paper is formed by random network of fibers, its wetting property is not only influenced by the surface free energy, but also, its morphology/roughness plays an equally important role. Both silanization and CF₄ plasma treatments create a low surface energy which rendered the handsheets hydrophobic. However, the contact angles for both unrefined Kraft and TMP fibers' handsheets are significantly higher than those of the refined ones. The optical profilometer results, on some selected handsheet samples, (Fig. 2.3), show higher roughness value on unrefined fibers' handsheets compared to refined ones. As the images show, it is easier to identify individual fibers on handsheets prepared with long fiber sizes (unrefined fibers) compared to shorter fiber sizes (highly refined ones). This

is due to the fact that the increase of refining energy results in smaller fiber sizes, which consequently increase the fiber's surface area and the hydrogen bonding between the fibrils. Therefore, the increase of hydrogen bonding causes creation of handsheets with lower porosity and roughness. The lower roughness results in the decrease of the roughness factor in the Wenzel equation, which is the reason for the decrease of the contact angle. Our hypothesis is that for handsheets prepared with long fibre sizes, namely KU, KR₁, TU, TR₁, the water droplet follows the Cassie-Baxter model due to the higher surface roughness of these sheets. On the other hand, for highly refined samples we are expecting to be in Wenzel wetting regime and the water droplet fills the roughness patterns of the handsheets resulting in lower contact angles.

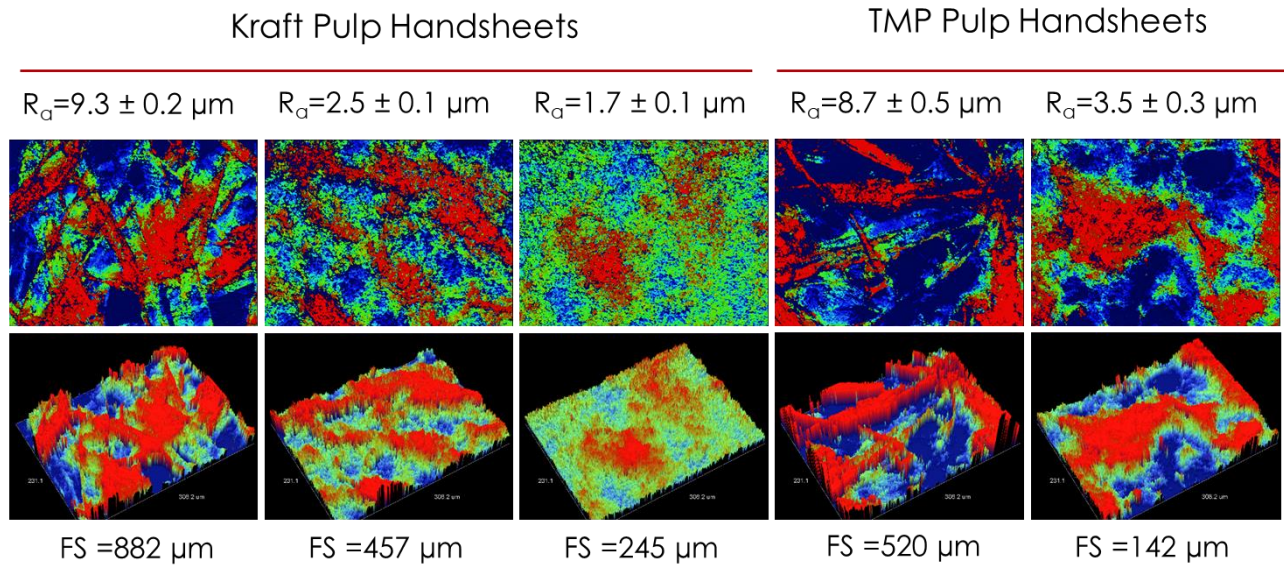


Figure 2.3. Profilometer images and average roughness (R_a) values on handsheets with unrefined and refined fibers. The scale bar is 58 μm .

We have tested this hypothesis by dispensing stained water droplets on handsheets substrates. A rhodamine fluorescent dye (purchased from Sigma-Aldrich) was used for staining the water. The dye was dispersed in distilled deionized water followed by sonication for 5 min. The droplets were dispensed on the surface of handsheets and removed off the surface after 20 seconds. When the

water droplet is withdrawn from the surface of the KU, KR₁, TU, and TR₁ handsheets, a small residue of stain remained on the surface that was visible only by microscope (Fig. 2.4a and 2.4c for KU and TU handsheets). Specifically, the water droplets roll off on the surface of O₂/CF₄ plasma treated handsheets and the surface was barely stained by the droplet (Fig 2.4e). According to the images, (Fig. 2.4a, 2.4c, and 2.4e), the residues of the stain are only evident on the very top surface layer of the handsheets (the red color area) which confirms formation of air pockets (black/dark color area) and heterogeneous wetting on these handsheets. However, on handsheets prepared with refined pulps, the water droplet sticks to the surface even after inversion of the handsheets, and when the droplet is removed from the surface, a visible stain remains on the handsheet's surface (Fig. 2.4b, 2.4d, and 2.4f).

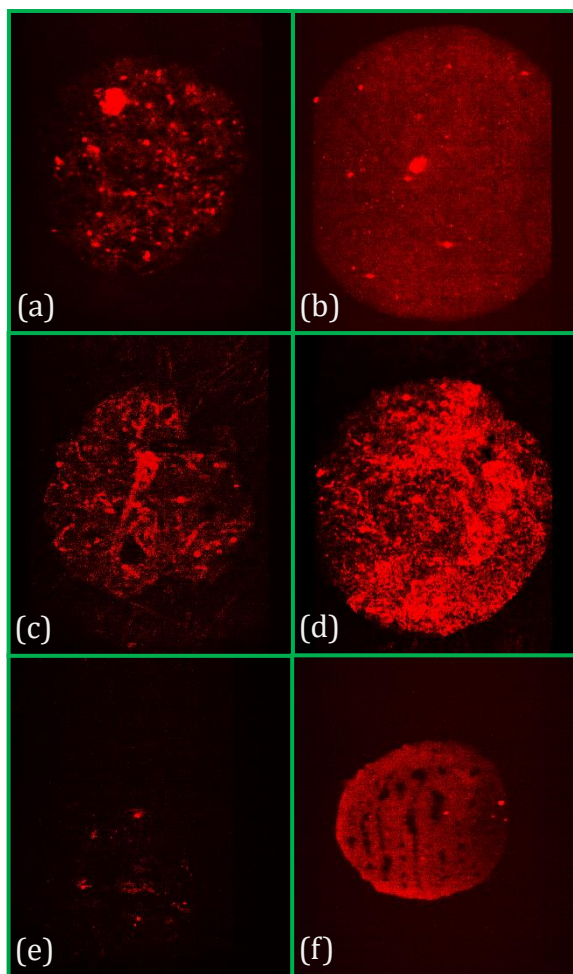


Figure 2.4. Fluorescent microscope image of stained droplet on (a) silanized KU (b) silanized KR (c) silanized TU (d) silanized TR (e) O₂/CF₄ deposited KU (f) O₂/CF₄ deposited KR handsheets

In addition to surface roughness, the number of free hydroxyl groups on the surface of a handsheet may affect the contact angle as well. FTIR-ATR results on handsheets prepared by unrefined and refined wood fibers showed that the number of -OH groups on the handsheets prepared with the unrefined fibers was greater (shown in chapter 3, Fig. 3.9). This is counterintuitive because it is known that pulp refining increases the number of -OH groups found in the refined fibers. However, when a handsheet is formed with refined fibers this may no longer be true because the -OH groups become bonded. In our view the implication of this is that the handsheets with refined fibers have less -OH available as reactive sites during the silanization

process, which is a dry process. On the other hand, handsheets made with unrefined fibers have more active (reactive) -OH sites available to respond to silanization and thus render the sheet more hydrophobic compared to refined ones. Also, according to Missoum et. al.⁶² nanofibrillated cellulose forms higher number of hydrogen bonds (due to higher number of hydroxyl groups on the surface of fiber) for the same volume comparing to native cellulose fibers.

The O₂/CF₄ plasma treated Kraft handsheets resulted in higher contact angles compared to silanized samples. This is due to the nano-scale roughness that was created on handsheets surface by O₂ plasma as illustrated in Fig. 2.5¹¹.

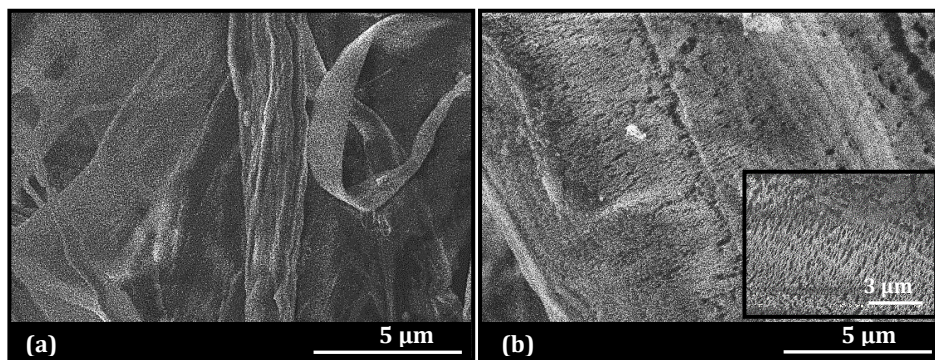


Figure 2.5. SEM images on handsheets (a) before and (b) after plasma O₂ etching

The water absorption on handsheets, shown in Fig. 2.6, follows the same trend as that of the contact angles. The green boxes on left graph categorized the samples with no water absorption (top box) and with water absorption (bottom box) over time. For bare handsheets, as the fibre size decreases the time it takes for water droplet to completely be absorbed into a handsheet (without leaving any sheen on the surface) increases due to the decrease of the porosity. For treated handsheets on the other hand, there was no water absorption on unrefined handsheets and the water droplets evaporate gradually over time. The water droplet contact angles over time on KU, TU, KR₁, and KR₂ handsheets also confirms no water absorption in these handsheets. As Fig. 2.6 (top

inset droplet images for KU (927 μm) over the first 28 min) shows, the water droplet retains its shape over time and the slight decrease in the contact angle values is due to evaporation. However, on refined handsheets (bottom inset droplet images for KR₇ (245 μm) over the first 28 min) the water droplet wicks and absorbs onto the handsheets over time, which results in a decrease of the contact angles.

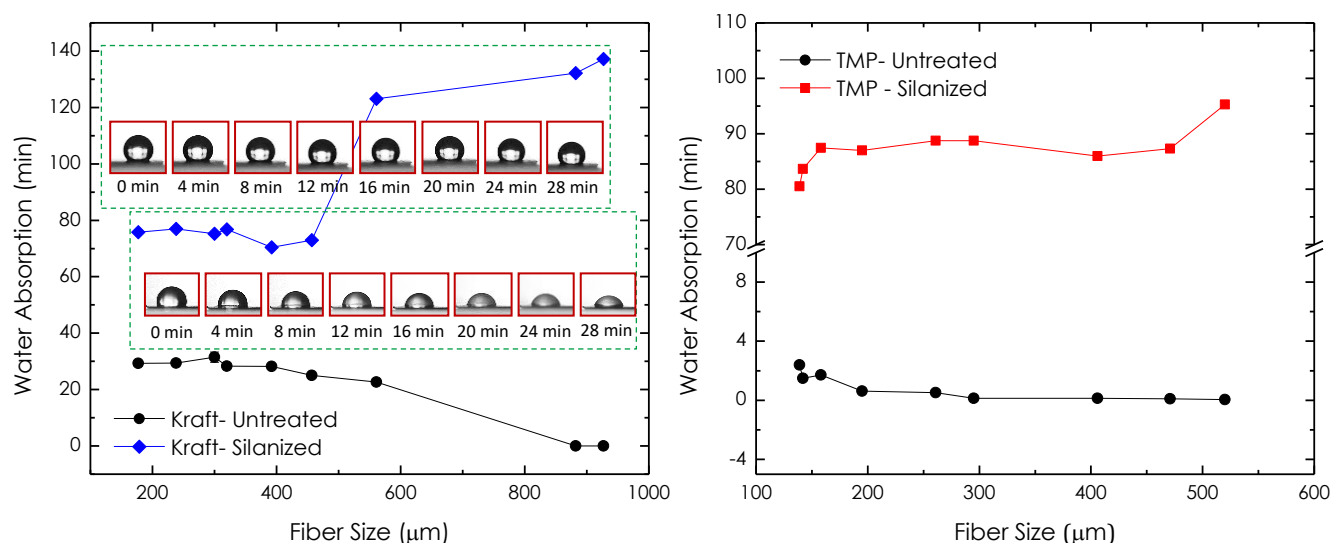


Figure 2.6. Water absorption on Kraft and TMP handsheets before and after silanization. The top and bottom inset droplet images are on KU and KR₇ handsheets respectively.

2.2.2 Effect of Vapor Phase Treatments on WVTR and Gas Permeability

The water vapor transmission rate of handsheets was measured at 23°C and 50% RH. The WVTR results are illustrated in Fig. 2.7. The decrease of fiber size resulted in reduction of WVTR values. This is due to the fact that refined fibers form denser handsheets with lower porosity and higher tortuosity. According to Fig. 2.7, the lowest WVTR for Kraft pulp handsheets was obtained with fibre size of 561 μm which is about 76 and 34 $\text{g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ before and after treatment respectively. The results show further refining of fibers, to obtain fibers smaller than 561 μm , did not affect the WVTR values significantly and even slightly increased WVTR values. The increase in WVTR

could be due to the decrease of tortuosity or diffusion path. Previous studies⁶³ have shown that nano-fibrillated cellulose (NFC) films have lower gas permeability than crystalline nano-cellulose (CNC) films due to higher fibre entanglement within NFC films which increase the diffusion path. The reported WVTR value for NFC film at standard conditions (23°C and 50% RH) is about 234 g.m⁻².day⁻¹¹⁵.

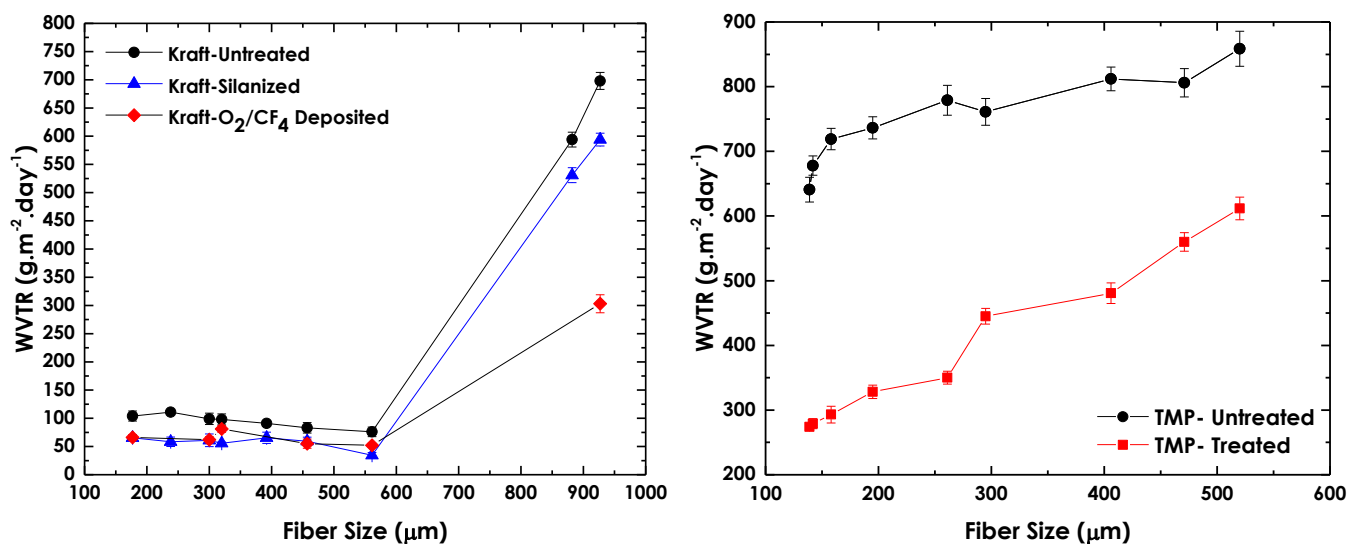


Figure 2.7. WVTR on Kraft and TMP handsheets before and after hydrophobic treatment

On average, the hydrophobic treatment decreased the WVTR by about 34% for Kraft handsheets. The reduction in fiber size before hydrophobic treatment reduced the WVTR by about 80% for KR₂ handsheets. For TMP handsheets the hydrophobic treatment decreased the WVTR by about 47%. The lowest WVTR of 274 g. m⁻². day⁻¹ was obtained for the smallest fiber size which was about 139 μm. Although TMP fibers before and after refining have smaller fiber sizes compared to Kraft fibers, they have significantly higher WVTR values. This is due to the rigidity of TMP fibers which cause formation of porous and higher bulk structure within a handsheet.

The air permeability of the handsheets were tested by Gurley method. For Kraft refined fibers, the sheets were impermeable, and the air permeability could not be quantified with Gurley tester. The air permeability results on TMP handsheets are shown in Fig. 2.8. The trend for air resistance results are consistent with WVTR results; the handsheets with smallest fiber size resulted in lower air permeability.

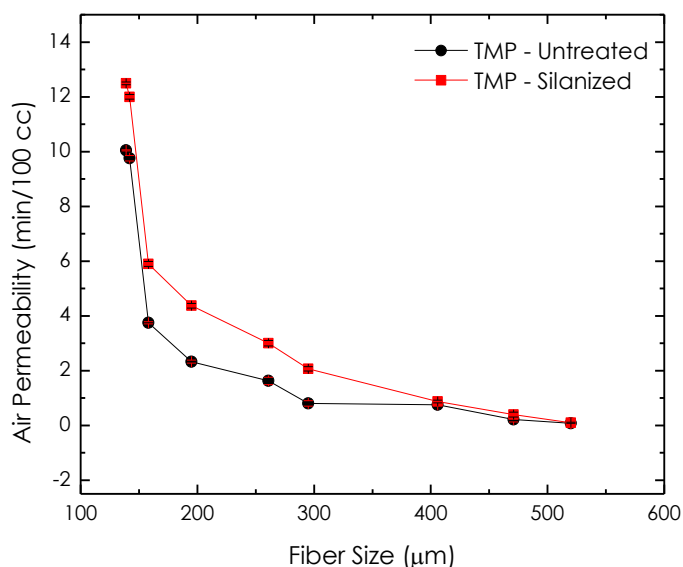


Figure 2.8. Air permeability of TMP handsheets before and after silanization

The fabricated hydrophobic paper in this study can be used as substrate for microfluidic applications, packaging applications, and possibly others. As an example, the highly refined Kraft fibers' handsheets were used as separators in the design of fast charging supercapacitors due to their high strength ⁶⁴, and they were found to be the best material to fulfill the demand for separators in electrochemical energy storage devices (Appendix A).

2.3 CONCLUSIONS

The present chapter describes the effects of fiber size and surface energy (hydrophobic treatment), on the wettability and gas permeability of cellulosic and lignocellulosic handsheets.

The refined Kraft fibers of 561 μm size, enabled fabrication of handsheets with WVTR value as low as 34 g. m⁻². day⁻¹ after silanization. The reduction in fiber size before hydrophobic treatment decreased WVTR by about 80-90% for Kraft refined handsheets. Both vapor phase silanization and O₂/CF₄ plasma processing rendered the handsheets hydrophobic. However, the contact angles are highly dependent to the handsheets surface roughness and the contact angles decreased with decrease of fiber size. This is due to the fact that highly refined fibers resulted in formation of handsheets with a smoother surface compared to unrefined fibers.

Chapter 3: Enhanced Barrier Performance of Engineered Paper by Atomic Layer Deposited Al₂O₃ Thin Films

Although, the decrease in fiber size in conjunction with vapor phase salinization reduced the water vapor transmission rate up to $34 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, it is still considered a high WVTR value for high performance packaging and paper electronics applications. In this chapter, we present another approach to the design and fabrication of hydrophobic thin paper substrates ($60 \text{ g}\cdot\text{m}^{-2}$). Our hypothesis is based on that using highly refined wood fibers in conjunction with ALD will produce papers with low water vapor transmission rate comparable to that of synthetic polymeric films. Moreover, we exploit the role of fiber size through the refining energy in order to identify its optimum value for the purpose of minimizing WVTR. Therefore, we first altered the average fiber size, to control inter-fiber spacing, by mechanical refining of cellulosic and lignocellulosic fibers, and we used the refined fibers to form paper substrates. Second, we exploit plasma assisted ALD to deposit thin Al₂O₃ coating on paper substrates in order to control the inherent wetting and hygroscopic properties of the fibers. To the best of our knowledge, this is the first report of engineered hydrophobic paper substrates free of coatings, chemicals, and additives present in commercial paper products with WVTR values as low as $2.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ by employing plasma assisted ALD.

3.1 EXPERIMENTAL METHODS

3.1.1 Pulp Refining

Micron-size cellulose fibers were prepared by mechanical treatment of wood pulp using refiner. Refining is a common technique used to render wood fibers suitable to improve the uniformity and strength properties of paper products ⁶⁵. During the refining process the pulp passes through

the refiner plates that compress and shear the wetted fibers, thereby ripping and fibrillating the individual wood fibers ⁶⁵. The detailed refining process explained in chapter 2. In this study, Bleached Softwood Kraft Pulps and Thermo-Mechanical Pulps (TMP) were obtained from a pulp and paper mill in central British Columbia. The results here present three fiber sizes for softwood Kraft pulps and two fiber sizes for thermo-mechanical pulps summarized in Table 3.1. For the ease of reference, the handsheets prepared with these pulps are addressed as Kraft Unrefined (KU), Kraft Refined 1 (KR₁), Kraft Refined 2 (KR₂), TMP Unrefined (TU), and TMP Refined (TR).

Table 3.1. Refined and unrefined fiber sizes

Handsheet Type		Fiber Size (μm)
Kraft-Unrefined	KU	882
TMP-Unrefined	TU	520
TMP-Refined	TR	142
Kraft-Refined 1	KR ₁	457
Kraft-Refined 2	KR ₂	245

It is known that the refining process influences the structural properties and surface chemical composition of fibers ^{61,66}. Specifically, the extent of refining significantly affects the cellulose fiber morphology and network in the handsheet. In this study, refining at different specific refining energies enabled us to control the fiber length and diameter, and consequently the fiber-fiber bonding and porosity of the handsheets. Fig. 3.1 presents the SEM images of cellulosic and lignocellulosic fibers before and after refining. Figure 3.1 (a) and (b) show KU and TU fibers. TMP fiber and kraft softwood fibers at the onset of delamination and fibrillation can be also seen in Fig. 3.1 (c) and (d) respectively. The arrows show fibrils as well as fracture and delamination of the fiber wall. Fig. 3.1 (e) and (f) show refined fibers of KR₁ and KR₂ respectively that have been used in this study. The increase in refining energy results in increase of the external surface

area of the fibers, which enhances the bonding ability of fibers due to the increase of hydrogen bonding ⁶².

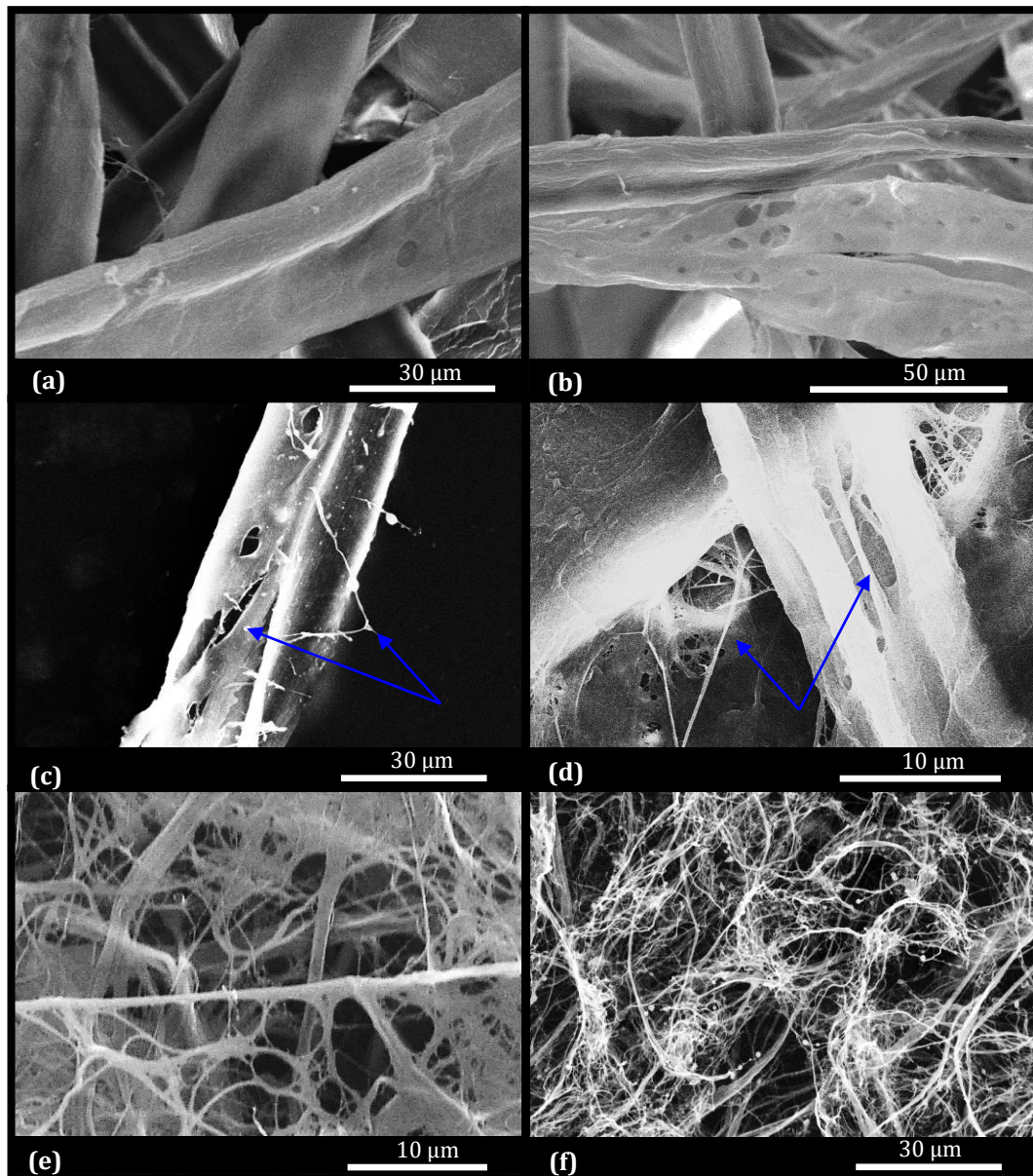


Figure 3.1. SEM images of (a) Kraft-Unrefined fibers (KU) (b) TMP-Unrefined fibers (TU) (c) TMP fiber at onset of fibrillation (d) Kraft fiber at onset of fibrillation (e) KR₁ fibers (f) KR₂ fibers

3.1.2 Cellulosic Handsheets Preparation.

In order to control the effect of treatments solely on fiber/fiber network, we fabricated our own paper substrates. These substrates are free of hydrophobic binders, chemical modifiers, fillers, and additives, present in commercial papers products, which can interfere with, or mask the effect of Al_2O_3 deposition. Therefore, the paper substrates in this study consist of only softwood natural fibers and referred to as handsheets in this study. The handsheets were prepared using two different procedures. For the unrefined pulps, the sheets were prepared using a modified former on an applied vacuum ¹¹. The former utilizes a simple filtration of pulp suspensions through a forming fabric mesh. However, for refined pulps, a different procedure had to be used. Using the handsheet former with refined pulps will result in low retention of fibers due to the small size of the fibers which will easily pass through the forming fabric mesh. Therefore, the sheets were prepared by a casting and drying method. In this method, a pulp suspension with consistency of 1% was placed under vacuum and stirred for 15 min. The suspension was slowly transferred into a petri dish followed by manual shaking to remove any entrained air. Then the suspension was dried at ambient temperature and humidity to form cellulosic handsheets. All handsheets in both methods were prepared with basis weight of $60 \text{ g}\cdot\text{m}^{-2}$. The handsheets were kept at 23°C and 50% RH before the treatment.

3.1.3 Plasma Assisted Atomic Layer Deposition of Al_2O_3

The Al_2O_3 films were grown on paper substrates by the atomic layer deposition (ALD) technique using trimethylaluminum (TMA) (97%, Sigma Aldrich) and O_2 plasma as precursors. Prior to Al_2O_3 deposition the handsheets were purged with N_2 gas in order to remove possible surface contaminants. The depositions were performed at 100°C in a FlexAL ALD reactor (Oxford

Instruments, base pressure 10^{-7} mbar) equipped with a remote inductively coupled plasma (ICP) source. An ALD cycle consists (Fig. 3.2) of a 0.75 s pulse of TMA exposure and a 2.5 s pulse of O_2 plasma. After every precursor pulse, the reactor is purged by an N_2 flow for 3 s to remove the unused precursor and reaction by-products. Under these experimental conditions, the growth rate of Al_2O_3 was 0.14 nm/cycle. The number of ALD cycles was adjusted according to the desired Al_2O_3 coating thicknesses of 10, 25, and 45 nm. Due to the porous structure of handsheets the actual thickness of coating was estimated by measuring the thickness of the Al_2O_3 layers deposited on Si substrates under the same experimental conditions (i.e., temperature, number of cycles). This thickness measurement was performed using *ex situ* spectroscopic ellipsometry.

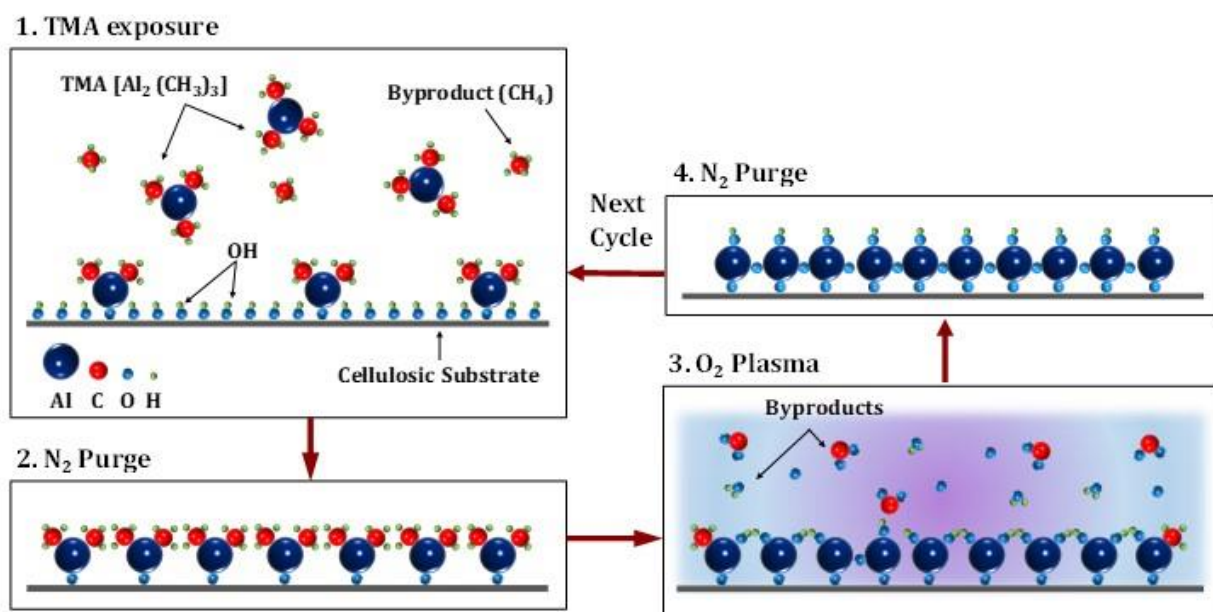


Figure 3.2. Atomic Layer Deposition reaction cycle

It should be noted that the existence of functional groups on the substrate plays an important role on the initial growth and nucleation of Al_2O_3 films by ALD²⁵. Therefore, the hydroxyl groups on cellulose substrates secure a good adhesion to the deposited Al_2O_3 films with high chemical and thermal stability.

3.1.4 Characterization of Cellulose Handsheets

Fiber Size Measurements. The average fiber size distribution in the wood fiber suspension was measured with the use of the Scircoco 2000 Malvern Mastersizer (Malvern Instruments Inc., Malvern, UK). The device uses static light scattering and the particle size is reported as a volume equivalent sphere mean diameter. The device size detection limit is within 0.02 to 2000 μm . The reported fiber size in this study is the average of five measurements and the errors associated with them are within $\pm 4 \mu\text{m}$ to $\pm 10 \mu\text{m}$.

Contact Angle Measurements. The advancing and receding contact angles ($\theta_{\text{Adv.}}$ and $\theta_{\text{Rec.}}$) were obtained by the “add and remove” volume method demonstrated in our previous work ^{11,67}. A 3 μL water droplet with dispense rate about 0.2 $\mu\text{L/s}$ was used for dynamic contact angle measurements. Static contact angles were determined by dispensing a 2 μL distilled deionized water droplets (resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 $^{\circ}\text{C}$, a total organic C content of <10 ppb, and pH 7) on paper substrates with a piston-driven air displacement pipet. The image of a water droplet on the substrate was captured with a high-resolution camera (Nikon D90) and analyzed with FTA32 version 2.0 software. Contact angles on Al_2O_3 deposited handsheets were measured a few days after deposition. All handsheets were kept in a controlled environment away from light, humidity, and contaminations prior to contact angle measurements.

Water Vapor Transmission Rate. The water vapor transmission rate of the handsheets was measured by the cup method at 23 $^{\circ}\text{C}$ and 50% RH. In this method, a paper sample was cut into 1.6 cm diameter disc, then sandwiched between two rubber washers (0.9 cm aperture) and mounted on a vial filled with anhydrous calcium chloride. A screw-cap with an aperture of 11 mm tighten on the vial, compressing the washers against the vial to secure good sealing. The paper disc was

about 1 cm above the calcium chloride desiccant. The weight of the whole set up increased as water vapor transported through the paper sample and absorbed by desiccant. All samples were preconditioned at the controlled environment for 48 hours prior to measurements. The weights were tracked for 10 days and the average values are reported. The Water Vapor Transmission Rate (WVTR) and Water Vapor Permeability (WVP) were calculated according to equations 3.1 and 3.2:

$$WVTR \text{ (g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}\text{)} = \frac{\Delta m \text{ (g)}}{A \text{ (m}^2\text{)}} \quad (3.1)$$

where Δm is the difference between the initial mass (g) and the mass after 24h (g), and A is the exposed area of paper sample.

$$WVP \text{ (g} \cdot \text{Pa}^{-1} \cdot \text{m}^{-2} \cdot \text{day}^{-1}\text{)} = \frac{WVTR \text{ (g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}\text{)}}{P_s \text{ (Pa)}(RH_1 - RH_2)} \quad (3.2)$$

where P_s is the saturation vapor pressure (2.81 kPa at 23°C), RH_1 is the relative humidity of condition room expressed as a fraction (0.5) and, RH_2 is the relative humidity in the vial expressed as a fraction (0).

Air permeability. The air resistance of handsheets was evaluated by the Gurley method. This method measures the time (s) that is required for 100 mL of air to pass through the handsheets at pressure of 1.22 kPa. The TAPPI standard method of T460 om-02 was followed for the measurements. The tests were performed at 23°C and 50% (RH).

Profilometer Measurements. Roughness measurements were conducted using the Wyko NT1100 Optical Profilometer. The average roughness values (R_a) were analyzed using the Vision software

(Veeco Instruments Inc.). The reported values in this study are the average values for three measurements.

SEM Imaging. The surface structure and morphology of cellulosic and lignocellulosic fibers and films before and after ALD deposition were examined with a Hitachi S-3000N-VP scanning electron microscope at operating voltage of 5-10 kV. All images were obtained at variable pressure mode since paper and Al_2O_3 films are insulators.

XPS Analysis. The elemental composition of the material surface was determined by X-ray photoelectron spectroscopy. The spectra were collected by the Leybold model MAX200 XPS with Al K- α X-rays and 15 kV, 20 mA emission current. The analyzed area for all samples was $4 \times 7 \text{ mm}^2$ with the X-ray spot size of $\sim 20 \text{ mm}$ diameter. The pass energies to measure the survey scan and narrow scan were 192 eV and 48 eV respectively.

FTIR-ATR Analysis. Fourier transform infrared spectra (FTIR) with attenuated total reflectance (ATR) were obtained with the Thermo Nicolet AVATAAR 360 FTIR spectrometer. The $0.5 \times 0.5 \text{ cm}$ cut samples were pressed against the ATR crystal using a flat metal with controlled pressure. The level of pressure kept constant for all test samples.

3.2 RESULTS AND DISCUSSION

3.2.1 Effect of Al_2O_3 ALD on Wettability

Film Thickness Effect. It is well established that low surface energy and surface roughness are the main parameters responsible for hydrophobic and superhydrophobic surfaces^{9–11}. Paper is composed of a random network of fibers. Therefore, its wettability is not only dictated by the surface free energy, but also by the morphology of the surface which plays an important role. Prior

to Al_2O_3 deposition all handsheets were hydrophilic. More specifically, the static water contact angles on KU and TU handsheets can be considered practically to be zero, since the droplet quickly absorbs and wicks onto the sheet upon contact. For KR and TR handsheets, due to their denser structure, it takes significant amount of time for a droplet to totally absorb. The static water contact angles on KR and TR are between 10° - 20° , immediately after the droplet dispensed on the surface. The deposition of Al_2O_3 films on handsheets renders them hydrophobic. To fully characterize and understand the effect of film thickness on the barrier properties of handsheets, we have studied three coating thicknesses of 10, 25, and 45 nm. The results for the advancing contact angles and the contact angle hysteresis (CA_H) (the difference between the advancing and receding contact angle values) of the three different film thicknesses are presented in Fig. 3.3. In this study, the aim was to deposit Al_2O_3 on one side of the sheets; however, the film growth on the other side could not be prevented and resulted in hydrophobic surfaces on both sides of the sheets. According to the results, the hydrophobicity of the handsheets was shown to slightly increase with Al_2O_3 film thickness. This is more significant for unrefined Kraft and TMP handsheets in comparison with handsheets formed with refined pulp fibers. As Fig. 3.3 demonstrates, handsheets with refined pulp fibers are relatively unaffected by the increase of the coating thickness.

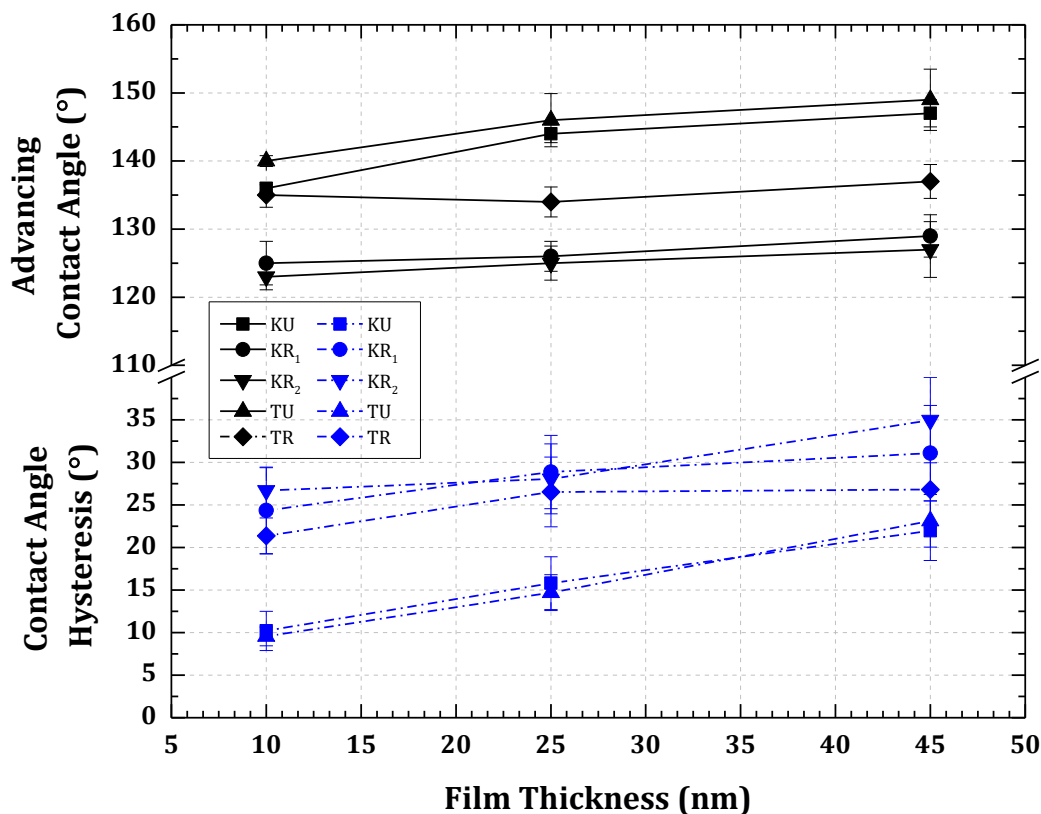


Figure 3.3. Advancing contact angles and contact angle hysteresis for handsheets after Al₂O₃ ALD at different film thicknesses

The effect of Al₂O₃ ALD (at deposition temperatures of 60° and 90°) on the wettability of woven cotton mats and cotton balls was reported by Lee et al.⁴⁸, showing that there is a wetting transition from hydrophilic to hydrophobic after the first few ALD cycles (2-3 cycles). However, the surface transitioned back to the hydrophilic state after about 15 ALD cycles. In our study we observed a distinctly different behavior for the cellulosic wood fiber handsheets. There was no transition from hydrophobic to hydrophilic state with increase of ALD cycles. We observed an increase in contact angle for KU and TU handsheets from 10 nm to 25 nm thicknesses which corresponds to 75 and 190 ALD cycles, respectively. However, for a coating thickness of 45 nm (300 cycles) the increase in contact angles is insignificant compared to that of 25 nm coating thickness. For handsheets with refined pulps (KR and TR), on the other hand, the increase in contact angle is small (about 1-2

degrees which is within experimental error) with increase of ALD cycles. On the contrary to advancing contact angles, the effect of film thickness is more evident on contact angle hysteresis as its value increases significantly with film thickness (specially on unrefined samples). This is due to the decrease of handsheet surface roughness (which is discussed further in the next section) as the film thickness increases. It is established that the contact angle hysteresis depends on chemical heterogeneity and surface roughness ⁶⁸. Therefore, although the increase of film thickness slightly enhanced the hydrophobicity of the handsheets (by lowering the surface energy), its effect on surface roughness by reducing it has resulted in higher contact angle hysteresis values.

Fig. 3.3 also illustrates that the contact angles on handsheets prepared with unrefined pulps (KU, TU) are higher than those of the refined pulps (TR, KR₁, and KR₂). Highly refined samples (KR₁ and KR₂) resulted in lowest contact angles after Al₂O₃ deposition. This behavior is attributed to the fact that refining results in higher specific surface area which in turn increases the number of fiber-fiber bonds. Therefore, during sheet formation the strong hydrogen bonding between the fibrils causes formation of a dense, nonporous, and smooth surface for highly refined samples. The relative reduced roughness causes the decrease of contact angle which is expected based on Wenzel equation. Fig. 3.4 illustrates advancing contact angles vs. fiber size.

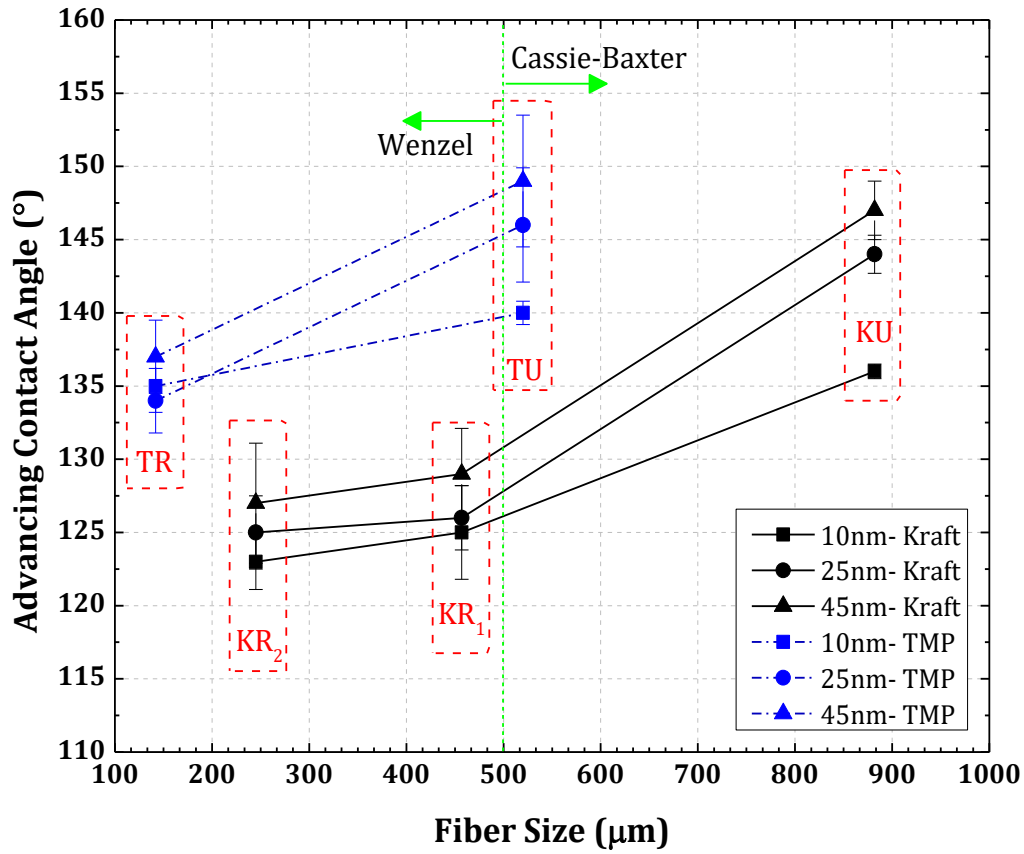


Figure 3.4. Effect of fiber size on wetting transition for handsheets with TMP and Kraft Pulp for the three film thicknesses

Depending on the fiber size, the handsheets are either in the Wenzel or in the Cassie-Baxter wetting state. In order to test our hypothesis, a 2 μ L stained water droplet was dispensed on the surface of the handsheets, and it was removed off the surface after 20 s by letting the droplet wicks into a Kimwipes. The stained water droplet on KU and TU could be removed without leaving any residual fluid on the handsheets that is visible by unaided eye. However, on TR, KR₁, and KR₂ (handsheets made with refined pulps) surfaces, water droplets pinned on the surface even after inversion, and the stain of water droplet remains on the surface when the droplet is removed. This implies that the droplet resides on the handsheet according to the Cassie-Baxter state for KU and TU handsheets. On the other hand, on TR, KR₁, and KR₂ the droplets reside in the Wenzel wetting

state, leading to higher adhesion to the fibers. Fig. 3.5 shows the stain of water droplet on the surface of handsheets using inverted fluorescent microscope. We stained the water with rhodamine (which is fluorescent) and took the images of the handsheets surface after withdrawing the droplet. The homogeneous wetting on KR₂ handsheet is evident based on Fig. 3.5 (a). As mentioned, macroscopically we did not observe stain residues on KU handsheet, but microscopically there is an evidence of droplet pinning on the very surface layer of the fibers. The smaller contact area that is formed by stain of the droplet on KU handsheet (for 25 nm Al₂O₃ thickness) and the heterogeneous coverage of stain on the surface confirms the Cassie-Baxter wetting state on these handsheets.

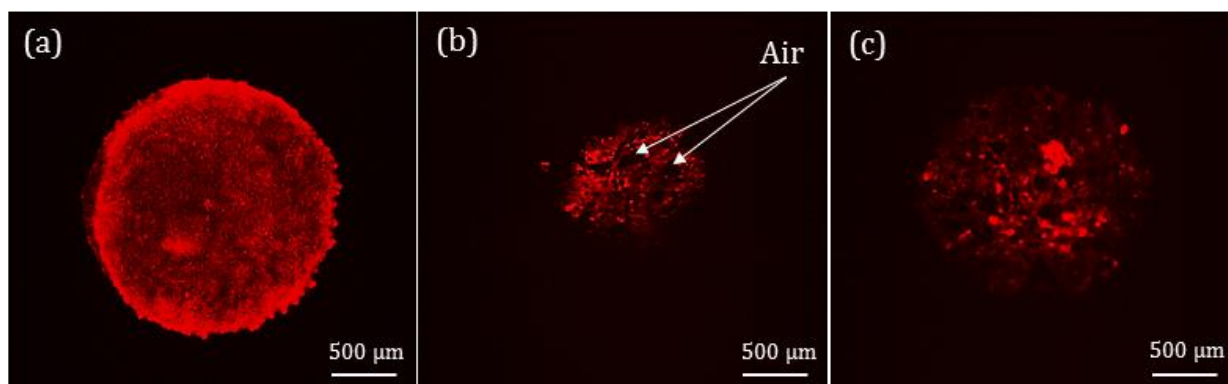


Figure 3.5. Stain of water droplet on (a) KR₂ handsheet with 25 nm Al₂O₃ (b) KU handsheet with 25 nm Al₂O₃ and (c) KU handsheet with 10 nm Al₂O₃.

The long-term stability of contact angles was tested in order to prove the wetting state hypothesis. Fig. 3.6 illustrates the static contact angles on handsheets with Al₂O₃ film thickness of 10 nm. The images of a water droplet were captured every minute up to 20 min. In order to minimize the evaporation effect, the droplet was covered, and the cover was removed only at the time of capturing the image. According to the results, on KU and TU handsheets the droplet shape remains stable over time and the slight decrease in contact angle, due to evaporation, is within the range of hysteresis contact angle results shown in Fig. 3.3. On handsheets with refined pulps, the contact

angles decreased over time. According to Fig. 3.6 the decrease of contact angle for KR₁ and KR₂ samples is about 40° over 20 min which is significantly higher than their hysteresis contact angle values reported in Fig 3.3. Specifically, after about 13 min, the handsheets are not hydrophobic anymore and have contact angle of about 87°. Since the droplets are in the Wenzel wetting state, there is higher adhesion of water droplet to the fibers. Therefore, over time the liquid may come into contact with underlying fibers and absorb into the substrate, causing the decrease of contact angles. Therefore, for refined samples the decrease of static contact angles can be mainly due to wicking and absorption over time.

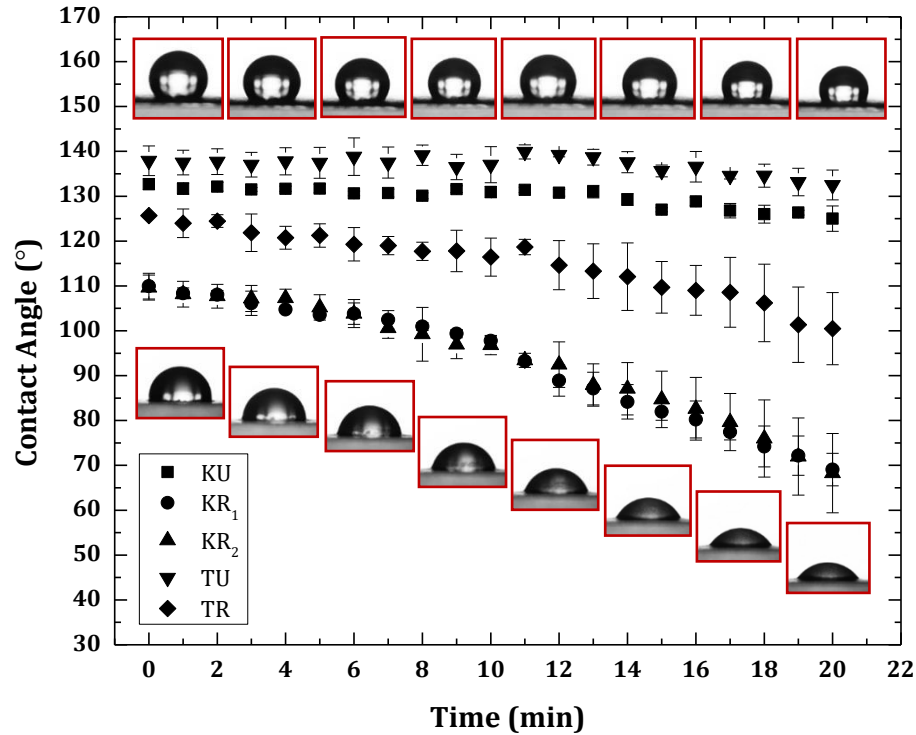


Figure 3.6. Long term static contact angles on handsheets with an Al₂O₃ film thickness of 10 nm

The Al₂O₃ ALD coated handsheets are not noticeably different from the original unmodified handsheets, having similar feel and flexibility. The SEM and profilometer images of handsheets coated with 25 nm Al₂O₃ are shown in Fig. 3.7. The shorter fiber size results in a decrease of the

handsheet porosity and individual fibers become harder to identify. For the refined pulp handsheets, the increase of surface area and higher number of hydrogen bonds between the fibrils creates aggregates that fill the pores in the fiber network leading to a smoother appearance of the handsheets¹⁰.

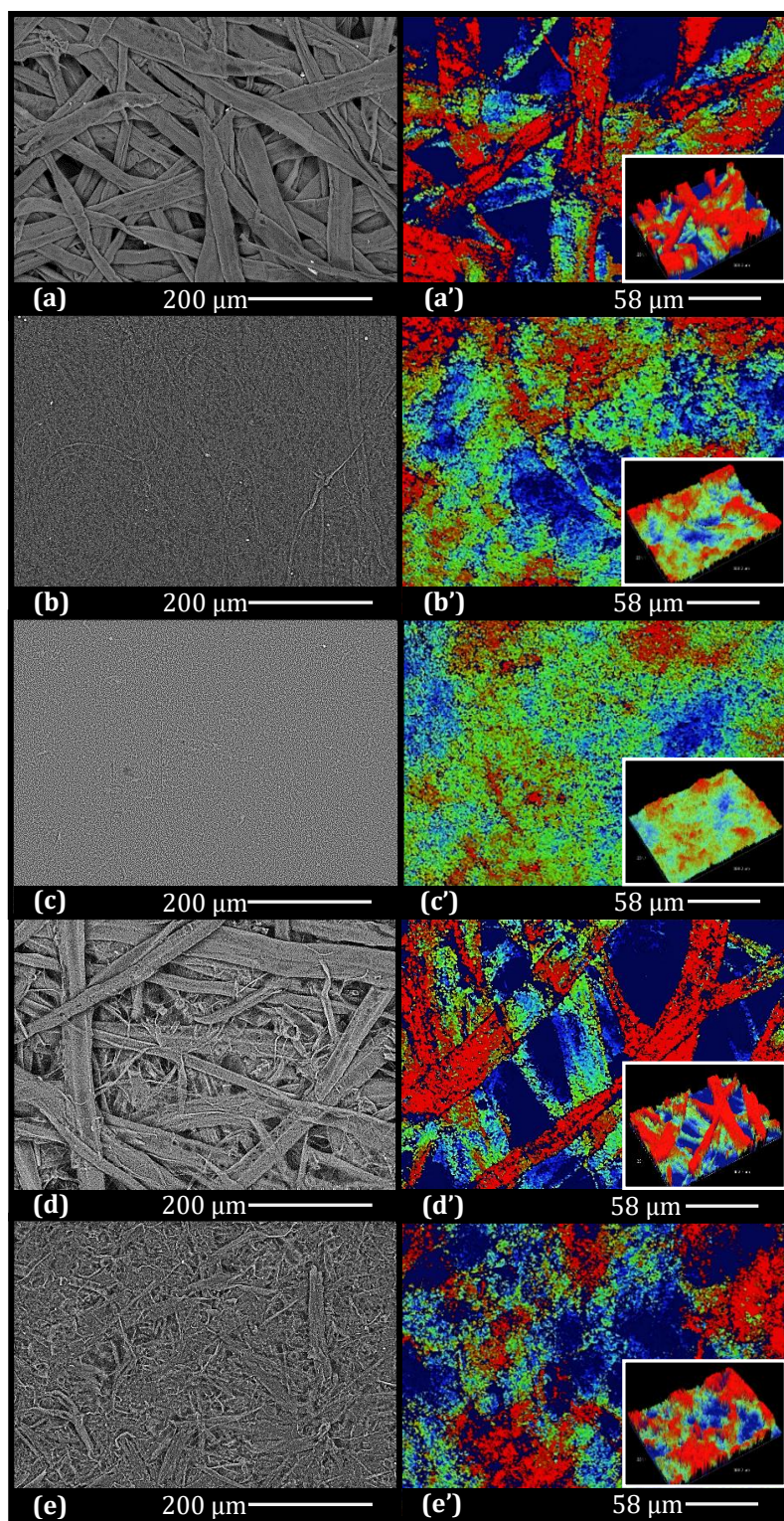


Figure 3.7. Profilometer images (right) and complementary SEM images (left) of handsheets prepared from (a, a') KU (b, b') KR₁ (c, c') KR₂ (d, d') TU (e, e') TR.

According to Fig. 3.3 and 3.4, the handsheets prepared by TMP pulps show higher contact angles than the Kraft pulps. This is due to the presence of hydrophobic substances such as lignin and extractives on TMP fiber surface. The wood fibers may consist of different amounts of cellulose, lignin, hemicellulose, and extractives depending on the pulping technique and this influences their wettability ^{11,69}.

Roughness Effect. As mentioned earlier, Al_2O_3 films on handsheets create a low energy surface, which renders the handsheets hydrophobic. However, the roughness of the handsheets highly affects the contact angle values. Table 3.2 presents the average surface roughness (R_a) before and after the Al_2O_3 deposition for refined and unrefined handsheets. According to Table 3.2 the roughness of the sheets is highly dependent on fiber size and coating thickness.

Table 3.2. Profilometer roughness values of handsheets before and after Al_2O_3 deposition

Handsheet Type	Fiber Size (μm)	Average Roughness Values (R_a) (μm)			
		Uncoated	10 nm	25 nm	45 nm
KU	882	9.3 ± 0.2	8.2 ± 0.6	7.1 ± 0.5	6.3 ± 0.1
TU	520	8.7 ± 0.5	7.9 ± 0.8	7.0 ± 0.4	6.2 ± 0.7
TR	142	3.5 ± 0.3	3.4 ± 0.3	3.2 ± 0.1	2.9 ± 0.4
KR ₁	457	2.5 ± 0.1	2.5 ± 0.1	2.2 ± 0.3	2.1 ± 0.3
KR ₂	245	1.7 ± 0.1	1.7 ± 0.1	1.2 ± 0.1	1.3 ± 0.1

Fig. 3.8 shows that handsheets with unrefined pulp (KU) resulted in the highest advancing contact angles due to the higher roughness, which is expected based on the Wenzel and the Cassie-Baxter wetting models. This is consistent in all three film thicknesses. However, as the coating thickness increases, it leads to lower roughness values and smoother surfaces which results in an increase in the contact angle hysteresis. Higher film thickness also results in higher coverage of surface by Al_2O_3 film and loss of porosity.

The higher contact angles of KU handsheets could be also due to the effect of free hydroxyl groups on the KU handsheets before deposition of Al_2O_3 .

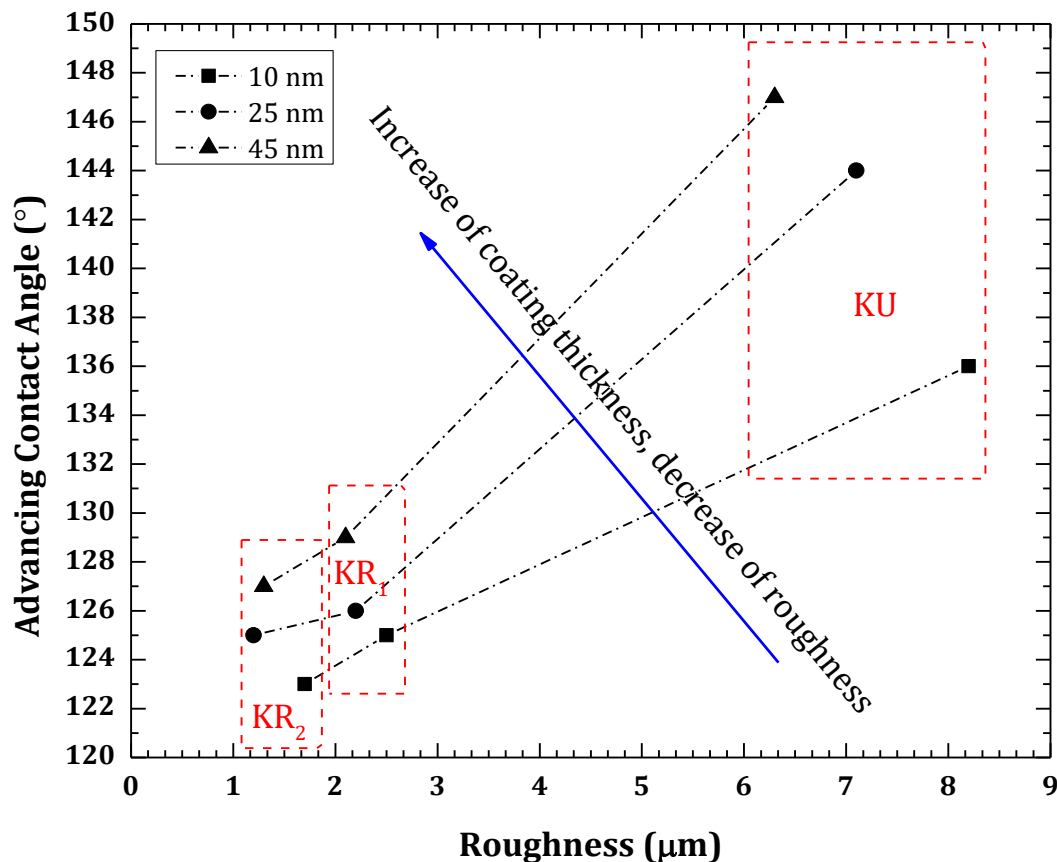


Figure 3.8. Effect of handsheet's roughness on advancing contact angles ($\theta_{\text{Adv.}}$) for handsheets prepared by Kraft pulp.

More specifically, the FTIR-ATR results (Fig. 3.9) on untreated samples reveal a higher number of hydroxyl ($-\text{OH}$) groups on unrefined pulp (KU) handsheets at peak wavenumber of 3327 cm^{-1}). The band intensity of $-\text{OH}$ peaks decreased for KR₁ and decreased furthermore for KR₂ handsheets. This is due to the fact that refining increases the number of hydroxyl groups on the fiber surface, and consequently increases the hydrogen bonding between the fibers during handsheet formation⁶² (i.e. higher number of $-\text{OH}$ groups at the surface of the fiber involve in interfibrillar hydrogen bonding, which causes formation of low porosity sheets). Therefore,

according to the FTIR-ATR results, unrefined fibers have large number of free or unbonded hydroxyl groups on the surface, which are more accessible for reaction with Al_2O_3 . It is known that the higher the number of free hydroxyl groups on a surface, the more the surface is prone to modification. Based on this, we believe the higher contact angles of KU handsheets is due to the presence of higher number of free/unbonded $-\text{OH}$ groups available to react with Al_2O_3 compared to the case of refined samples with lower number of free $-\text{OH}$ groups.

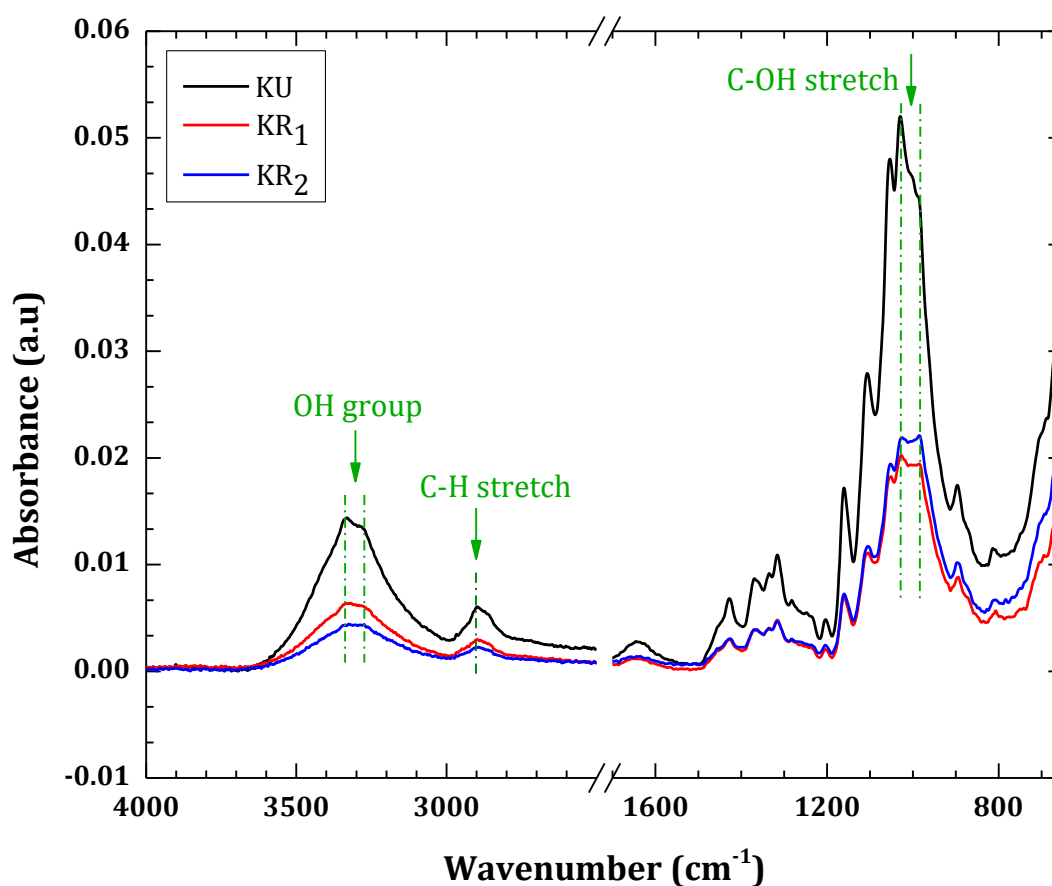


Figure 3.9. FTIR-ATR spectra on bare (untreated) Kraft pulp handsheets

The surface chemistry of plasma assisted Al_2O_3 ALD using infrared spectroscopy on pure Al_2O_3 films shows dependency of the surface groups to the deposition temperature⁷⁰. Basically, the study

⁷⁰ shows at lower deposition temperature (25°C), the number of hydroxyl groups on the surface created by O₂ plasma increased compared to depositions at 100° and 150°C.

In this study, XPS was employed to identify the elements and chemical bonds on the surface of uncoated and Al₂O₃ coated handsheets. The survey scan spectra of an untreated handsheet mainly show the presence of oxygen (O_{1s}: 27.09%) and carbon (C_{1s}: 70.83%) elements with oxygen to carbon (O/C) ratio of 0.38. The existence of chemical bonds on the surface was determined by high resolution XPS carbon (C_{1s}) spectra. The resulting deconvoluted three major peaks of C_{1s} for untreated and 10 nm Al₂O₃ deposited handsheets are shown in Fig. 3.10 (a) and (b) respectively. The C₁ peak at 285.0 eV corresponds to carbon-carbon (C-C) or carbon-hydrogen (C-H) bonds, the C₂ peak at 286.6 eV is due to bonding of carbon to a single non-carbonyl oxygen (C-O), and the C₃ peak at 288.0 eV represents bonding of a carbon atom to one carbonyl oxygen (C=O) or to two non-carbonyl oxygens (O-C-O). The three peaks are consistent with the literature data for cellulose ^{11,49,71}. The intensity of C₁, C₂, and C₃ peaks decreases after 10 nm Al₂O₃ ALD deposition (Fig. 3.10 (a) and (b)). It should be noted that the C₃ peak on an uncoated handsheet shifts to a higher binding energy of 289 eV after ALD coating which can correspond to one carbonyl oxygen and one non-carbonyl oxygen (O-C=O) bonds to carbon atom. Also, the O/C elemental ratio increased from 1.61 (10 nm coating thickness) to 1.97 for the 45 nm coating. This is due to the formation of Al₂O₃ (Al-O) which is confirmed by the O_{1s} peaks at 531.5 eV (Fig. 3.10 (c)). The O_{1s} peak also confirms O-C bond at 533 eV on the uncoated handsheet. After the Al₂O₃ deposition, the O-C peak position shifts to a lower binding energy consistent with oxygen binding mainly to aluminum (Fig. 3.10 (c)). Also, the Al₂O₃ peaks become dominant after 10 nm and 45 nm deposition. This is consistent with Al₂O₃ bonds on Al_{2p} peaks for both coating thicknesses as demonstrated in Fig. 3.10 (d). The intensity of the Al_{2p} peak increased with respect to increase in

coating thickness. According to Lee et. al ⁴⁸ the presence of Al-O-C peak at binding energy of 532.4 eV was the reason for hydrophobicity of cellulosic cotton mats after a few cycles of ALD. Their study shows, that the formation of Al-(O-C-)₃ bonding units during interaction of trimethylaluminum with -OH units on cellulose surface is the reason for hydrophobicity. In addition, the air exposure of the sample after Al₂O₃ deposition caused adventitious carbon adsorption which resulted in hydrophobicity of the cotton mats even after subsequent ALD cycles ⁴⁸. Our XPS results here also shows the presence of carbon on the surface of handsheets after Al₂O₃ deposition, which could originate from the adsorption of carbon from environment or the presence of Al-O-C, which both affect the wettability of the surface.

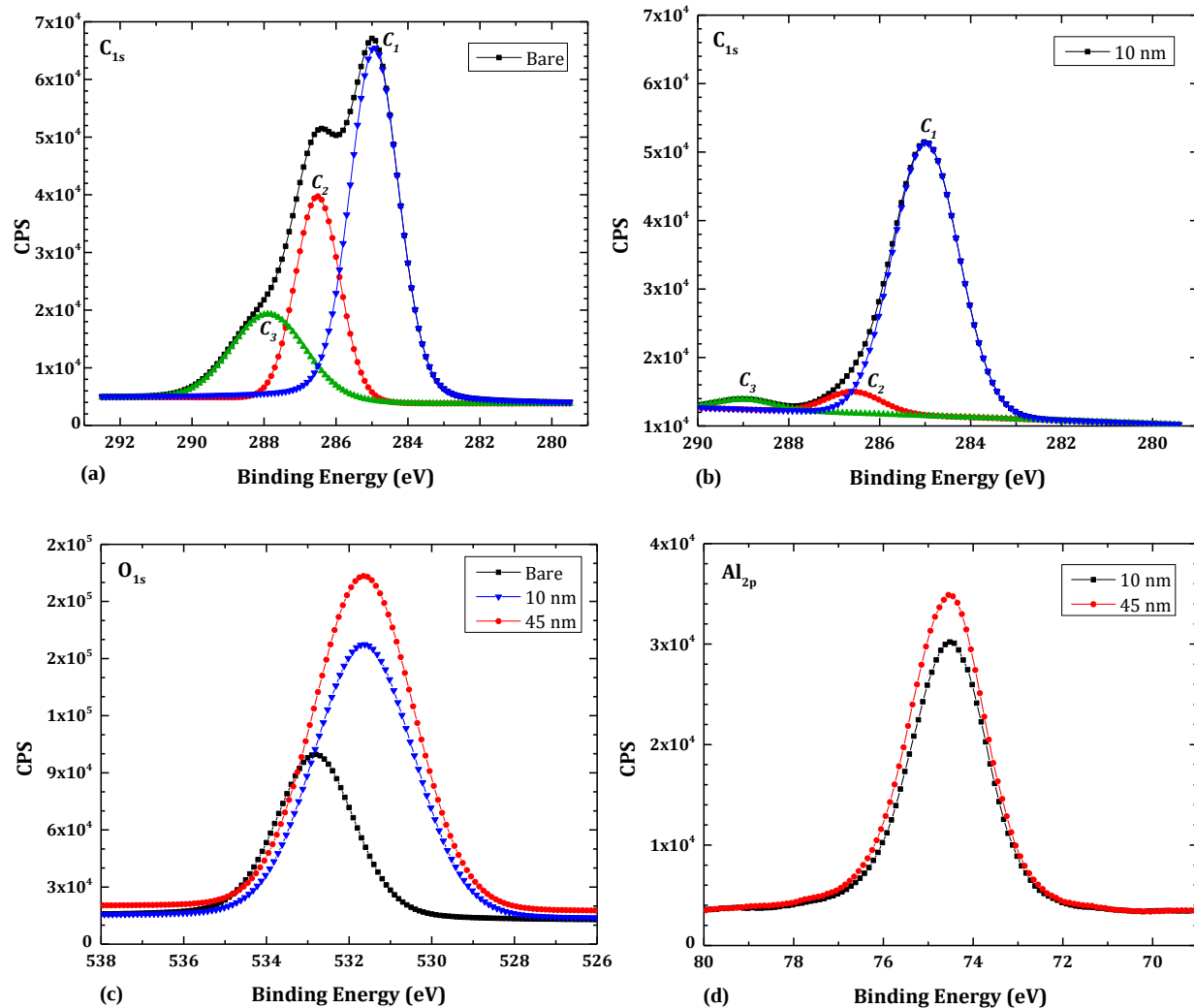


Figure 3.10. KR₂ handsheets' XPS high resolution spectra of (a) C_{1s} for bare sample (b) C_{1s} for 10 nm Al₂O₃ ALD (c) O_{1s} and (d) Al_{2p}.

3.2.2 Effect of Al₂O₃ Film Thickness on Gas Permeability

The water vapor transmission rates (WVTR) and water vapor permeability (WVP) at 23°C and 50% RH for handsheets before and after ALD modifications are presented in Tables 3.3 and 3.4 respectively. Although ALD modification greatly improves the wettability of unrefined Kraft and TMP handsheets, it did not affect their WVTR significantly. The reduction in WVTR value at 45 nm coating thickness is about 15% for KU handsheets and about 36.6% for TU handsheets. However, for refined Kraft pulp handsheets, the WVTR decreases 97% for KR₁ and 98% for KR₂

after Al_2O_3 deposition. The reduction of fiber size results in decrease of WVTR by 87% for KR_1 and 84% for KR_2 . Table 3.3 clearly shows the effect of fiber size on WVTR values. For both handsheets prepared by Kraft and TMP pulps the decrease in fiber size results in decrease of WVTR values. This is due to the larger surface area of fibers after refining. Accordingly, as mentioned before, the enhanced bonding between the fibers results in a dense fiber network with smaller pores and uniform dimensions⁶³. Therefore, the tortuosity increases within the sheets due to the formation of this dense network, which lowers the permeability. In addition to fiber size, fiber entanglement plays an important role in the increase of tortuosity⁶³. Studies have shown that nano-fibrillated cellulose (NFC) has longer fiber sizes compared to crystalline nano-cellulose (CNC)⁶³. However, the gas permeability of the CNC film is higher than that of the NFC film due to the higher entanglement of fibrils within the NFC films which results in increase of the tortuosity factor⁶³. The reported WVTR value (at 23°C and 50% RH) for NFC film (with thickness of 42 μm) is about $234 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ⁷ which is higher than the WVTR values for the KR_1 and KR_2 handsheets in this work. Although KR_1 fibers are longer than KR_2 (Table 3.3), the lowest WVTR value for untreated samples are for handsheets prepared with KR_1 fibers. Therefore, it can be concluded that there is an optimum fiber size that results into the lowest permeability. This can be due to the highest possible fiber entanglements that increase tortuosity and consequently reduce gas permeability to a minimum possible value.

Table 3.3. Water Vapor Transmission Rates for handsheets before and after Al₂O₃ ALD modification

Handsheet Type	Fiber Size (μm)	Sheet Thickness (mm)	WVTR (g·m ⁻² ·day ⁻¹)			
			Uncoated	10 nm	25 nm	45 nm
KU	882	0.21	694.8 ± 11.5	615.9 ± 2	606.6 ± 8.9	589.9 ± 15.1
TU	520	0.34	858.6 ± 16.1	602.1 ± 12.6	566.0 ± 10.6	544.6 ± 14.2
TR	142	0.11	640.9 ± 13.2	452.0 ± 13.5	443.2 ± 8.7	392.0 ± 11.1
KR ₁	457	0.07	88.6 ± 4.6	2.3 ± 0.2	2.5 ± 0.4	2.5 ± 0.2
KR ₂	245	0.06	107.1 ± 2.5	2.2 ± 0.9	2.1 ± 0.2	2.2 ± 0.5

Table 3.4. Water Vapor Permeability for handsheets before and after Al₂O₃ ALD modification

Handsheet Type	Fiber Size (μm)	Sheet Thickness (mm)	WVP (g·m ⁻² ·day ⁻¹ ·kPa ⁻¹)			
			Uncoated	10 nm	25 nm	45 nm
KU	882	0.21	495 ± 8.2	438 ± 1.4	432 ± 6.3	420 ± 10.7
TU	520	0.34	611 ± 11.5	429 ± 9.0	403 ± 7.5	388 ± 10.1
TR	142	0.11	456 ± 9.4	322 ± 9.6	315 ± 6.2	279 ± 7.9
KR ₁	457	0.07	63 ± 3.3	1.6 ± 0.14	1.8 ± 0.30	1.8 ± 0.14
KR ₂	245	0.06	76 ± 1.8	1.6 ± 0.64	1.5 ± 0.14	1.6 ± 0.40

The WVTR values for KR handsheets remarkably reduced after Al₂O₃ ALD compared to KU handsheets. However, there is not a significant difference in the WVTR values between the KR₁ and KR₂ handsheets after Al₂O₃ deposition. The results also show that the increase in coating thickness does not affect water vapor permeability by a great amount for KR₁ and KR₂ handsheets. Therefore, the combination of Al₂O₃ coating thickness of 10 nm and fiber sizes as small as 457 μm (as in KR₁) would be enough to achieve WVP values as low as about 1.6 g·m⁻²·day⁻¹·kPa⁻¹. It should be noted that although the refined TMP fibers have smaller fiber size compared to refined Kraft, the WVTR values for TR sheets are significantly higher than RK sheets. This is due to the presence of lignin in TR fibers, which hinders hydrogen bonding and forms more pores, resulting in higher WVTR values⁶³. As mentioned earlier, for the purpose of this study all WVTRs were obtained at 23 °C and 50% RH and the effect of treatment on handsheets at higher relative humidity

were not investigated. Generally, for uncoated paper-based materials at higher relative humidity, the WVTR is expected to increase due to the swelling of fibers⁶³.

The Gurley air permeability test was used to obtain the time required for air to pass through a unit area at a given pressure. The air permeability values for untreated and 25 nm Al₂O₃ ALD handsheets at 23 °C and 50% RH are presented in Table 3.5. Handsheets prepared with refined pulp fibers have remarkably lower air permeability compared to handsheets prepared with unrefined pulp fibers.

Table 3.5. Gurley air permeability for untreated and 25 nm Al₂O₃ ALD coatings

Handsheet Type	Fiber Size (μm)	Air Permeability (s/100cc)	
		Uncoated	25 nm
KU	882	1.3 ± 0.1	5.7 ± 0.54
TU	520	3.2 ± 0.1	17.6 ± 0.3
TR	142	222.9 ± 25.5	362 ± 20.1
KR ₁	457	352800	Impermeable
KR ₂	245	Impermeable	Impermeable

The trend in air permeability agrees with the WVTR results. According to table 3.5, the air permeability before and after treatment for the unrefined pulp handsheets (KU and TU) is in the order of few seconds. However, for KR₁ handsheets before the treatment, it takes 98 hours for the 100 cc of air to pass through the sheet. The KR₁ and KR₂ samples after 25 nm coating can be considered impermeable and the air permeability could not be quantified with Gurley method. As mentioned earlier this is due to the decrease in fiber size as well as filling of the pores after Al₂O₃ ALD coatings which results in lower permeability.

Thus, the major finding in this work is that it demonstrates the requirements to achieve an effective water vapor barrier by: (i) use of refined fibers (reduction in fiber size) to obtain a densely packed cellulosic film; and (ii) deposition of Al₂O₃ to reduce the surface energy as well as porosity

of the sheets. A major target of highest gas barrier property with the lowest number of coating thicknesses was achieved with the Al_2O_3 ALD method. A maximum water vapor barrier improvement of ~98% (WVTR value of $2.1 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$) was determined after ALD treatment for Kraft refined handsheets. The reduction in Kraft pulp fiber sizes reduces the WVTR by 87% for KR_1 and 84% for KR_2 prior to ALD treatment. For comparative reasons the WVTR of commercially available coatings and packaging materials such as polyvinylidene chloride coated cellulose films, cellulose acetate films, and PET films are 6, 14, and $4 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ respectively at 35 °C and 25% RH ⁷² which are inferior to some of the coated papers elaborated in this study. Contrary to polymers, these handsheets, regardless of the process, are produced from a renewable material. The potentials are in packaging applications and some may not be foreseen.

3.3 CONCLUSIONS

The present study demonstrates that the use of refined wood fibers of suitable size in conjunction with atomic layer deposition of Al_2O_3 enables the fabrication of paper with a water vapor transmission rate that is superior to some of the commercially available coated films. The permeability is greatly reduced due to the formation of dense networks within the sheets by smaller and more uniform fibers dimensions. The deposited Al_2O_3 has its maximum effect on gas permeability with the paper produced with Kraft refined pulp. We observed the lowest WVTR for cellulosic sheets prepared by 450 μm fiber sizes from refined Kraft pulp. This is due to the higher fiber entanglements within the cellulosic sheets that increase the diffusion path for gas molecules. Further refining of the cellulose fibers to 245 μm reverses the effect and caused increase in WVTR values. The coatings also effectively modified the surface energy of handsheets and converted the highly hydrophilic cellulose surface to a hydrophobic one. However, the hydrophobicity of the

sheets is highly dependent on surface roughness. The fabricated sheets in this study are comparable with commercial synthetic polymers. Therefore, the preparation of hydrophobic and water vapor barriers by Al_2O_3 ALD approach on engineered paper is a promising tool in renewable material science and technology.

Chapter 4: Self-assembly of Cellulosic Micro Fibers on Surfaces with Different Wetting Properties

In this chapter, mechanically refined fibers with diameter ranging from 80 nm to 10 μm were utilized for the preparation of cellulosic films. The fiber suspension is referred as Microfiber (MF) throughout this chapter. The MF films were prepared by casting Microfiber (MF) suspension on two surfaces with different wettability. The objective of this work was to demonstrate the effect of the substrate's wettability on the optical, physical, and mechanical properties of the MF films. We were thus able to produce MF films with tunable optical properties, which have low water vapor barrier properties, and high mechanical strength comparable to their counterparts.

4.1 EXPERIMENTAL SECTION

4.1.1 Microfibers Preparation.

Bleached Softwood Kraft Pulps, obtained from a pulp and paper mill in central British Columbia, were refined in two optimized stages at pilot plant in the Pulp and Paper Centre at the University of British Columbia (Vancouver, B.C., Canada). The detailed method is reported in Chapter 2. The pulp suspension was not subjected to any enzymatic pretreatment prior to mechanical refining. A microfiber aqueous suspension with consistency of 1.07% was obtained after refining. The suspension was directly used as the starting material for the preparation of microfiber films without any post treatment.

4.1.2 Fiber Size Measurement

Fiber size distribution in suspension was obtained by using the Scirocco 2000 Malvern Mastersizer (Malvern Instrument Inc., Malvern, UK). The device uses laser diffraction to

determine the particle size distribution, reports it as a volume equivalent sphere mean diameter. The detection range of the device is from 0.02 to 2000 μm .

4.1.3 Film Preparation.

The Microfiber suspension was diluted with water to the final consistency of 0.5%, followed by mixing at 1500 rpm using magnetic stirrers (IKA RH Basics) for 30 min. The suspension was degassed for 15 min with a water vacuum pump and then transferred into hydrophilic CORNING[®] glass and hydrophobic Teflon[®] FEP film liners petri dishes. The dishes were shaken manually to remove any entrained air and the samples dried at 23°C and 50% relative humidity. To prepare films with basis weight of 30 and 60 $\text{g}\cdot\text{m}^{-2}$, 35 g and 71 g of the suspension was used respectively. The thickness of the sheets was measured by using the L&W Micro Calliper.

4.1.4 Freeze Drying.

The microfiber suspension was freeze-dried using the Flexi-Dry TM Manifold Freeze dryer. The suspension (50 g at 0.05% consistency) was poured into glass and Teflon petri dishes and kept at 23°C and 50 % relative humidity for 24 h. Subsequently, the dishes were put into a freezer for another 24 h prior to freeze-drying.

4.1.5 Characterization of Films

SEM Imaging. The morphology of the freeze-dried fibers and the structure of the films were observed using S3000N Variable-Pressure Scanning Electron Microscopy at operating voltage of 5-10 kV.

X-ray diffraction. The XRD patterns for the films were obtained by Rigaku Multiflex diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 20 mA over the angular range $2\theta = 2^\circ - 50^\circ$. The

microfiber films were individually mounted in the sample holder and X-ray beam passed through them. The degree of crystallinity or crystallinity index (CI) for each film was calculated using equation 4.1⁷³.

$$CI = \frac{(I_{max} - I_{am})}{I_{max}} \times 100\% \quad (4.1)$$

where I_{max} is the maximum intensity of the principal pick (or lattice diffraction) near $2\theta = 22.5^\circ$, and I_{am} , is the minimum value of intensity near $2\theta = 18^\circ$, attributed to the intensity of diffraction for the amorphous region of the cellulose.

Tensile Index. The tensile index (kNm/kg) of the microfiber films were obtained using L&W Tensile Strength tester. The devise setup is based on TAPPI method T494. Prior to tensile measurements, the films were preconditioned at 23°C and 50% RH for 48 h and then were cut into 15 mm wide strips to conform to TAPPI T494 standard. Five specimens were tested for each sample and the average values are reported.

Water Vapor Transmission Rate (WVTR). The water vapor transmission rate of microfiber samples was obtained using the cup method. The detailed procedure is described in chapter 2. The samples were preconditioned for 48 h at 23°C and 50% relative humidity. The weight of the samples was measured for 10 days and the average value is reported. The WVTR values were calculated using equation 4.2.

$$WVTR (g \cdot m^{-2} \cdot day^{-1}) = \frac{\Delta m (g)}{A (m^2)} \quad (4.2)$$

Where Δm is the difference between the initial mass and the mass after 24 h (g) and A is the exposed area of the film (m^2).

Porosity. The apparent density of the films was obtained by measuring the weight and dimensions of each specimen. The corresponding film porosity was then determined using equation 4.3⁷⁴.

$$Porosity = \left(1 - \frac{\rho_{film}}{\rho_{cellulose}}\right) \times 100\% \quad (4.3)$$

where ρ_{film} is the apparent density of the microfiber film and $\rho_{cellulose}$ is the density of pure cellulose which is 1,500 kg/m³.

Light Transmittance. The visible light transmittance for microfiber films was obtained at a wavelength range from 400 to 800 nm using the Optometrics® tunable monochromator following Forughi et al. procedure^{75,76}.

Roughness. The surface roughness of the films was measured using the Wyko NT1100 optical profilometer. The Vision software (Veeco Instruments Inc.) was employed to obtain the average roughness values (R_a) of the film's surface.

Contact Angles. The static and dynamic contact angles on glass and Teflon substrates were determined by dispensing a 5 μ L droplets on the surface with a piston-driven air displacement pipet. A high-resolution camera (Nikon D90) was used to take the droplet images on the substrate following the procedure reported by Kietzig et. al.^{11,67}. Then, the images were analyzed with FTA32 version 2.0 software to determine the contact angle.

4.2 RESULTS AND DISCUSSION

4.2.1 Morphology of Unrefined and Refined Fibers and MF Films

The average fiber size before and after refining was 927 $\pm$ 5 μ m and 259 $\pm$ 10 μ m respectively. Figure 4.1a and 4.1b are the scanning electron microscope images of the unrefined and refined

fibers respectively. Figure 4.1b illustrates the impact of mechanical refining on the fibers that creates microfibrils. The microfibrils are the main components of the suspension which contains fibers, fiber fragments, fines and fibrils (Fig. 4.1b-arrows show fiber fragments). Based on the SEM images, the diameter size distribution of fibers is within 80 nm- 10 μ m which is significantly higher than the diameter of MFC (10- 50 nm) reported in literature ²⁹. During the drying of the MF suspension, the fibers densely packed together and created a high-density MF film. It is particularly notable that depending on the surface on which the MF suspension was casted, films with distinct differences in morphology and microstructure were formed. The hydrophilic glass surface resulted in the formation of opaque (OP) films, while the hydrophobic Teflon surface resulted in the formation of translucent (TL) films. The surface micrograph of OP films, Fig. 4.1c, shows micro-sized cellulose fibers with some visible pores as well as a network structure on the surface. On the other hand, the surface of TL films (Fig. 4.1d) shows a denser and compact arrangement with no visible network structure. The cross-section images of the films also confirm a denser structure on TL films compared to OP films (Fig. 4.1f and 4.1e). On OP films the microfibrils were self-assembled into layers of macro-sized cellulose fibers in which the fibers stood out from the fractured surface (Fig. 4.1e). The TL films also have a layered structure (Fig. 4.1f). However, the fracture surface of TL films shows microfibrils that are self-assembled to form aligned and parallel plate-like layers with less visible pores (inset image of Fig. 4.1f).

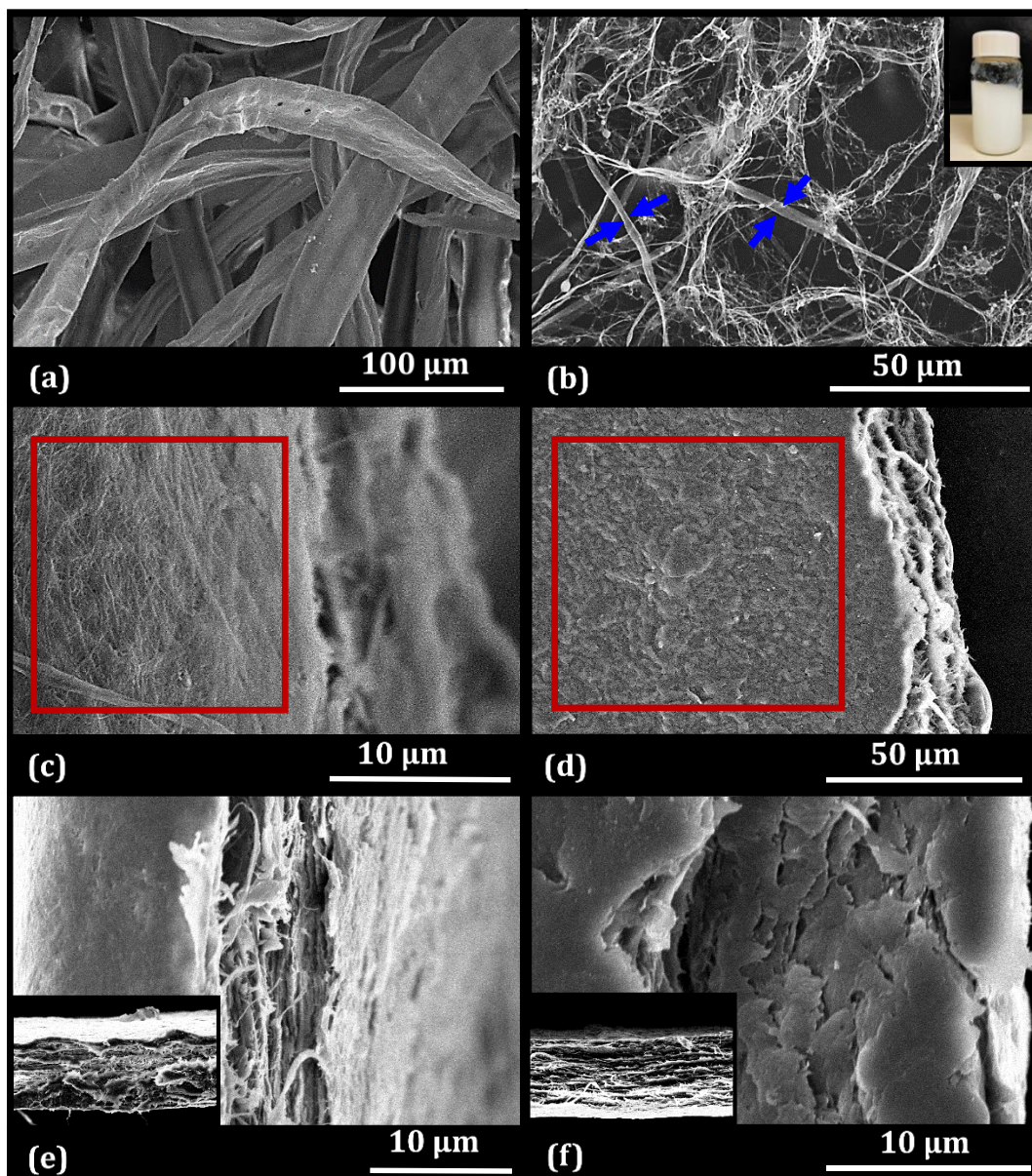


Figure 4.1. SEM micrographs of (a) unrefined fibers (b) mechanically refined fibers. The arrows indicate the existence of fibers and fines in the suspension after mechanical refining, the inset image shows the dispersion state of microfibers at 1wt% concentration (c) fiber network structure and visible pores on the surface of OP films (d) compact denser film structure on the surface of TL films with no visible fiber network structure (e) cross section of OP films with fibres standing out from the fractured surface (f) cross section of TL films with parallel and plate-like layers of microfibers.

4.2.2 Crystallinity Index of Films by XRD

The XRD Pattern of the films are shown in Fig. 4.2. The sharp diffraction peak ($I_{\max}$ or I_{200}) appearing at $2\theta=22.72^\circ$ corresponds to crystalline part of cellulose fibrils (200 lattice plane), and

it is characteristic of natural plant cellulose. The measured crystallinity index (CI) in this study was about 75% for OP films and 79% for TL ones. The crystallinity of NFC film is very dependent on its manufacturing (fibrillation) process as well as the drying mechanism. Previous studies have shown that while mechanical fibrillation did not change cellulose polymorphs⁷⁷⁻⁷⁹, the enzymatic or chemical pretreatments resulted in decrease of NFC film's crystallinity^{74,78}. Heat and humidity are other factors which cause the increase in crystallinity of cellulosic films^{74,78,80,81}.

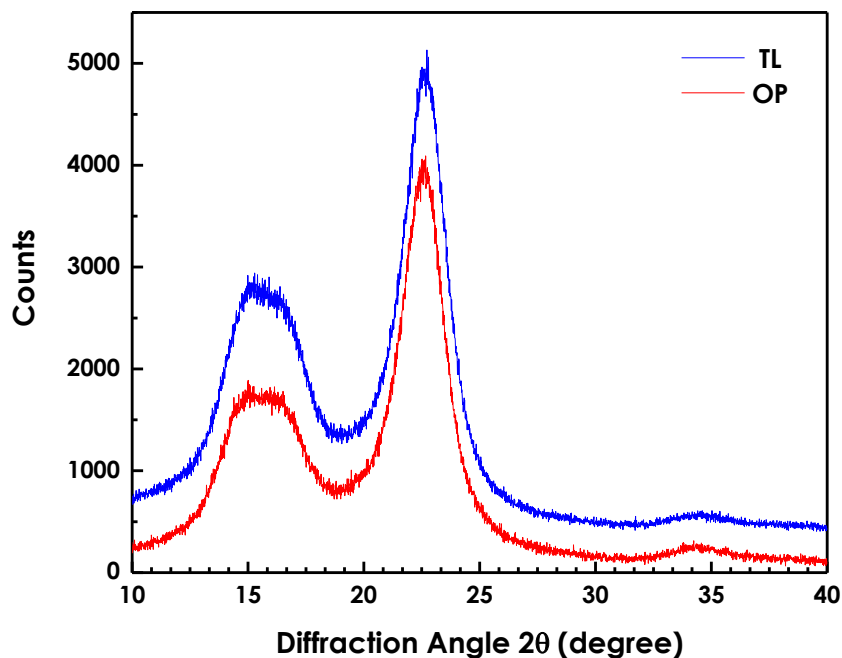


Figure 4.2. XRD patterns for OP and TL microfiber films

In this study, the slightly higher crystallinity of TL films can be related to the denser structure of TL films. For TL films, the hydrophobic surface causes microfibers to populate more closely during drying and create tight aggregates due to the higher number of hydrogen bonds among hydroxyl groups of the cellulose chains. This results in enhancing the crystalline structure⁷⁸. In addition, rearranging of microfibers during air drying is another factor which results in higher crystallinity of TL films⁷⁸.

4.2.3 Optical Transmittance of Microfiber Films

The optical properties of MFC films depend on the degree of fibrillation and the fabrication method. The higher the degree of fibrillation the more the transparency of the MFC material due to formation of optically inactive fibrils²⁸. Such fibrils have diameters less than 20 nm and can form dense structures with almost no air cavities within the film and low light scattering^{28,77,82}.

The visual appearance of TL and OP films is shown in Fig. 4.3a-c. The TL film appears transparent when it is placed on the background image (Fig. 4.3a). However, by holding the TL film 3 cm above the background image, the translucency of the film is more evident (Fig. 4.3b) due to light scattering. Fig. 4.3d shows a MF film formed by casting the MF suspension on a surface with hydrophobic/hydrophilic stripe pattern. The image shows alternating translucent and opaque stripes on the film corresponding to the respective hydrophobic and hydrophilic stripes of the substrate. The light transmittance of various MF films is compared in Fig. 4.3e. The transmittance of TL film (37%) is about three times higher than that of the OP film (12%) at wavelength of 600 nm for samples with basis weight of 30 g.m⁻². The light transmittance is lower for sample with basis weight of 60 g.m⁻² (3% vs. 12% for OP and 31% vs. 37% for TL films, respectively) at 600 nm wavelength. This is due to the higher thickness of these samples compared to samples with basis weight of 30 g.m⁻² (51 μ m vs. 25 μ m). This is explained by the Beer-Lambert law which states that the absorption of light exponentially reduces with thickness. Other factors such as packing density of fibers, large fiber fragments or fiber aggregates, and surface roughness impact light transmittance of the films⁸².

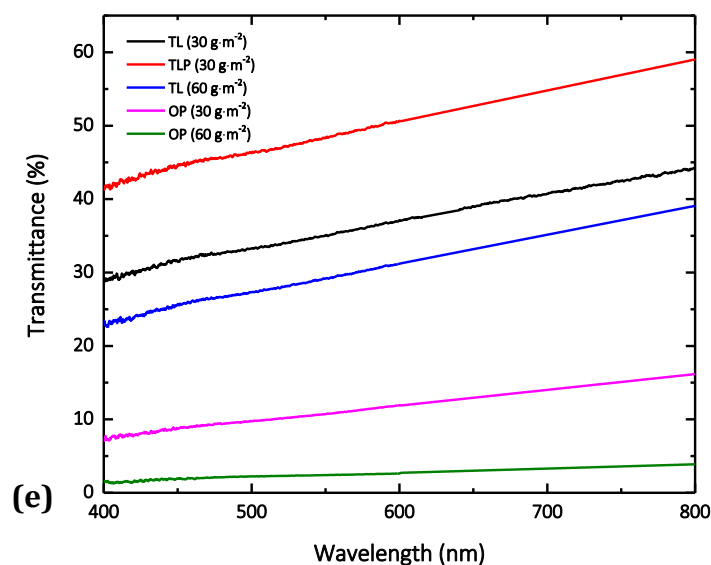
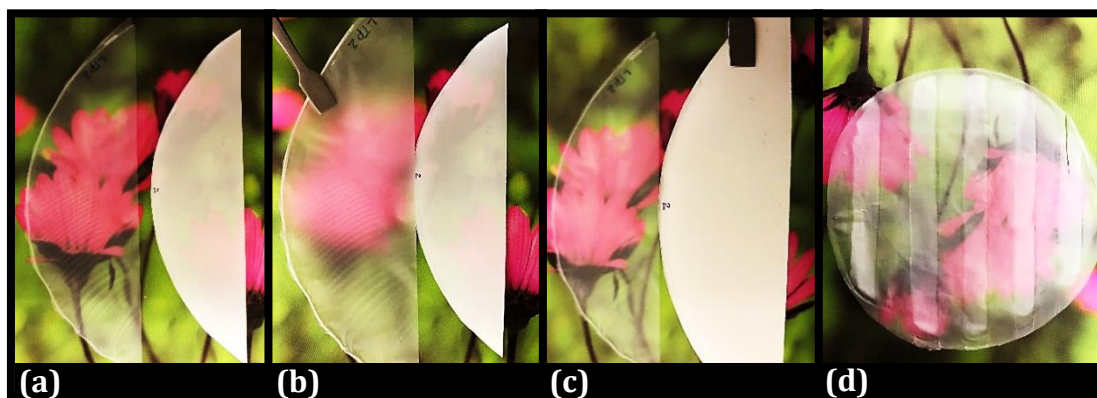


Figure 4.3. (a-d) The visual appearance of the two MF films (TL and OP): (a) both films are on the surface of the background image (b) the TL film is 3 cm away from the background image (c) the OP film is 3 cm away from the background image (d) a film with transparent and opaque stipes formed on a hydrophobic-hydrophilic surface. (e) The light transmittance of TL and OP film (TLP stands for translucent polished film).

The higher light transmittance in TL films is due to their higher packing density compared to OP films. Surface roughness also affects light scattering at the surface. This is due to different refractive indices of cellulose and air. We have further improved the light transmittance of TL films to 51% (at wavelength of 600 nm) by polishing the top surface of the film using emery paper. The thickness of the film was 25 and 22 μm before and after polishing respectively.

4.2.4 Microstructure of Self-Assembled Microfibers During Freeze-Drying

To understand the effect of surface wettability on the self-organization of the microfibers during drying, MF samples with 0.05 wt % concentration were prepared and casted on glass and Teflon petri dishes. The samples were kept at room temperature overnight to let the self-assembly of fibers take place prior to freeze-drying. Fig. 4.4 shows the morphology of the freeze-dried MF suspension which forms foam like structure upon freeze-drying.

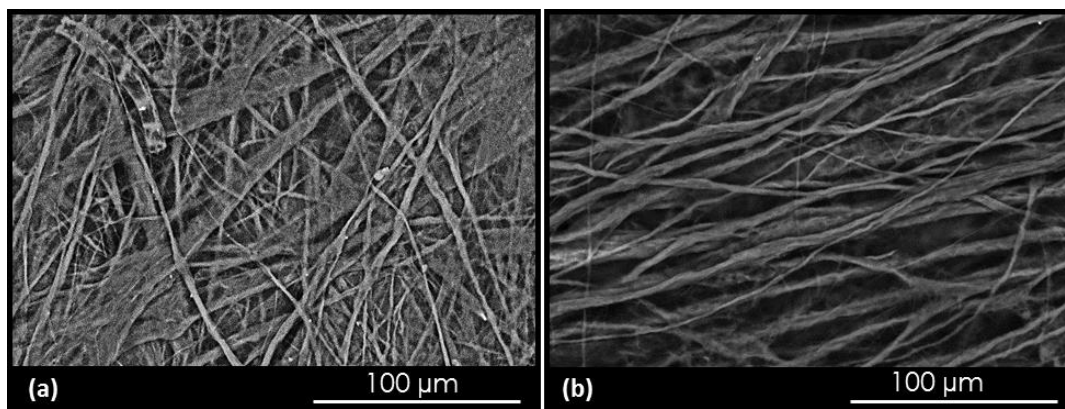


Figure 4.4. SEM Images of (a) MF fibers casted on glass substrate shows a random fiber network (b) MF fibers casted on Teflon substrates shows an aligned fiber structure.

As seen in figure 4.4, on the hydrophilic glass surface (Fig. 4.4a) the MF fibers self-organized into a more random structure compared to MF fibers casted on the hydrophobic surface (Fig. 4.4b). On the hydrophobic substrate (Fig. 4.4b), the microfibers self-assembled into an aligned structure. In addition, a denser foam structure is formed on the hydrophilic glass surface compared to Teflon surface.

4.2.5 Drying Mechanism of Cellulose Microfibers

Little is known about the self-assembly behavior of MFC and NFC during casting evaporation. The MF suspension forms a convex meniscus on the hydrophobic surface and the contact area of the dried film is smaller than the initially pinned contact area. On the other hand, the MF

suspension forms a concave meniscus on the hydrophilic glass surface and the dried films have the same contact area as the initially pinned contact area. The edges of the film casted on the hydrophilic glass substrate are translucent as seen in Fig. 4.5a. For the MF films casted on the hydrophobic surface although the films are translucent, there are bumps or a foot like structure at the edge of the film (Fig. 4.5b).

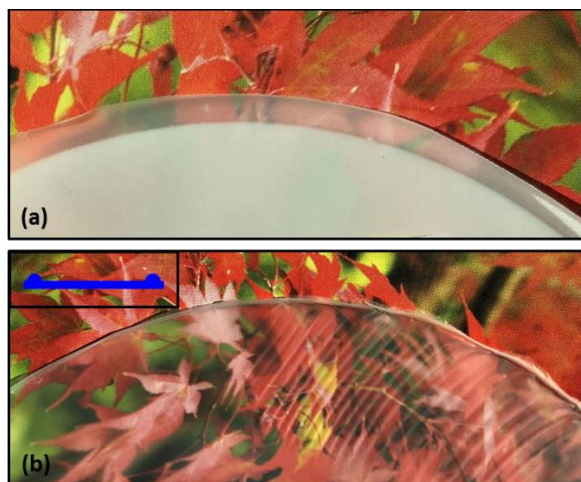


Figure 4.5. (a) Translucent edge of the OP films dried on hydrophilic glass substrate (b) bump/foot like structure at the edge of TL films, the inset image is the 2D schematic of the foot like structure at the edge.

There may exist certain alignment and denser accumulation of fibers at the edges of the films dried on both, the hydrophobic and hydrophilic surfaces, which can be explained by the coffee ring effect⁸³. On the hydrophilic surface, since the evaporation flux is faster at the dry line boundary (air/suspension/substrate triple line) compared to the center, the suspension flows to the perimeter and the fibers pin and adsorb on the contour of contact area. Therefore, convection results in condensation (deposition) and causes pile up of fibers at the edge. Consequently, the fiber concentration gradient toward the edge results in thickness gradient toward the edge and denser structure of the dried film at the edge. This can be the reason for the translucency of OP films at the edge (Fig. 4.5a). In addition, there might be certain alignments of fibers at the edge due to Surface Tension Torque (STT)⁸⁴. According to Mashkour et al.⁸⁴, a fiber approaches the

triple line by the capillary outward flow (convective flow) of the liquid until one of its ends contacts the triple line. The fiber may stay at this contact point, but since the contact line is energetically more favorable, the exerted torque on the other end of the fiber due to liquid flow will turn the fiber parallel to the contact line. This acts as a nucleation point and other fibers from the suspension follow the same arrangement and can accumulate onto the deposited fibers on the triple line upon evaporation of the liquid (Fig. 4.6, the fibers are depicted as smooth rods although in reality are long and flexible).

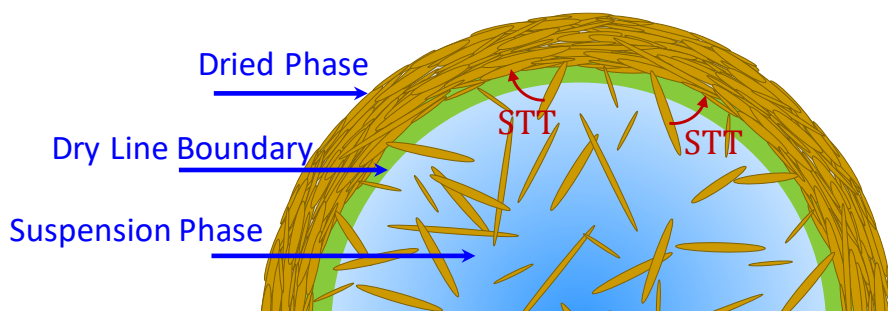


Figure 4.6. Drying mechanism of the MF suspension on a hydrophilic glass substrate

Due to the dense structure of the films we were not able to observe the alignment at the edge by SEM. We believe that the higher concentration and denser structure of fibers at the edge is the reason for the edge translucency. However, the SEM images of the freeze-dried sample on Fig. 4.7 shows some alignment for MF films dried on Teflon (Fig. 4.7b) compared to Glass (Fig. 4.7a).

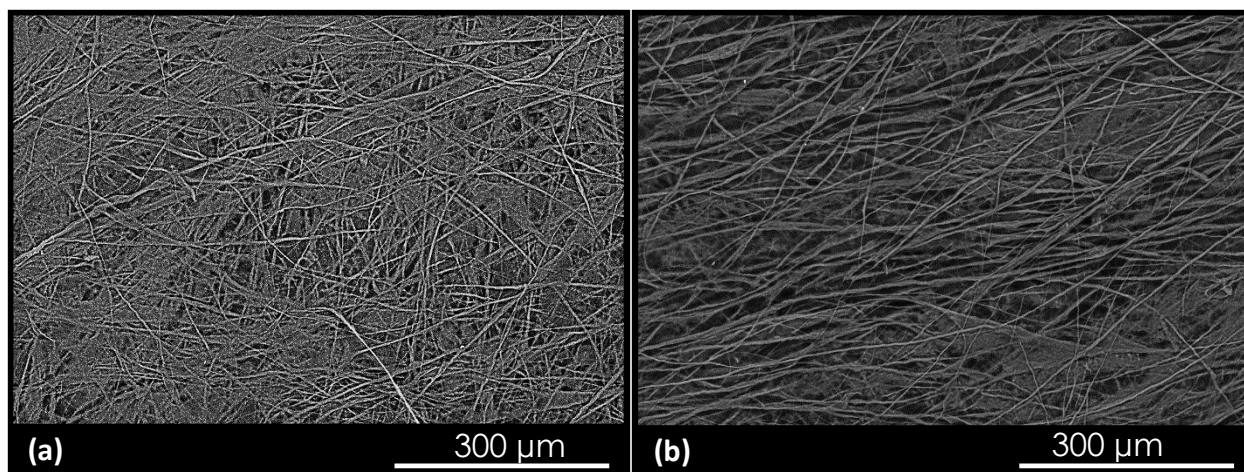


Figure 4.7. (a) Random network of fibers on the hydrophilic glass surface (b) relatively aligned MF structure on the hydrophobic Teflon surface.

The mechanism of drying on the hydrophobic surface is slightly different⁸⁵. At the initial stage of drying on the Teflon substrate, the adsorption of the fibers at the outline of the contact area was not observed. As the drying proceeded, the fibers start to aggregate and when the concentration reached a critical value, at which the system transitions from fluid to gel-like⁸⁶, the fiber-aggregates moved by convection, and deposited at the dry line boundary to form a gel foot structure. The gel foot grows over time and results in the rise of the solid-vapor interface above the gel which creates instability and formation of inward mass transport to the center, counterbalancing the capillary flow. Therefore, the contact line depins and recedes until it finds a new equilibrium state. The fiber aggregates are gathered at the center of the contact area with decrease of suspension volume. After complete drying of the MF suspension a freestanding TL film is formed.

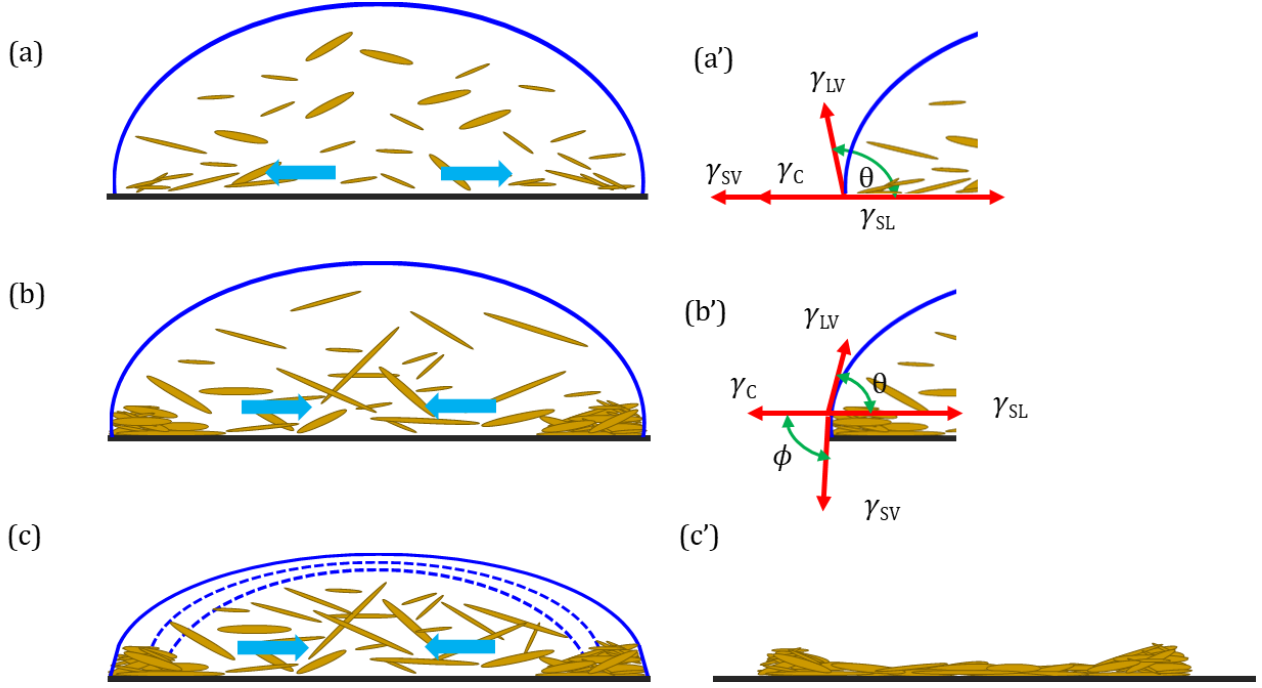


Figure 4.8. Schematic of the mechanism of fluid flow in an evaporating MF suspension on a hydrophobic Teflon substrate. (a) capillary flow deposits fibers at the contact line (a') magnified view of the four interfacial tension forces acting at the contact line at equilibrium (b) depinning and transport of MF toward the center (b') magnified view of suspension at the contact line after depinning and the raise of the solid-liquid interface above the gel foot (c) multiple cycles of pinning and depinning and deposition of fibers toward the center due to circulatory fluid flow (c') dried MF film.

Figure 4.8 shows the mechanism of MF drying on the hydrophobic surface⁸⁷. The forces acting at the contact line are the surface tension of the solid/vapor interface (γ_{SV}), solid/liquid (γ_{SL}), liquid/vapor (γ_{LV}), and the pinning tension due to the capillary force (γ_C). At equilibrium the surface force balance is given by Eq. 4.4 (Fig. 4.8a')

$$\gamma_{SL} = \gamma_C + \gamma_{SV} + \gamma_{LV} \cos(\pi - \theta) \quad (4.4)$$

where θ is the contact angle at the surface.

The gel foot starts to form at the bottom of the dish when there is no attachment of the fiber suspension to the wall of the dish. This is due to the fact that pinning of the fibers at the wall was not observed. In addition, the diameter of the dried film is smaller than the diameter of the dish, and at the film's edge the foot like structure is evident (Fig. 4.5b).

The growth of the gel foot shifts the solid/vapor interface above the gel (Fig. 4.8b and b') and results in an imbalance of forces in the system (Eq. 4.5).

$$(\gamma_{SL} + \gamma_{LV} \cos \theta) - (\gamma_C + \gamma_{SV} \cos \phi) > 0 \quad (4.5)$$

where ϕ is the angle of the gel foot. This results an unbalanced force acting inwards and depins the contact line in search for a new equilibrium state (Fig. 4.8c). Consequently, the fluid above the deppined contact line flows inward. Multiple cycles of pinning and depinning occur and microfibers transport inward and upon complete drying the TL film forms.

The pinning and depinning occurs due to low contact angle hysteresis of the smooth Teflon substrate. To confirm our hypothesis, we track the evaporation dynamics of a 50 μ L pulp suspension droplet on the hydrophilic glass and hydrophobic Teflon substrate. Figure 4.9 shows the contact angle ($^\circ$) and base diameter (normalized by the initial diameter) of pulp suspension droplet on both substrates over time (normalized by the final time).

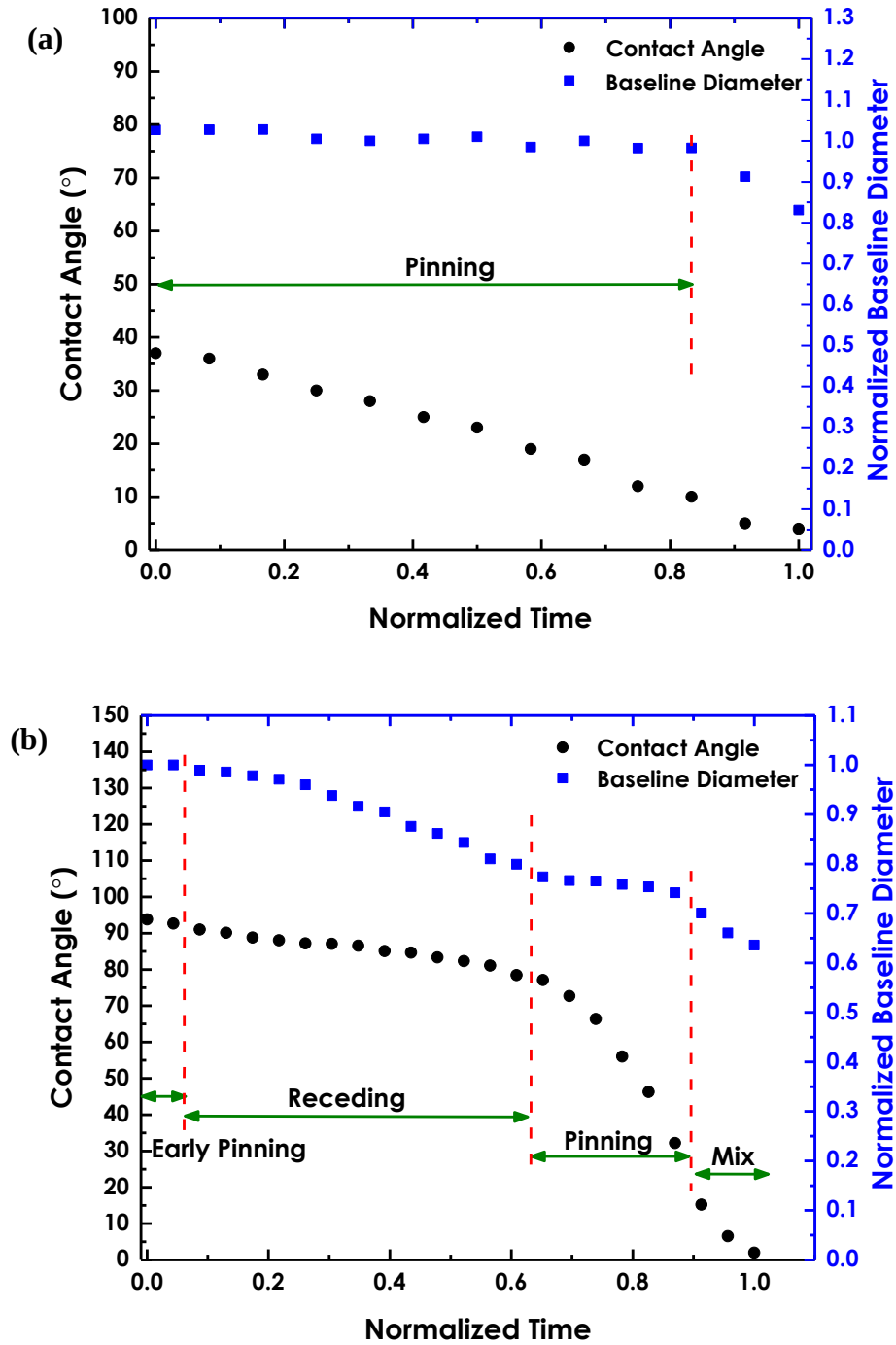


Figure 4.9. Evaporation dynamics of an MF suspension droplet on (a) hydrophilic glass substrate and (b) hydrophobic Teflon substrate

On the hydrophilic glass substrate (Fig. 4.9a) the contact angle steadily decreases over time, while the base diameter of the droplet remains approximately constant until the final stage of

evaporation. During the final stage, the contact angle levels off at about 5° while the base diameter decreases until the suspension is dried completely. On the hydrophobic Teflon substrate, the evaporation of suspension droplet involves four distinctive modes⁸⁸: short early pinning mode (constant contact droplet diameter), receding mode (constant contact angle), pinning (constant diameter), and a final mixed mode in which both the contact angle and contact diameter are not constant. According to Fig. 4.9b, initially there is very short early pinning mode of the MF suspension droplet (during the first 5% of the total evaporation time). During this time the contact angle decreases while the base diameter remains constant. The short pinning time is due to the hydrophobicity and low contact angle hysteresis (~18°) of the Teflon surface. When the contact angle reaches the receding contact angle, the triple contact line starts receding and shrinking toward the center of the droplet. During this time the contact angle remains roughly constant up to 65% of the total evaporation time of the droplet. Consequently, the contact angle decreases sharply during the late pinning mode followed by the mixed mode of evaporation.

4.2.6 Physical and Mechanical Properties of Cellulose Microfiber Films

Table 4.1 summarizes the physical and mechanical properties of OP and TL films. Clearly films prepared on the hydrophobic substrate have superior physical and mechanical properties.

Table 4.1. Physical and Mechanical Properties of OP and TL films prepared on hydrophilic and hydrophobic surfaces respectively

	WVTR (g·m⁻²·day⁻¹)	Density (kg·m⁻³)	Porosity (%)	Tensile (MPa)	Thickness (μm)
Opaque Film	105.6 ± 2.7	1325±19	12±2.0	144.0±3.1	21±2.1
Translucent Film	91.6 ± 2.1	1396±13	7±0.9	163.6±3.9	25±2.8

The TL films have higher tensile strength, lower water vapor transmission rate, and lower porosity compared to OP films due to their denser structure.

The profilometer images of the films (Fig. 4.10) show roughness values on both sides of the OP and TL films. The top side (the side exposed to air) of the OP film is 4.7 times rougher than its bottom side (the side attached to glass surface). Based on the profilometer image (Fig. 4.10b), the fibers pinned and adsorbed to the surface of glass substrate formed a smoother film.

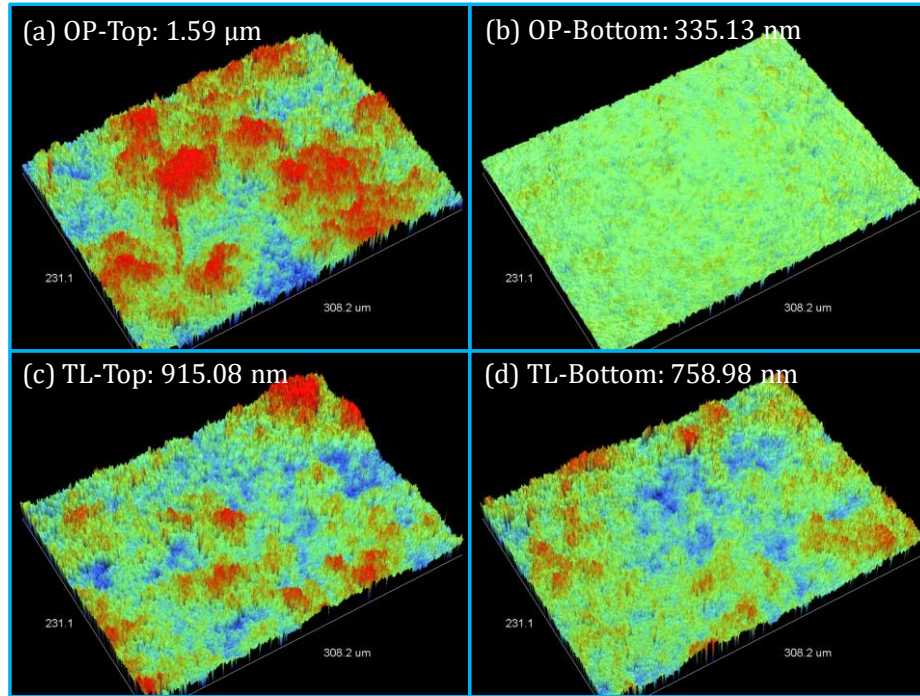


Figure 4.10. Surface roughness and profilometry images on (a) top surface of OP film (b) bottom surface of OP film (c) top surface of TL film (d) bottom surface of TL film

On the hydrophobic Teflon substrate (Fig. 4.10c, d), the roughness values on both sides of the TL films are similar. This is due to the absence of adhesion and pinning of TL films to the substrate during drying of the films.

4.3 CONCLUSIONS

In this study translucent and opaque microfiber films were fabricated by casting microfiber suspensions on hydrophobic and hydrophilic substrates, respectively. We have demonstrated that the wettability of the substrate significantly impacts the physical, optical and mechanical properties

of the formed film. Thus, the fabricated microfiber TL films have tunable optical properties while maintaining good mechanical properties. In addition, their physical and mechanical properties are comparable to Micro and Nano-fibrillated Cellulose films reported in literature^{27,74,89,90}. During drying, the microfibers moved towards the edge of the drying film by convection, condensed, and aligned at the contact line boundary. This results in translucency of the edge of films dried on the hydrophilic surface. However, on the hydrophobic substrate, due to the movement of the triple boundary line and tendency of the suspension to minimize its contact with the hydrophobic surface, the microfiber suspension becomes highly concentrated and hydrogen bonding occurs directly among the hydroxyl groups of the cellulose chain and form a dense translucent film. Since the efficient production of Micro and Nano-fibrillated cellulose is still challenging due to high energy consumption, by refining fibers at lower energy levels and casting suspension on a low surface energy substrate, a film with desirable properties comparable to MFC and NFC can be obtained.

Chapter 5: Fabrication of Janus Cellulosic Paper Using Dual Functional

Fillers

Mineral fillers are widely used in paper making for enhancing the physical properties of paper. In this chapter, Janus hydrophobic/hydrophilic silica and TiO₂ fillers are fabricated. The effect of filler's dual functionality on the barrier properties of cellulosic handsheets is investigated. In addition, the distribution and retention of dual functional fillers on handsheets is determined.

5.1 EXPERIMENTAL METHODS

5.1.1 Materials

Highly pure spherical silica particles (1.5 μm in diameter) and titanium dioxide (particle size of 100 nm) were supplied by Tokuyama America Inc. (Illinois, USA) and Spectrum Chemical MFG Corp. respectively. Paraffin wax with melting point ranging from 53-57°C, aminopropyl triethoxysilane (APS) (99%), Fluorescein isothiocyanate isomer I Celite[®] (FITC), didodecyldimethylammonium bromide (DDAB) (98%), Chloroform ($\geq 99.5\%$), and dichlorodimethylsilane (DCDMS) ($\geq 99.5\%$) were purchased from Sigma-Aldrich.

5.1.2 Fabrication of Janus Fillers

Amphiphilic Janus particles were prepared as described by Hong et al.⁹¹. Briefly, Silica and Titanium dioxide (TiO₂) were dispersed in paraffin wax at 85 °C and then mixed with DDAB-water solution with concentration of 0.05 mg/mL for silica particles and 0.005 mg/mL for TiO₂ particles. The chemical dosages as well as experimental conditions are shown in Table 5.1.

Table 5.1. Chemical Dosages for Synthesis of Janus Fillers

Filler	W (g)	Wax (g)	DDAB (mL)	T (°C)	RPM	t (min)
SiO₂	1.5	9	22.5	85	1300	15
TiO₂	0.15	7	35	85	1300	15

Fig. 5.1 shows the process for fabrication of Janus filler. The emulsions were prepared by stirring the mixture with a magnetic stirrer at 1300 rpm for 15 min. The vigorous agitation resulted in absorption of the hydrophilic filler particle onto the liquid/liquid interface (oil in water emulsion) and formation of colloidosomes. The colloidosomes were cooled at room temperature at which the paraffin wax is solid. Then they were washed with deionized water three times and dried at room temperature for 48 hours. Then the exposed surface of fillers became hydrophobic by vapor phase silanization at room temperature. The reaction occurred by bubbling N₂ gas through the liquid silane reagent to vaporize it, and then the colloidosomes were exposed to the silane vapour to make them hydrophobic. In the final step, the paraffin wax was dissolved by chloroform to release the filler particles.

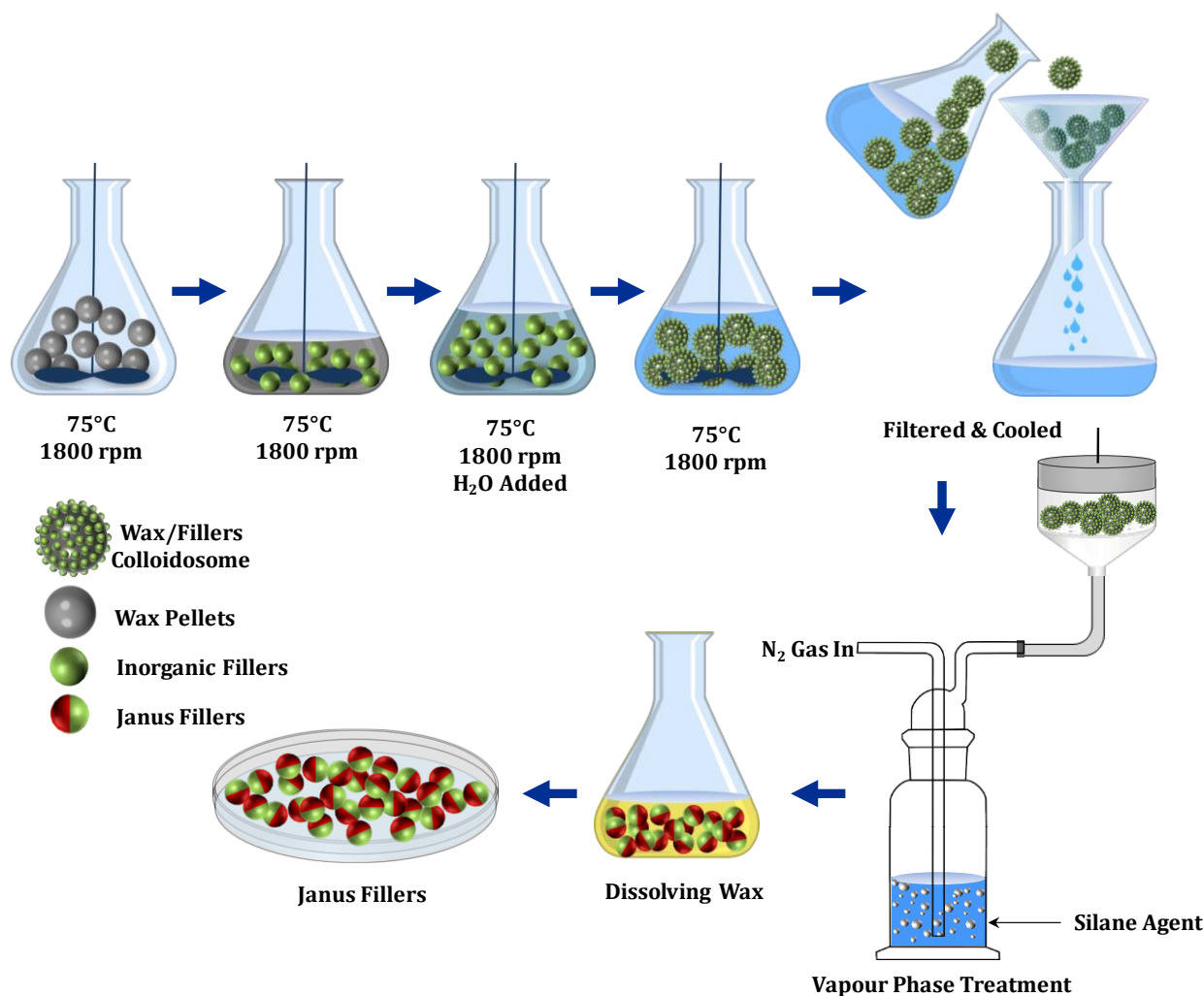


Figure 5.1. Janus fillers fabrication process

5.1.3 Fabrication of Janus Paper Substrates

Refined and unrefined bleach Kraft softwood pulp with fiber size of 927 and 496 μm (measured by Scirocco 2000 Malvern Mastersizer, Malvern Instruments, Inc., Malvern, U.K.) was used to prepare paper substrates. The pulp was provided by Canfor pulp and paper mill in British Columbia. The paper substrates that are referred to as handsheets in this manuscript were prepared using two different procedures. In the first method, the Janus fillers as well as a cationic flocculant were added to the pulp suspension and the handsheets were prepared using a modified former by

filtration. This method is referred as filtration method. In the second method, the pulp suspension which contained fibers and a cationic flocculant (cationic polyacrylamide) were added to the sheet former and after the dewatering/filtration step the dispersed Janus fillers in water were deposited onto the wet handsheets and let the water drain. The filler deposition repeated one more time. This method is referred as layer by layer deposition (LBL). In both methods, the sheets were dried at 23°C and 50% relative humidity (RH). The target basis weight of the handsheets were 60 g. m⁻² with Janus filler concentrations of 10, 20, and 40%. The cationic flocculant of acrylamide copolymer with concentration of 0.011% was used, and it was supplied by Eka chemicals. For each concentration of filler and fiber size, three different handsheets prepared.

5.1.4 Characterization of Paper Substrates

Contact Angle Measurements. The contact angles were measured by the sessile drop method. A 3 µL distilled deionized water droplet was dispensed on the surface and the images of water droplets were captured with a high-resolution camera (Nikon D90) under a light source. Then the images were analyzed with FTA32 version 2.0 software. The contact angles reported are average of 30 measurements.

Water Vapor Transmission Rate. The cup method was used to measure the water vapor transmission rate (WVTR) of handsheets. The detailed procedure is described in chapter 2. The tests were performed at 23 °C and 50% RH. All the samples were preconditioned at the controlled environment for two days before measurements.

SEM Imaging. The morphology of colloidosomes and handsheets was examined with Hitachi S-3000N-VP scanning electron microscope at operating voltage of 5-10 kV. The images were obtained at variable pressure mode since the samples are insulators.

5.2 RESULTS AND DISCUSSION

5.2.1 Effect of Fillers Dual Functionality on Barrier Properties

Amphiphilic Janus silica and TiO_2 particles modified by DCDMS were prepared according to the method developed by Hong et. al.⁹¹. The closed packed coverage of silica and TiO_2 particles on the wax colloidosome surface prior to vapor phase silanization is shown in Fig. 5.2.

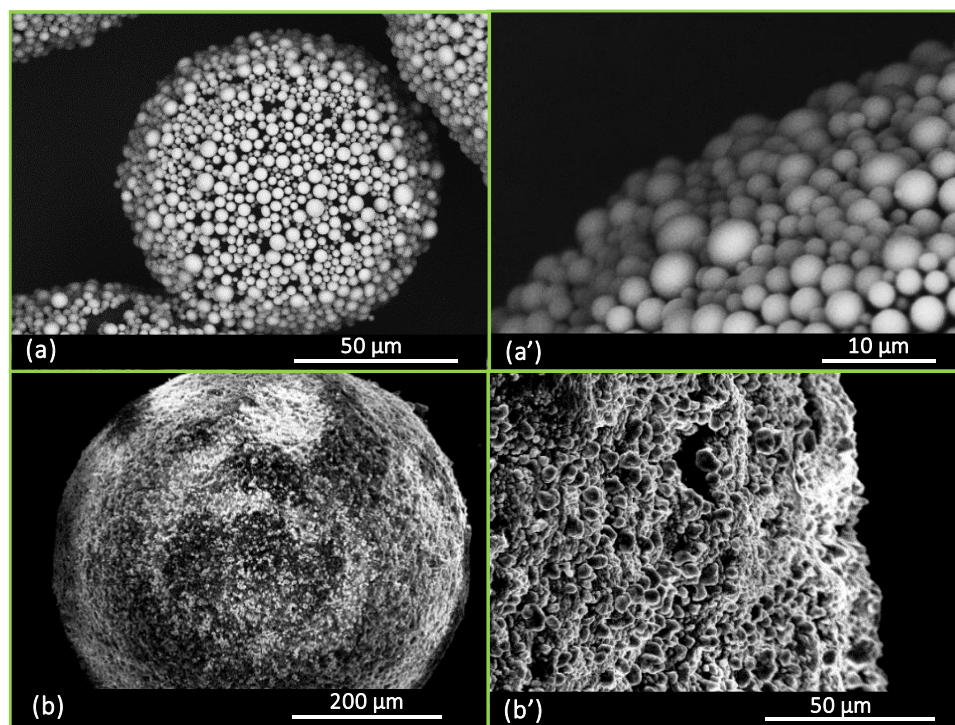


Figure 5.2. Colloidosomes of (a, a') silica and (b, b') TiO_2

To prove the Janus character of the particles, fluorescent-label APS (APS-FITC) prepared using the procedure reported in literature⁹². The Janus particles were dispersed in 5 mL of ethanol solution containing 1mM APS-FITC followed by 1 hour of sonication. Fig. 5.3 shows the labeled Janus silica particles which confirms the Janus characteristics. The bright side of the particle is the APS-FITC labeled side, and the other side which is not visible in the image is the hydrophobic side. For TiO_2 particles the detection of Janus character was not possible due to their asymmetrical

geometry (Fig. 5.2 b, b'). However, by dispersing the modified Janus fillers in water, a monolayer of TiO_2 particles forms on the surface of water without any agglomeration of particles which can confirm the dual functionality.

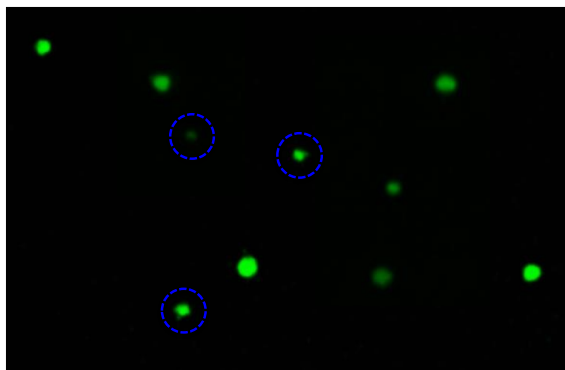


Figure 5.3. Fluorescent dye labeled Janus silica particles

Three different concentration of Janus fillers (10%, 20% and 40%) and two different fiber sizes, unrefined and refined fibers (927 and 496 μm respectively), used in the fabrication of handsheets. For the handsheet prepared by filtration, the larger fiber size in conjunction with all three filler loadings resulted in hydrophilic handsheets (Fig. 5.4). As the filler loading increases, the contact angle also increases. The contact angles are higher on handsheets prepared with refined fibers, compared to unrefined ones. However, the handsheets are still hydrophilic. The layer by layer deposition (LBL) method resulted in handsheets with higher water contact angle compared to filtration method. In this method, at 40% filler loading the handsheets surface is superhydrophobic. However, as soon as the droplet contact the underlying exposed fiber networks, which is poorly covered by Janus fillers, it immediately absorbs to the handsheet. Fig. 5.5 shows droplets of water on both sides of the handsheets prepared with Janus Silica filler at 40% loading by the LBL method. The paper is also Janus, i.e. the side with Janus particles on its surface is hydrophobic, while the other side of the handsheet is hydrophilic where water absorbs to the paper.

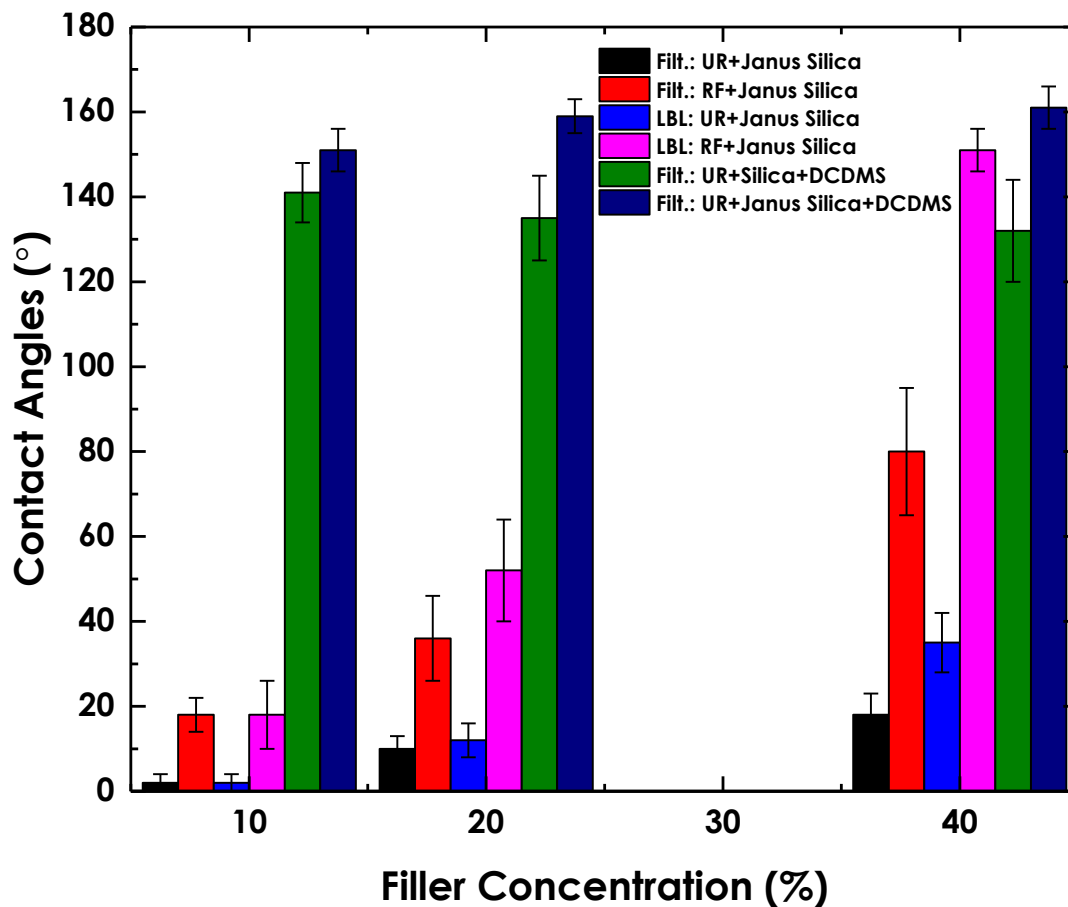


Figure 5.4. Contact angles on handsheets prepared with silica fillers by filtration (Filt.) and Layer by Layer (LBL) deposition methods. URF and RF stand for Unrefined and Refined Fibers, respectively.

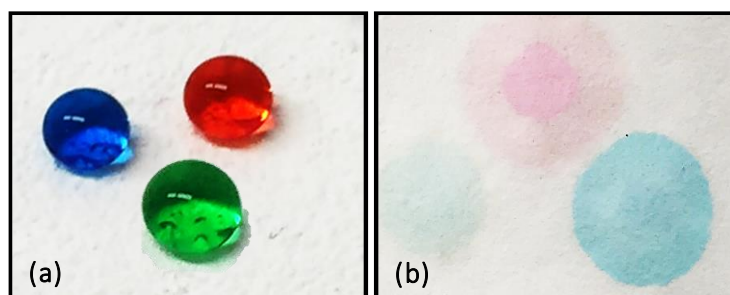


Figure 5.5. (a) Water forms droplet on felt/top side of handsheet surface with Janus silica on the surface (b) water absorbs on the other side (bottom/wire side) of the handsheet

Although higher filler loading resulted in superhydrophobic surface, the adhesion of the fillers to the fiber networks is weak. We did an adhesive tape test to check the adhesion of fillers on

handsheets prepared by LBL method with filler loading of 40%. We observed some of the fillers removed from the surface by the adhesive tape.

We silanized the handsheets (prepared by filtration method) with untreated fillers and Janus fillers using DCDMS agent for 30 s at room temperature. According to the contact angle results shown in Fig. 5.4, the handsheet become hydro/superhydrophobic after silanization. The increase in Janus filler concentration resulted in increase of contact angles. On handsheets prepared with 40% loading of Janus fillers, the droplet easily rolled on the surface. This is due to the fact that even 30 s of vapor phase silanization of handsheets can significantly reduce the wettability of surface due to hydrophobization of cellulose fibers. In this regard, the increase of untreated silica filler's loading on handsheets resulted in decrease of contact angle, while this is reverse for the case of Janus silica filler, i.e. as the loading of Janus filler increases the contact angle also increases. This is due to the fact that (1) the effect of silanization on fibers is dominant compared to silica fillers, and higher filler loading results in reduction of contact angles and (2) since during filtration the Janus silica fillers mostly retained on the surface of the handsheets, their hydrophobicity in addition to the hydrophobicity of the handsheets due to silanization enhanced the hydrophobicity of the surface, and higher filler loading resulted in higher contact angles.

The water vapor transmission rates for handsheets with silica fillers is given in Fig. 5.6. The WVTR is higher for handsheets prepared with unrefined fibers (URF) compared to handsheets prepared with refined fibers (RF). For refined fibers the larger surface area of fiber results in higher number of interfiber hydrogen bonding and formation of dense fiber network with less porosity compared to unrefined samples. The increase of filler loading also resulted in the increase of WVTR. This is due to the fact that fillers hinder the hydrogen bonding between the fibers and

increase the porosity of the handsheets. The silanization of handsheets results in reduction of WVTR values for handsheets prepared with unrefined fibers. The lowest WVTR value of $231 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ was observed for handsheets prepared with unrefined pulps with 10% Janus filler loading. The WVTRs of silanized handsheets with untreated fillers are higher compared to those prepared with Janus fillers.

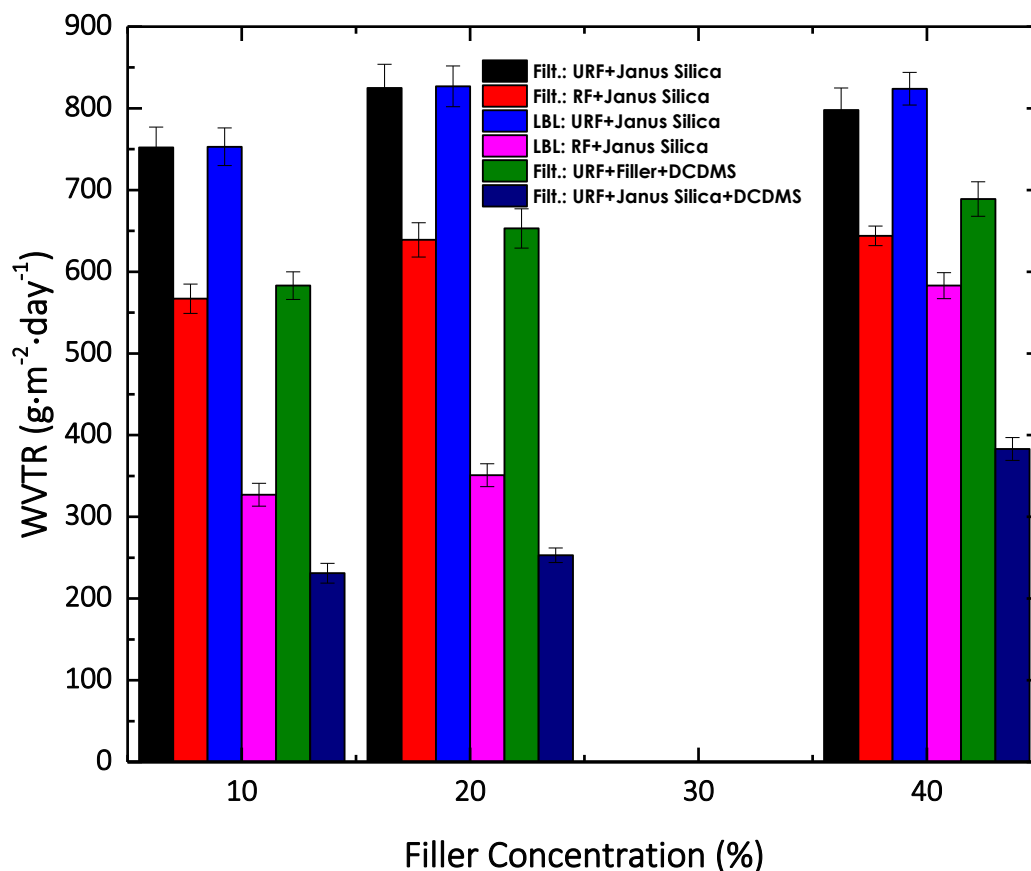


Figure 5.6. WVTR of handsheets with silica fillers

The handsheets prepared with TiO_2 Janus fillers are hydrophilic and water droplet absorbs to the surface of handsheets prepared with filler loadings of 10% and 20%. For these cases the contact angle measurements were not possible due to quick water absorption. Figure 5.7 shows the contact angle results for handsheets with TiO_2 fillers at 40% loading. The hydrophobicity only observed

in handsheets that were treated with DCDMS. The handsheets with Janus TiO₂ have higher contact angles compared to those prepared with untreated fillers after silanization.

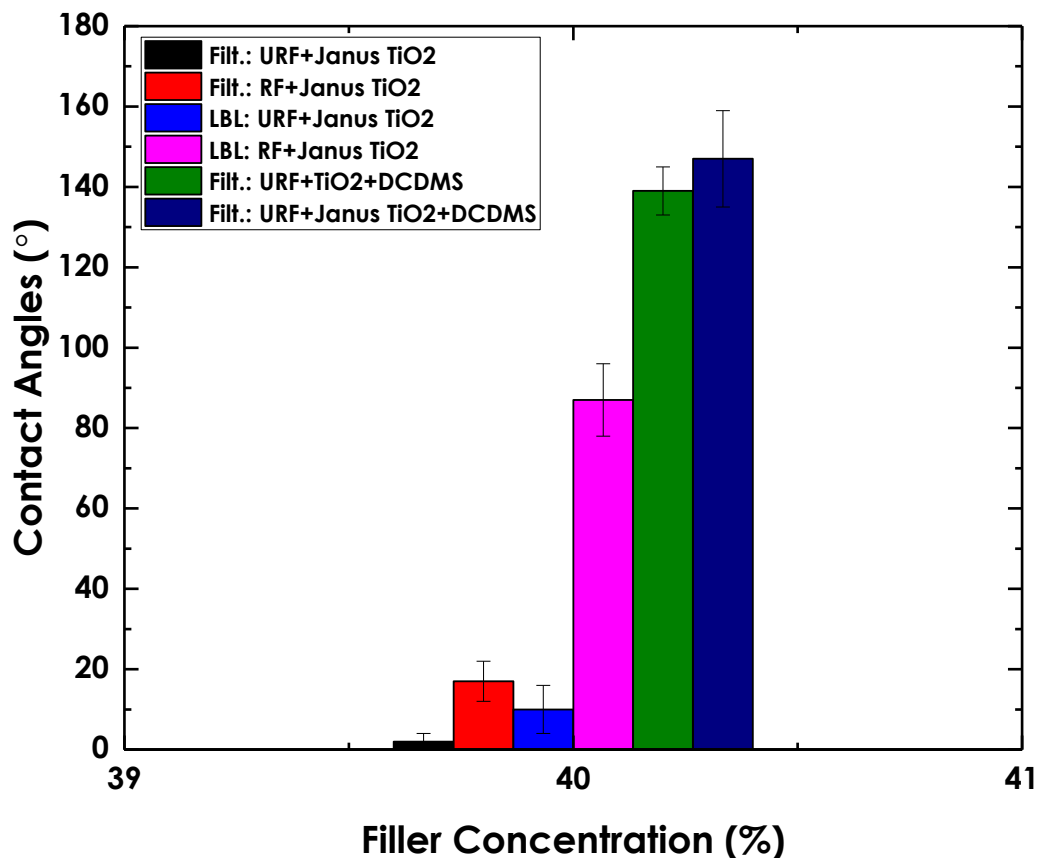


Figure 5.7. Contact angles for handsheets with 40% loading of TiO₂

The WVTRs of handsheets with TiO₂ fillers are shown in Fig. 5.8. There is no significant change in WVTRs for unrefined handsheets loaded with 10-40% Janus TiO₂ fillers prepared by filtration method. This can be due to the poor retention of Janus TiO₂ fillers during filtration. The WVTRs are lower for handsheets prepared with LBL deposition of Janus TiO₂ using refined fibers. This is due to the higher retention of Janus fillers in conjunction with lower porosity of the handsheets. For the silanized handsheets the lowest WVTR value of 237 g·m⁻²·day⁻¹ was obtained for handsheets with 10% loading of Janus TiO₂. The WVTR values for handsheets with Janus TiO₂ fillers are relatively lower than those with SiO₂ ones. This can be due to the smaller size of the

TiO₂ (particle size of 100 nm) fillers. The smaller size of TiO₂ fillers results in lower retention of the fillers and consequently less disruption of hydrogen bonding between the fibers.

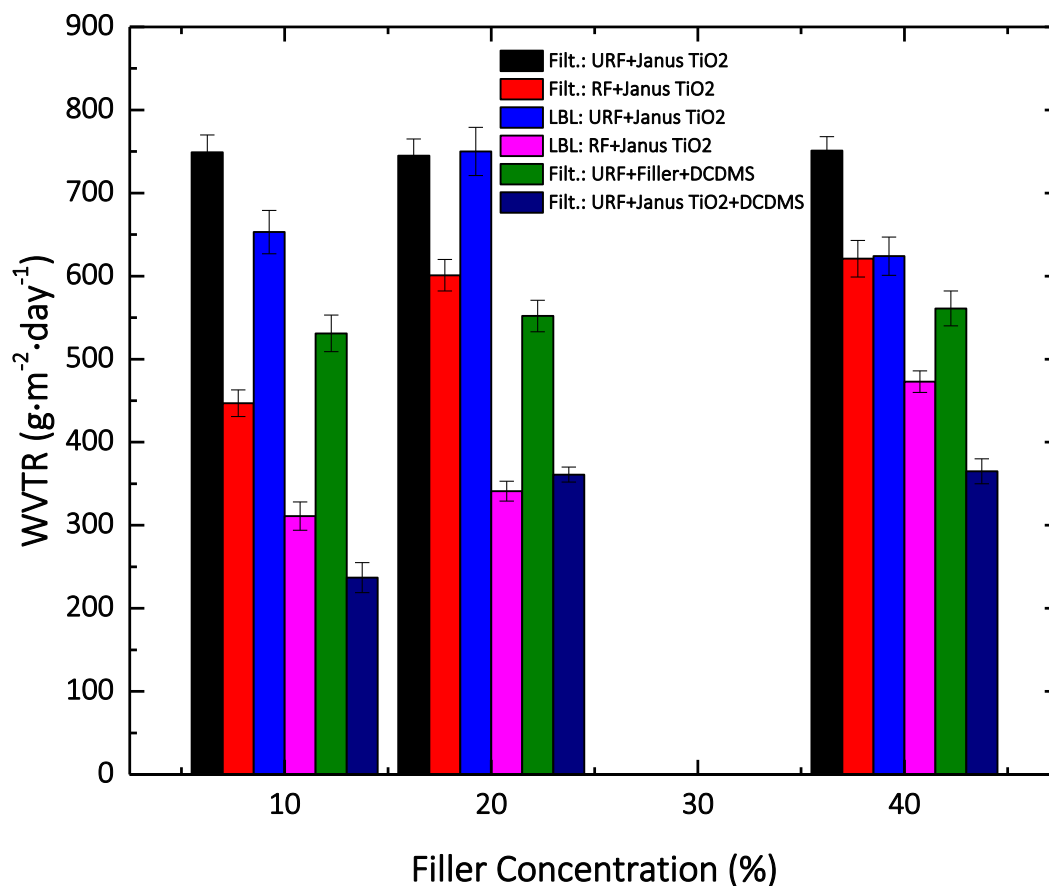


Figure 5.8. WVTR of handsheets with TiO₂ fillers

5.2.2 Effect of Fillers Dual Functionality on Their Distribution in Handsheets

The distribution of SiO₂ fillers at 40% loading on handsheets prepared by unrefined fibers was observed by SEM (Fig. 5.8). The retention of fillers on a handsheet with Janus fillers (Fig. 5.8b) is significantly higher than in one with untreated fillers (Fig. 5.8a). The Janus fillers mainly retained on the felt side of the handsheet while this is the opposite for untreated fillers. Their concentration on the wire side of the handsheet is higher. The SEM images of the handsheet's

thickness also confirms a higher concentration and retention of Janus fillers on the felt side of the sheets compared to handsheets prepared with untreated fillers.

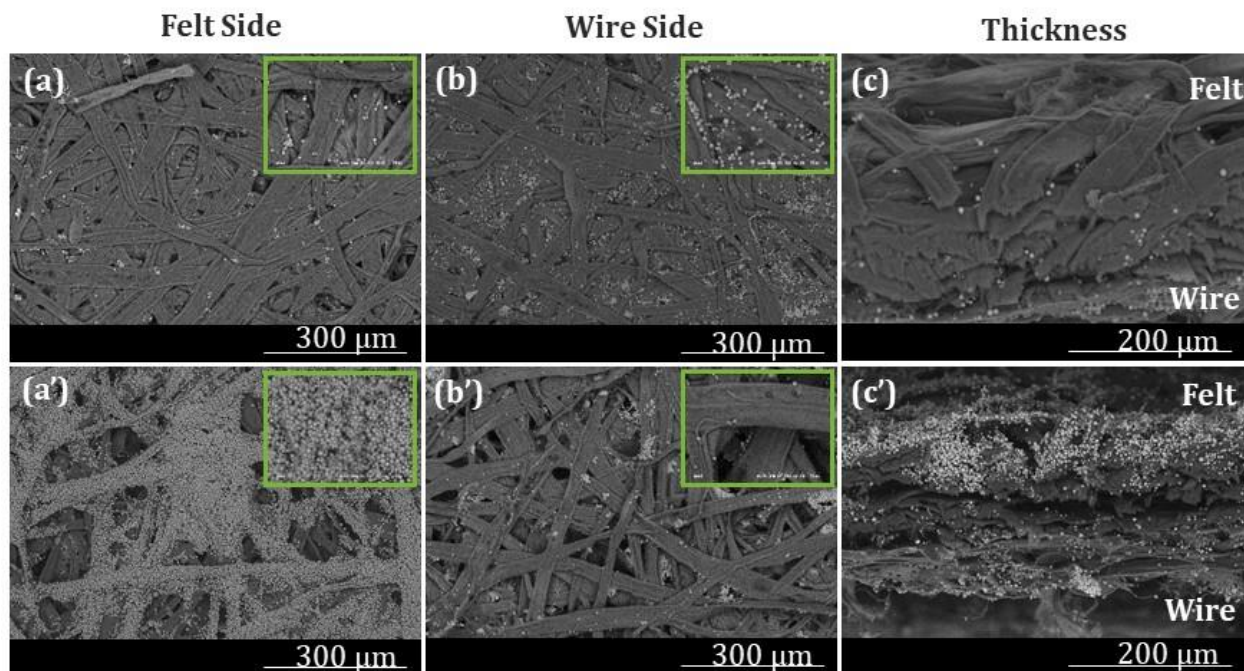


Figure 5.9. Filler retention on handsheets prepared with unrefined fibers (a) felt side of handsheet with untreated filler (a') felt side of handsheet with Janus filler (b) wire side of handsheet with untreated filler (b') wire side of Handsheet with Janus filler (c) thickness of handsheet with untreated filler (c') thickness of handsheet with Janus filler. The inset images show higher magnifications.

The higher retention of Janus fillers is due to their dual functionality. During drainage and filtration, the Janus fillers form a monolayer and remain on the surface of the water/suspension until complete filtration of water which leaves the fillers on the surface of the fibers. The distribution of fillers on the surface can minimize the adverse effects of filler addition on the strength of the paper. However, the adhesion of Janus fillers to the surface needs to be improved.

5.3 CONCLUSIONS

In this work Janus silica and TiO_2 particles prepared and used for fabrication of handsheets. Handsheets were prepared with three different filler concentrations (10, 20, and 40%) and two

different fiber sizes (927 and 496 μm , unrefined and refined fibers respectively). The highest contact angle was observed in handsheets with refined fiber and 40% Janus filler concentration. However, the droplet absorbed to the paper on the exposed area where it is not covered by Janus fillers. To avoid water adsorption, the handsheets were silanized for 30 s and superhydrophobic sheets were fabricated with contact angles ranging from 151° to 161° . The water vapor transmission rates are relatively high for Janus papers. The lowest WVTR value of $231 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ was obtained for silanized handsheets with Janus filler concentration of 10%. The fabrication of Janus fillers instead of hydrophobic fillers can remove the high shear requirement for dispersion of fillers in the pulp suspension. In addition, the dual functionality of fillers results in distribution of the fillers on the surface/felt side of the sheets which can increase the tensile strength of the handsheets since fillers do not hinder hydrogen bonding between the fibers.

Chapter 6: Conclusions

In this thesis, three different chemical vapor deposition techniques were utilized to deposit barrier coating on lignocellulose substrates. The effects of precursor type, deposition technique, and fiber size on the wettability and gas permeability were investigated. The drying mechanism of cast cellulose microfibers on surfaces with different wettability was also studied. In addition, dual functional fillers were fabricated and utilized for handsheet formation to impart hydrophobicity on handsheet substrates.

This chapter summarizes the important conclusions obtained from the work reported in this thesis as well as recommendations for future studies.

6.1 Conclusions

Key conclusions and contributions to the knowledge are described as following:

- The reduction of Kraft fiber size by refining can decrease the water vapor transmission rate by 80- 90% in papers prepared with these fibers. At certain fiber size, 561 μm , the WVTR reaches its minimum value and further reduction of fiber size does not significantly affect this value.
- The vapor phase silanization reduces the WVTR value by 34 %. The highest water contact angle was obtained for handsheets prepared with unrefined fibers after vapor phase silanization and O_2/CF_4 PECVD. The O_2/CF_4 plasma treated handsheets have significantly higher contact angles compared to silanized ones. This is due to dual scale roughness on the surface of handsheets imparted by O_2 plasma etching.
- The Al_2O_3 atomic layer deposition on paper substrates resulted in the lowest WVTR value of $\sim 2 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for Kraft refined fibers. In terms of barrier properties, the fabricated papers

with this method are comparable with commercial synthetic polymers with the advantage of being green and sustainable. The fabricated films from refined fibers are suitable substrate for paper electronics applications due to their low gas permeability, desired optical properties, and transparency of the Al_2O_3 coatings.

- The physical, mechanical, and optical properties of cellulose substrates is dependent on their drying mechanism. Casting and drying of microfibers on a hydrophobic surface resulted in the formation of translucent films with mechanical and barrier properties similar to micro and nano-fibrillated cellulose films. Therefore, the high energy consumption to produce MFC/NFC can be minimized by using lower refining energies to produce microfibers and casting them on a hydrophobic surface to obtain films with desirable features like MFC and NFC.

- The inclusion of Janus mineral fillers on handsheets results in formation of a Janus handsheet with one side being hydrophobic and the other side hydrophilic. This is due to the distribution of Janus fillers on the surface of the handsheets. However, the long-term wettability of handsheets can be guaranteed by short time silanization of the Janus handsheets.

6.2 Recommendations for Future Studies

The following suggestions can be considered for future studies:

- In this work the lowest WVTR was obtained for highly refined paper samples deposited with Al_2O_3 ALD. However, in terms of wettability, although the samples are hydrophobic, water droplets absorb to the paper over time. Since the O_2/CF_4 samples resulted in the highest contact angles, the combination of these two methods is suggested in order to enhance the wetting barriers of Al_2O_3 deposited samples.

- Utilizing the Al_2O_3 ALD film for paper electronic applications, such as organic light emitting diodes and organic solar cells is suggested. This is due to the fact that in addition to their high barrier properties, the fabricated films in this work have good light scattering which makes them a promising candidate for optical diffusers in LED lighting.
- The formation of MF films by casting and evaporation requires long drying time. Therefore, fabrication of microfiber films using sheet former with hydrophobic mesh/filter is suggested to reduce the drying time. In this work, the MF films that were prepared on a hydrophobic surface are optically translucent. Studying the optical, physical, and mechanical properties of MF films casted on a superhydrophobic surface is also recommended.
- The Janus silica and TiO_2 fillers fabricated and loaded in pulp suspension to form Janus paper. Although the handsheets are hydrophobic, the adhesion of Janus fillers to the fibers is still an issue which needs further investigation. In addition, further work on quantifying the retention of Janus fillers is recommended.

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Appendix A : Application of MF Films in Energy Storage Devices-High Performance Supercapacitors from Niobium Nanowire Yarns⁶⁴

Separators are important components of capacitor and supercapacitors. Using cellulosic papers as separators in energy storage devices has several advantages: (1) It is from a renewable source, (2) It possesses outstanding properties such as high ionic conductivity and chemical stability, and (3) it has superior thermal stability comparing to polymeric separators which might meltdown due to overcharging or short circuiting. In this study the impact of physicochemical properties of cellulosic separators on the performance of niobium nanowire yarn supercapacitors are studied.

A.1 EXPERIMENTAL METHODS

Separators Preparation. Different separator sheets were prepared by using cellulosic wood pulp fiber of different sizes. The sizes are such that the fibers can be classified as microfibers (MF). The fiber sizes reported in Table 6.1.

Thickness Measurements. The thickness of the separator sheets was measured using an L&W Micrometer (1 μm resolution).

Electrolyte Uptake. The electrolyte uptake of the separator sheets was obtained by measuring the weight of dry sheets and then immersing the sheets in 1M sulphuric acid for 2 hours. Finally, the sheets were removed from electrolyte and wiped with filter paper and the weight of the wet sheet was recorded. The electrolyte uptake was then calculated by Eq. 6.1.

$$EU = (m_{wet} - m_{dry})/m_{dry} \quad (6.1)$$

where m_{wet} is the mass of the wet sheet and m_{dry} is the mass of the dry sheet.

Tensile Strength. The tensile strength of the sheets is obtained using a QC-II tensile tester. To determine the wet strength of the sheet in electrolyte solutions, the sheets were cut into 7 mm stripes and kept in 1M sulphuric acid solution for 2 hours prior to tensile testing.

A.2 RESULTS AND DISSCUSSION

Various separators (such as Glass fibers, Nafion membrane, and Millipore membrane) were tested and cellulosic-based thin sheets (made of Microfibers) had the highest ionic conductivity ($3.4 \text{ S}\cdot\text{m}^{-1}$ in 1M Sulphuric acid) with electrolyte uptake of up to 600%. Having a highly ionically conductive separator reduces the equivalent series resistance and this directly increases the power density. Due to the hydrophilicity and exceptionally high tensile strength of microfiber cellulose film based materials, they are an excellent candidate for use in the design of energy storage devices

The properties of the separators are included in Table A.1. The formation of a very thin film of MF with thickness of 9 μm was only possible with MF fibers with fiber size of 177 μm .

Table A.1. Mechanical properties of some of the separators used in the design of the supercapacitor.

Fibre Size in Pulp Suspension (μm)	Thickness of Sheet (μm)	Areal Density (g/m^2)	Electrolyte uptake (%)	Tensile Strength (Nm/g)	Wet Tensile strength (Nm/g)
977	179	60	209	53.5	0.9
561	60	58	151	104.7	1.1
339	11	12	264	36.6	2.7
177	9	10	602	70.9	6.37
Kim wipes	104	20	200	4.9	0.71

The surface morphology of MF separators is shown in Fig. A.1. In order to clearly see the structure of microfibers, the samples were freeze dried for SEM imaging to prevent collapse or shrinkage of cellulosic fiber.

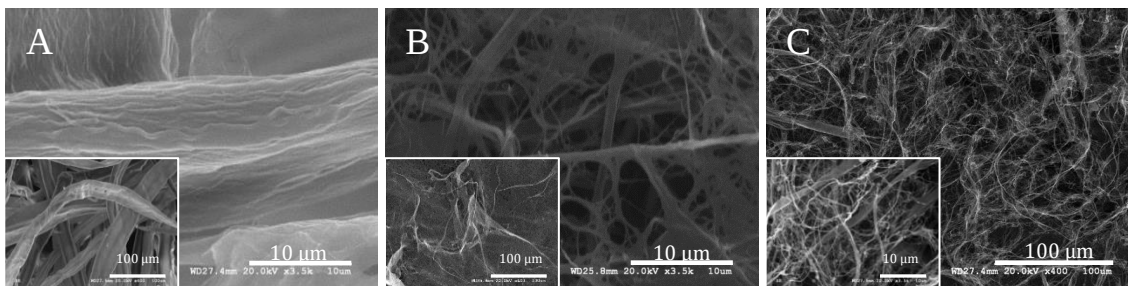


Figure A.1. SEM of different cellulosic wood fibers used for three different separators with fiber sizes of (A) 977 μm , (B) 399 μm , and (C) 177 μm .

The 9 μm thick separator made from 177 μm fibers showed the best performance for aqueous electrolytes. Generally, separators with low thickness, as long as it does not adversely affect the mechanical strength, results in high energy and power densities in capacitors. The small size of fibers facilitates formation of very thin and strong films due to higher number of hydrogen bonding between the fibers.

A.3 CONCLUSIONS

Different materials were tested as separators for the Nb nano wire yarns supercapacitors. The cellulosic thin film (9 μm thickness) with electrolyte uptake of up to 600% resulted in best performance due to their highest ionic conductivity. The high ionic conductivity reduces the equivalent series resistance which directly cause the increase of the power density.