SUPERHYDROPHOBIC FIBRE NETWORKS LOADED WITH FUNCTIONALIZED FILLERS

by

Mehr Negar Mirvakili

B.A.Sc., University of British Columbia, 2011

A THESIS SUBMITED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Chemical and Biological Engineering)

The University of British Columbia (Vancouver)

December, 2012

© Mehr Negar Mirvakili, 2012

ABSTRACT

In this thesis a series of fluorocarbon plasma treatment experiments (Plasma enhanced chemical deposition (PECVD)) were performed to study the effect of filler type and concentration on the wetting behavior of handsheets which are made from pulp using precipitated calcium carbonate (PCC), kaolin clay, and talc as a filler. The plasma treatment was performed in two steps; first using oxygen plasma in order to create nanoscale roughness on the surface of the handsheet; and second fluorocarbon deposition plasma in order to add a layer of low surface energy material. The contact angle of droplets of deionized water on all of the handsheets increased after plasma treatment. However, although some of the handsheets have low concentrations of filler, and therefore the fibre effect should be dominant after the treatment, it was found that the type of filler has a significant effect. It was also observed that roughness of the surface plays a key role in the wettability of handsheets and increased the hydrophobicity. The water vapor transmission rate values show that plasma hydrophobization does not prevent vapor uptake into the paper, although it is good barrier to water. The same plasma treatment was performed on the surface of PCC and kaolin clay fillers in order to fabricate partial hydrophobic fillers. The goal was to use these treated fillers in handsheets and study their wetting behavior. The plasma treatment on the surface of kaolin clay increased its contact angle, however no effect on PCC fillers was observed immediately after the treatment.

TABLE OF CONTENTS

11
iii
iv
viii
X
. xi
1
1
3
4
6
6
7
8
9
.11
.12
.12
.15
.16
.17
.19
21

3.1 Experimental Set-up, Equipment and Materials	21
3.2 Experimental Methods	21
3.2.1 Handsheet Preparation	21
3.2.2 Preparation of Fillers for PECVD	24
3.2.3 Surface Plasma Treatment	25
3.2.4 Contact Angle Measurements	25
3.2.5 Surface Analysis	25
3.2.6 Handsheet Properties Measurement	27
3.3 Limitations of Study	
3.4 Experimental Approach	
CHAPTER 4: RESULTS AND DISCUSSION	
4.1 Handsheet Treatment	32
4.1.1 "Roll off" and "Sticky" Water Droplet, Roughness Effect	32
4.1.2 Plasma Processing on Filled Handsheets, Filler Type and Con Effect	centration
4.1.3 Effect of CF ₄ Plasma Flowrate on Hydrophobicity	41
4.1.4 Advancing and Receding (Dynamic) Contact Angles, Wenzel v Regimes	7s. Cassie 44
4.1.5 Handsheet Properties Tests, Tensile, WVTR, and Cobb Values	46
4.2 Fillers Treatment with PECVD	53
CHAPTER 5: CONCLUSION AND RECOMMENDATION	55
BIBLIOGRAPHY	56
APPENDIX A: Advancing and Receding CAs, and Static CAs	64
APPENDIX B: Tensile Index Figures	67
APPENDIX C: Water Vapor Transmission Rates	68

APPENDIX D: ATR-FTIR Spectra	
------------------------------	--

LIST OF TABLES

Table 3.1: Pulp suspension 24
Table 3.2: PECVD operation parameters
Table 3.3: Tensile strength values for L&W tensile tester and COM-TEN tester
Table 4.1: Contact angle results before and after plasma treatment 33
Table 4.2: Contact angles on classified fibres after plasma treatment 36
Table 4.3: Air permeability results for handsheets before and after plasma treatment 51
Table 4.4: Cobb values for handsheets after plasma treatment 51
Table 4.5: Contact angles of droplets over 1 min 52
Table 4.6: XPS analysis, At% of elements after CF4 deposition 54
Table A.1: Static CAs on handsheet: containing starch, O_2 treatment of 20min, CF_4 flowrate o 40 cm ³ /min
Table A.2: Static CAs on handsheet: without starch, O_2 treatment of 15min, CF_4 flowrate of 40 cm ³ /min
Table A.3: Static CAs on handsheet: containing starch, O_2 treatment of 20min, CF_4 flowrate o 40 cm ³ /min
Table A.4: Static CAs on handsheet: without starch, O_2 treatment of 15min, CF_4 flowrate of 40 cm ³ /min
Table A.5: Static CAs on handsheet: with starch, O_2 treatment of 15 min, CF_4 flowrate of 30 cm ³ /min
Table A.6: Static CAs on handsheet: with starch, O_2 treatment of 20 min, CF_4 flowrate of 30 cm ³ /min
Table A.7: Static CAs on handsheet: with starch, O_2 treatment of 20 min, CF_4 flowrate of 10 cm ³ /min
Table A.8: Dynamic CAs on handsheet: containing starch, O_2 treatment of 15 min, CF_4 flowrate of 40 cm ³ /min

Table A.9: Dynamic CAs on handsheet: containing starch, O_2 treatment of 20 min, CF_4 flowrateof 40 cm³/min67

LIST OF FIGURES

Figure 2.1: (a) Cellulose structure (b) Molecular organization in a cellulose microfibril	7
Figure 2.2: World filler use in printing and writing paper	8
Figure 2.3: Liquid droplet in homogeneous wetting and heterogeneous wetting regime	9
Figure 2.4: Actual contact angle and apparent contact angle	10
Figure 2.5: A set of advancing and receding analysis of a droplet	11
Figure 2.6: (a, d) Janus films (b, c) Janus particles	17
Figure 2.7: Reaction mechanism for plasma surface modification	19
Figure 3.1: Schematic of the handsheet former	22
Figure 3.2: SEM images of fillers (a) PCC (b) Talc (c) Clay	23
Figure 3.3: (a) film of PCC on microscope slide (b) Pellet of PCC	25
Figure 3.4: EDX analysis sampling procedure	26
Figure 3.5: Handsheets treatment approach	30
Figure 3.6: Fillers treatment approach	31
Figure 4.1: (a) Rolling off droplet (b) sticky droplet when the droplet is dragged on the surfa	ce
	33
Figure 4.2: SEM results on plasma treated handsheets	34
Figure 4.3: Effect of plasma etching time on hydrophobicity	35
Figure 4.4: Felt side contact angle of handsheets after plasma treatment (CF4 flowrad	te of
40cm ³ /min, Left Plot: 15min O ₂ etching, Right Plot: 20min O ₂ etching)	37
Figure 4.5: Filler distribution on top and wire side of handsheets with filler loading wt% of 3	35 39
Figure 4.6: Filler distribution on z-direction of handsheets with filler loading wt% 35	40
Figure 4.7: Effect of plasma flowrate on wire side contact angle of the handsheets filled	with
PCC	41

Figure 4.8: Comparison of contact angle on felt side and wire side for talc filled (20 min	O_2
etching and CF_4 deposition with flowrate of 10, 20, and 40 cm ³ /min)	43
Figure 4.9: The roughness that is created on wire side due to the forming fabric	43
Figure 4.10: Advancing and receding contact angle for handsheet filled with PCC	44
Figure 4.11: Static contact angle	45
Figure 4.12: Tensile index of handsheet before and after plasma treatments	47
Figure 4.13: Effect of filler type on tensile strength after plasma treatment	48
Figure 4.14: WVTR of handsheets before and after plasma treatment	49
Figure 4.15: Water vapor path in handsheet filled with platy fillers and spherical fillers	50
Figure 4.16: FTIR spectra for handsheets made with 100% fibre	52
Figure 4.17: XPS Analysis for PCC thin films before and after washing	53
Figure 4.18: The kaolin clay samples (a) before and (b) after plasma treatment	54
Figure B.1: Tensile index values for all fillers	68
Figure C.1: WVTR values for all handsheets	70
Figure D.1: FTIR spectra for all handsheets	72

NOMENCLATURE

Symbol	Definition	Units	
r	Roughness factor	-	
\mathbf{f}_{SL}	Solid liquid fraction	-	
γ	Surface tension	N/m	
θ_Y	Young contact angle	degree	
$\theta_{\rm W}$	Wenzel contact angle	degree	
θ_{CB}	Cassie-Baxter contact angle	degree	
AKD	Alkyl-Ketene Dimer	-	
ASA	Alkenyl Succinic Anhydride	-	
PBA	Poly-Butyl Acrylate	-	
TEOS	Tetraethoxysilane	-	
TCMS	Trichloromethylsilane	-	
PDDA	Polyelectrolyte poly-Diallyl-Dimethyl Ammoniumchloride	-	
HMDSO	Hexamethyldisiloxane	-	
PECVD	Plasma Enhanced Chemical Vapor Deposition	-	

ACKNOWLEDGMENTS

First and foremost, I would like to express my sincere appreciation and gratitude to my supervisors Dr. Peter Englezos and Dr. Savvas Hatzikiriakos for their guidance, patience and support. They have provided me with plenty of academic freedom in order to reach my research goals. I have been indebted in preparation of this thesis to Dr. Englezos whose patience and kindness, as well as his academic experience have been invaluable to me. I admire Dr. Hatzikiriakos continuous encouragement which helped me to be creative and independent in research.

I am grateful to the entire past and present members of our research group for helping me with ideas and making my graduate life a wonderful learning experience. Special thanks to Madjid Farmahini Farahani for helping me and kindly doing the WVTR tests at University of New Brunswick.

I am really grateful to my family from the bottom of my heart. I owe a lot to my mother. I cannot find words to express my gratitude to her. Her constant love, support and encouragement has always been there for me. She is the sole reason for why I am doing what I am doing now. Special thanks to my brother for his encouragement and support in my endeavors. He always cares a whole lot about my studies and career. My deepest gratitude and affection goes to my beloved husband. He provided me the support with his patience, love, and inspiration. I am the luckiest to have him in my life.

Finally and most importantly, I dedicate this thesis to my deceased father, who always had confidence in me and provide me the best possible environment to grow up. My greatest pleasure would be to share this moment with him.

CHAPTER 1: INTRODUCTION

1.1 Motivation of the Study

Changing the wetting behavior of a surface to reach superhydrophobic status may facilitate the development of novel materials in a plethora of potential applications. Interestingly, most of the fabricated superhydrophobic surfaces are not renewable, sustainable, and biodegradable (Balu et al., 2008). On the other hand, rendering the cellulosic surface hydrophobic can open the door for value added applications based on a biodegradable, renewable and sustainable biopolymer that is abundant in nature.

Paper is produced from an aqueous suspension of lignocellulosic fibres in a filtration process (Smook, 2002). The fibres are produced from wood and non-wood plants. This is a sustainable, renewable, and biodegradable resource and can play a key role in advancing the green economy (Shen et al., 2012). The cellulosic paper is inherently hydrophilic due to the presence of hydrophilic groups mainly hydroxyl and carboxyl groups. This inherent water loving property poses some limitations in the applications, where hydrophobicity is highly required. For example, in packaging applications water and moisture resistance property is a necessity (Shen et al., 2012). The water and moisture resistance can be improved by internal sizing, surface sizing, and conventional barrier coating layers. There is a limitation however, due to the high cost of thick coating layers. Poor recyclability is an additional limitation.

Fluorocarbon thin films that are produced by plasma enhanced chemical vapor deposition (PECVD) bring several advantages over the conventional methods. The plasma deposited films are chemically inert, pinhole-free, insoluble, mechanically tough, thermally stable and highly coherent and adherent to a variety of substrates (Vaswani, 2005). The amount of fluorochemicals that is deposited on the surface of paper can be controlled depending on the degree of water or oil repellency that is required. However, the Food and Drug Administration (FDA) regulations had determined a limit for usage of fluorine in paper products that are in contact with aqueous and fatty foods (Vaswani, 2005). This limit is in the range of 0.09% to 0.26% depending on the basis weight of paper. The fluorocarbon films that are deposited by PECVD are thin and breathable and do not require the considerable challenge in recycling of the coated papers comparing to thick layers of coating in conventional methods (Vaswani, 2005). Also a single thin film of deposited fluorocarbon on the surface of cellulosic paper will eliminate the need of

multiple layer coatings to achieve barrier properties. This will reduce the processing cost (because of the many processing steps for certain types of barrier packaging) and also the cost that is related to recycling of the coated papers.

Recently, several studies focus on the use of hydrophobic mineral fillers for fabrication of hydro/superhydrophobic surfaces. The paper industry uses more filler in paper in order to reduce the papermaking cost and to improve the optical properties and printability of paper (Yoon et al., 2006). However by increasing the filler content, the paper strength and stiffness usually decrease. Mineral fillers are cheaper than the organic hydrophobic materials that are used for making the surface of cellulosic paper hydrophobic. By producing hydrophobic fillers and use those in the paper to turn it hydrophobic, their efficiency increase and the costs of paper products will decrease accordingly (Shen et al, 2012). However, the challenge is the dispersion of the modified hydrophobic fillers in water.

The wettability and repellency of a surface are important characteristic properties from both the fundamental and practical points of view (Vaswani, 2005). The wettability depends on surface energy, an intrinsic property, and surface roughness. The wettability of a surface is typically quantified in terms of the static and the dynamic contact angles (advancing and receding) of a water droplet on that surface. The contact angle characterizes the hydrophobicity or hydrophilicity of a surface. Generally, hydrophilic surfaces have contact angles of less than 90°, while the contact angles on hydrophobic surfaces are greater than 90°. The surface tension, which defines the energy of the boundary of different material phases, as well as the contact angle, which is a quantitative measure of liquid attraction to the surface, are fundamental concepts in interfacial phenomena studies (Courbin and Stone, 2007). The wettability is controlled by surface tensions acting at the three phase interface, which are in balance; and the formed contact angle is called the equilibrium contact angle given by the well known Young-Laplace Equation. The superhydrophobic surfaces, which refer to non-wettable surfaces with a high water contact angle of above 150° and low sliding angles, have received tremendous attention in industrial applications as well as academic research. However, control and modification of the surface chemistry as well as the surface roughness of a material, the two main factors for creating superhydrophobic surfaces, are challenging issues (Groenendijk, 2008; Goncalves et al., 2008).

Superhydrophobic paper is quite a new research area and a limited number of scientific publications are available especially on the use of plasma and hydrophobic mineral fillers for its fabrication. The atmospheric non-thermal plasma processing provides some advantages over the typical surface modification methods. It is a dry method which can be 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 (Pykonen, 2010).

This thesis presents the results of the study of the effect of CF_4 plasma deposition on (a) the wetting behavior of the surface of handsheets filled with three types of fillers (precipitated calcium carbonate, kaolin clay, and talc) at three levels of concentration and (b) the surface properties of mineral fillers.

1.2 Objectives of the Study

The focus of most studies on plasma treatment was on cellulose paper free of mineral fillers. There is a need to study and elucidate the effect of plasma treatment on fillers and filler containing paper at different levels of filler concentration. Moreover, the effect of different fibre size that the paper is made of is another parameter of interest, since it affects the roughness of the sheet and consequently may affect its degree of hydrophobicity.

The modification of fillers in order to render them hydrophobic and the inclusion of these hydrophobic fillers in cellulose paper are also of interest. The challenge here is the partial hydrophobization of filler without sacrificing its dispersability in the aqueous fibre suspension. In addition, the hydrophobicity of paper needs to be assessed when it is in contact with water for a long period of time. Durability and stability of the superhydrophobic paper are important factors when considering use of this paper for consumer good applications.

The work undertaken in the present study is part of a larger project. The objectives of this project are as following:

- 1- To investigate the effect of plasma treatment on the wettability of paper containing different fillers, namely precipitated calcium carbonate, clay, and talc at different concentrations ranging from 25% to 45%.
- 2- To investigate the effect of handsheet surface roughness on the hydrophobicity of handsheets.
- 3- To investigate the effect of plasma treatment on paper properties, such as tensile strength, water absorption, and water vapor transmission rate.
- 4- To fabricate dual functional filler and control water absorbance and water repellence of paper containing the dual functional filler.
- 5- To investigate the synergistic effect of dual functional filler in the suspension of the fibre and on the surface of the final handsheet that is formed.
- 6- To fabricate hydrophobic and superhydrophobic paper using dual functional fillers.

Objectives 1 to 3 have been set for the work undertaken in this thesis. Our focus is on the fabrication of filled handsheets and their subsequent treatment using plasma enhanced chemical vapor deposition. The goal is to examine the wetting behaviour of the handsheets as well as their superhydrophobic behaviour. It is of interest to know how untreated fillers affect the handsheet wetting behaviour after plasma treatment.

1.3 Organization of the Thesis

The thesis is divided into five chapters.

Chapter 1 Introduction: The motivation for fabrication of hydro/superhydrophobic fillers and paper as well as the objectives of the study are described.

Chapter 2 Background: The theory behind the non-wetting surfaces, the chemistry and physical property of cellulosic paper, as well as the relevant literature and recent reports on modification of hydrophobic fillers and cellulose paper are presented.

Chapter 3 Materials and Methods: This Chapter is dedicated to the materials and methodology as well as the experimental procedures used in this study. The study parameters, the pieces of equipment, and the adopted methodology are explained. This chapter also discusses the limitations in this study.

Chapter 4 Results and Discussion: The analysis of the results, the wetting behaviour, tables and figures are discussed and presented in this chapter.

Chapter 5 Conclusions and Recommendations: The conclusions of this research study as well as the recommendations for future studies in this area are given in this chapter.

Some of the details of the experimental findings as well as several additional figures are presented in an Appendix.

CHAPTER 2: BACKGROUND

2.1 Paper and Fibre Network

Paper is defined as a thin flat sheet which is made on a fine mesh from an aqueous suspension of wood or other plant fibres. It is noted that nearly any plant material can be used for making paper. However, there are a number of factors that limit their usage for papermaking. For example, the plant must be abundant, grows in an accessible area, grows quickly, contains a high proportion of cellulose fibre, and has a long and strong fibre (Wilcon, 2006).

Paper has played a significant role in the continuous progress of humankind. Despite the progress in digital communication, paper is still a necessity and requires being flexible to answer the needs of modern life applications. The term "paper" was originated from the stem of a reedy plant called papyrus, which ancient Egyptians used to create the world's first writing material (Smook, 2002). However, the first actual paper making in the form as we know it today arose in China in 105 AD and it was considered an art for several centuries. A number of significant inventions in the early 19th century provided the basis for the modern papermaking machinery. For the past two centuries a large fraction of paper and paper board production was used for packaging, printing and writing applications.

Wood fibres consist of four main components, cellulose, hemicelluloses, lignin and extractives. Cellulose is the most important component in papermaking (Smook, 2002). As shown in Figure 2.1 cellulose molecules $(C_6H_{10}O_5)_n$ are polymeric chains of β -d- glucose residues that are covalently coupled by glucosidal linkages. Cellulose molecules consist of crystalline and amorphous domains. The crystalline segments form the microfibrils that are bundled together to make macrofibrils. The physical properties, the chemical behavior and the reactivity of cellulose, are highly affected by arrangement of the cellulose molecules with respect to each other (Ciolacu et al., 2011). Most of the chemical reactants penetrate only the amorphous regions of cellulose and the reaction can take place on the surface of crystallites without affecting the intracrystalline regions (Ciolacu et al., 2011).



Figure 2.1: (a) Cellulose structure (Adapted from Balu, 2009) (b, c) Molecular organization in a cellulose microfibril ((b) Adapted from Balu 2009, (c) Adapted from Tischer, 2010)

2.2 Fillers and Pigments

The paper fillers are fine, white pigment powders that are usually produced from natural minerals. The purpose of using fillers in paper making is to make the surface of the paper smooth and to improve its printability by filling the pores between the fibres (Neimo, 1999). Fillers also provide a substitute for the expensive fibre and reduce the manufacturing cost because most fillers are cheap (Baker, 2005). There are also certain disadvantages in using fillers for paper making. Fillers cause loss of bonding between the fibres and affect the tensile strength and stiffness of paper. Fillers are added at levels up to 20%-35% in the paper (Neimo, 1999). The most common fillers that are widely used in printing and writing papers are Calcium Carbonate (Precipitated Calcium Carbonate (PCC) and Ground Calcium Carbonate (GCC)), Kaolin, Talc, and Titanium Dioxide (TiO₂) (Wilson, 2006). Figure 2.2 shows the world consumption of fillers for printing and writing paper (Wilson, 2006). In North America PCC is the most widely used filler due to the high availability of limestone. The lime that is produced from limestone is

converted to PCC on site at the paper mill. By manufacturing the PCC filler a good control of the chemical and physical properties of the particle, such as particle size, particle size distribution, surface area, and particle shape can be achieved. Therefore, some special treatment of the fillers that require specific shape or size would be more efficient.



Figure 2.2: World filler use in printing and writing paper (Adapted from Wilson, 2006)

2.3 Wettability

Total wetting of the surface of a material results from the high affinity of the water molecules to the solid surface in which the contact angle approaches zero and causes formation of a liquid film on the surface (Quere, 2003). In contrast, when the liquid forms a droplet on the surface this is because the affinity of the water molecules to themselves is higher than their affinity with the solid surface. In this case partial wetting of the surface occurs. The general definition for hydrophobic surfaces is the existence of static water contact angle of more than 90°. For superhydrophobic surfaces this value should be greater than 150°.

In principle, on rough surfaces superhydrophobicity may be associated with two different wetting states namely homogeneous and heterogeneous (Bittoun et al., 2009). In the homogeneous state as shown in Figure 2.3 the liquid penetrates into the roughness grooves and the whole surface is wetted. However, in the heterogeneous state air is trapped inside the roughness grooves under the liquid and the interface become composite including vapour-solid, vapour-liquid and liquid-solid (Bittoun et al., 2009).



Figure 2.3: Liquid droplets on homogeneous and heterogeneous wetting states (Adapted from Im et al., 2010)

2.3.1 Theory

The measurement of the contact angle is a method for the characterization of the wettability of a solid surface. The contact angle is defined as the angle between the tangent lines to the liquid-vapor and solid-liquid interfaces at the contact line of the three phases (Marmur, 2006). Depending on the surface structure and degree of roughness, the equilibrium contact angle can be expressed by different equations. In the early 1800s, Young developed an equation for the measurement of the contact angle on an ideal (perfectly smooth) solid surface. According to Young's (or Young-Laplace) equation the equilibrium contact angle, θ_Y is defined by the surface tensions acting at the three phase interface:

$$\cos\theta_{\gamma} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{VL}} \tag{2.1}$$

where γ_{SV} , γ_{SL} , and γ_{VL} are the surface interfacial tension between solid-vapor, solid-liquid, and vapor-liquid respectively (Groenendijk, 2008).

The Young's ideal solid surface is defined as a smooth, rigid, chemically homogeneous, non reactive and insoluble surface. The focus of Young's equation is on the physico-chemical property of the three phases without any dependency on the effect of gravity on the droplet shape (Marmur, 2006).

However, by the addition of micro structures or roughness to the surface, the Young's equation cannot be applied anymore. In such cases two types of contact angles, the actual and the apparent contact angles, will be formed on the surface. The actual or intrinsic contact angle is the angle between the liquid-vapor interface tangent line and the real liquid-solid interface tangent line. The apparent contact angle is also defined as the angle between the tangent lines of the

liquid-vapor interface and the nominal solid-liquid interface (Marmur, 2006). The apparent and actual contact angles are shown in Figure 2.4.



Figure 2.4: Actual contact angle and apparent contact angle (Adapted from Marmur, 2006)

In 1936, Wenzel introduced the effect of roughness on the contact angle by multiplying the Young (or Young-Laplace) contact angle (θ_Y) by a roughness factor according to Equation 2.2.

$$\cos\theta_W = r\,\cos\theta_V\tag{2.2}$$

Where θ_W , is the Wenzel contact angle, and *r* is the roughness factor defined as the ratio of actual surface area to the projected surface area (smooth surface). This ratio is always greater than one (Groenendijk, 2008). According to the Wenzel relation, roughness decreases the contact angle of the droplet for a hydrophilic material and increases the contact angle for a hydrophobic material. In other words, roughness makes a hydrophilic surface more hydrophilic and a hydrophobic one more hydrophobic. One limitation of the Wenzel relation is for cases where the right of the equation is greater than one, which defines a nonphysical state. Another limitation is that the Wenzel equation fulfills the measurement of one single apparent contact angle for a homogeneous wetting regime, while 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).

The limitations of the Wenzel equation for heterogeneous surfaces, led to further studies on roughness and contact angle. Cassie and Baxter in 1944 studied the composite surface depicted in Figure 2.3. In this case the water droplet does not wet the entire surface, and air pockets are formed between the liquid and the surface. The Cassie-Baxter contact angle is defined as:

$$\cos\theta_{CB} = f_{SL}r \,\cos\theta_Y + f_{SL} - 1 \tag{2.3}$$

where f_{SL} is the fraction of the droplet in contact with the solid surface and r is the roughness ratio of the wetted area (Groenendijk, 2008). It is noted that when f_{SL} is 1 (complete wetting), Equation 2.2 is recovered.

2.3.2 Static vs. Dynamic Contact Angle

According to recent studies, the measurement of a single static contact angle is not sufficient for characterizing the wetting behavior of a material. In reality, the microstructure details in heterogeneous surfaces are barriers to the motion of the contact line, which cause the existence of a wide range of apparent contact angles on a surface (Marmur, 2006). This range lies between the advancing and receding contact angles. The advancing contact angle is defined as the contact angle while the droplet is spreading on the surface. On the other hand, the receding contact angle is defined when the droplet is contracted (Johnson et al., 1969, Wang, 2006). The static contact angle value is typically between the advancing and receding contact angle showing how to measure the advancing and receding contact angles. This method of measurement is called dynamic contact angle measurement. The second image from left is the advancing contact angle and the forth image is the receding contact angle.



Figure 2.5: A set of advancing and receding analysis of a droplet

The difference between the advancing and receding values of contact angle is called contact angle hysteresis. A high value for a contact angle with a small hysteresis value is an essential requirement to characterize a surface as superhydrophobic (Gao, 2006, Wagterveld, 2006). When the volume of the droplet increases, the hydrophobic domain will pin the motion of the contact line and cause an increase of the apparent contact angle due to the effect of gravity. Similarly, when the volume of the droplet decreases, the hydrophilic domain will prevent the draining motion of the contact line and causes a decrease in the contact angle. This analysis implies the sensitivity of the advancing contact angle to the hydrophobic domain and the receding contact angle to the hydrophilic domain (Johnson et al., 1969, Wang, 2006).

2.3.3 Lotus Effect

The superhydrophobic behaviour of the surface of some plant leaves in nature has gained considerable attention (Otten, 2004, Ma, 2006, Kietzig et al., 2009). The creation of artificial superhydrophobic surfaces by mimicking the structural and behavioural properties of natural superhydrophobic creatures has been investigated since the 1990s (Ma, 2006, Liu, 2006). The superhydrophobicity of the lotus leaf is the focus of many research studies because of its self-cleaning property. Water droplets on the surface of the lotus leaf tend to minimize their surface and form spherical shapes due to the high surface tension of water. These drops wash off contaminants and dirt as they readily roll on the leaf's surface. This so called the lotus effect and it was first studied by Dettre and Johnson (1964).

The water repellency and self-cleaning (lotus effect) mechanism of the lotus plant are explained by the micro-scale bumps, nano-scale hair like structure, as well as waxy chemical composition of the leaf (Lai, 2003, Cheng, 2006). The self-cleaning phenomenon was studied for the first time by Neinhuis and Barthlott (1997).

The diameter of the micro scale bumps on the surface of a lotus leaf is about 5-9µm with the height of 10-15µm. The nano-scale hair like structures on top of each micro bump has a typical diameter of 124.3nm and is made of epicuticular wax crystalloids. The reported contact angle on the lotus leaf surface is about 161.0° with a hysteresis value of 2° which can be described by the Cassie-Baxter relation (Equation 2.3) due to the formation of air pockets between the liquid and the surface (Feng, 2002).

In order to mimic the lotus effect for creating a superhydrophobic surface the mentioned two scale roughness is essential. However, in order to achieve the optimal roughness structure to get the same water repellency the height and diameter of the micro scale bumps as well as the bumps' distance from each other should be optimized as they play an important role.

2.4 Surface Modification of Wood Fibres and Paper to Impart Hydrophobicity

One of the important properties of cellulose fibre in the paper making process is its hydrophilic nature. This characteristic makes the bonding of the fibres possible and allows the production of paper (Balu, 2009). Due to this hydrophilic property as well as the cellulose surface chemistry and morphology, its usage is limited in some industrial applications.

Wettability is determined by the contact angle of a liquid droplet on the surface. Controlling the wettability of the paper surface is crucial for applications such as packaging and printing. For example, in paper cups, milk cartons, and packaging papers it is desired to prevent the penetration by aqueous liquids. In printing and writing papers it is demanded to avoid a situation where the ink does not spread laterally or feather.

The contact angle of water on paper can be increased by the creation of a low surface energy, hydrophobic surface. One of the traditional methods for controlling the wettability of the paper is the sizing which can be divided into two sub categories: internal sizing and surface sizing. Internal sizing, which refers to the control of water penetration within the bulk, can be obtained by using natural or synthetic sizing agents such as rosin, or alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA) to the pulp suspension during stock preparation (Wang et al., 2000). Unsized or "waterleaf" paper absorbs water e.g. facial tissues are usually unsized. Well-sized paper has a contact angle of 90°-100°. The main drawbacks 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 (Roberts, 1996). Surface sizing, which addresses the penetration through the surface of the paper, is performed in the final stage by filling the pores using low surface energy waxes and chemicals (water repellent substances).

It is well understood that for any material superhydrophobicity requires a certain roughness of the surface, ideally on two length scales, to result in the Wenzel or the Cassie-Baxter states (Tuteja et al., 2008; Gao and McCarthy, 2006a). Many of the recent reports on methods to produce superhydrophobic paper show a certain roughness on the paper's surface is an important criterion. Superhydrophobicity implies a contact angle greater than 150° and contact angle hysteresis less than 10° ("roll off" or lotus effect) or more than 10° ("sticky" or high adhesion and small contact area) (Balu et al., 2008). Different ways were chosen to obtain this roughness and to further hydrophobize the surface, as described below.

Quan et al. (2009) used the traditional way via AKD combined with roughness to obtain contact angles of 173°. They roughened paper with an emery cloth and subsequently coated the paper with nano- to micro-sized particles of AKD by use of the rapid expansion of supercritical (RESS) process.

Similarly, Tajedo et al. (2009) experimented with common paper making sizing agents, such as AKD, ASA, *poly-butyl acrylate* (PBA), tetraethoxysilane (TEOS) and trichloromethylsilane (TCMS), to make cellulose fibres hydrophobic. The highest contact angles of about 150° were obtained with silanized (TCMS) fibres. The authors reported on the wet web strength but no further information was given on the roughness and contact angle hysteresis.

Another way via traditional paper making additives was chosen by Larsson et al. (2009), who exploited oppositely charged polyelectrolytes to form polyelectrolyte multilayer as the base to further adsorb anionic paraffin wax particles on them. Contact angles of about 151° were reported, although no information on the obtained surface roughness and hysteresis was provided.

Hu and Deng (2009) avoided the use of the traditional wax sizing agents with focusing on the surface roughness and using chemicals acceptable for food packaging. They used a fatty acid precipitate calcium carbonate coating in combination with internal sizing with potassium stearate to obtain paper surfaces with contact angles close to 150°. However, again the resulting surface roughness and hysteresis were not reported.

Swerin et al. (2009) developed a superhydrophobic fluoro based coating which resulted in contact angles above 150°. AFM images illustrate the nano- and micro- roughness of surface, but detailed information about the contact angle hysteresis was not given.

Yang and Deng (2008) and Goncalves et al. (2008) both combined structuring of the surface by silica particles with rendering the surface hydrophobic via fluorination. Yang and Deng (2008) exploited the paper inherent microstructure and achieved a nanostructure on top by a multilayer self-assembly deposition with silica particles. Using a perfluorooctyltriethoxysilane coating they achieved contact angles of 155° and reported hysteresis of 5°. Therefore, it can be stated that these paper surfaces are truly superhydrophobic probably similar to a Cassie Baxter (composite) state.

Goncalves et al. (2008) created a micro-roughness on cellulose fibres by sizing them with silica particles. To further achieve a nano-roughness five bylayers of the polyelectrolyte polydiallyldimethylammonium chloride (PDDA) were deposited on the SiO₂/cellulose composite. The final hydrophobization was achieved by coating the fibres with fluorosiloxane. The resulted contact angle was reported to be about 147° without further reference to the contact angle hysteresis.

Cho et al. (2009) also rendered paper hydrophobic with siloxane. They applied a 3:1 hexamethyldisiloxane (HMDSO)/toluene glow discharge plasma on filter paper that resulted in contact angles of 157°. Reference to the initial or obtained roughness of the paper was not given; also the contact angle hysteresis was not investigated further.

Balu et al. (2008) exploited the existing fibre network of paper at the micro-scale, to create a dual scale roughness. The nano-roughness was achieved by exposing the network to selective oxygen plasma etching, with the amorphous regions being more susceptible to the plasma etching. Subsequently, a fluorocarbon film was deposited on the etched fibres from pentafluoroethane by plasma enhanced chemical vapor deposition (PECVD). This process resulted in contact angles of about 167° and hysteresis of about 3.4°. To assess the impact of the dual scale roughness they also coated fibres, which were not subject to the plasma treatment and found that the hydrophobicity obtained by the fluorocoating on the fibre inherent micro-roughness alone only resulted in contact angles of 145° and hysteresis values of almost 80°. This situation results in water sticking to the surface. In agreement with theory, these findings indicate that the nano-roughness is an important feature to obtain the Cassie-Baxter hydrophobicity with air trapped between the surface and the water (composite interfaces).

Other methods such as mechanical treatments (roughening and polishing), wet chemical treatments, and vapor phase treatments can be used to modify wood fibres in paper in order to achieve a variety of paper surface properties. Recently, the vapor phase modification using cold plasma gained considerable attention due to its flexibility to render the fibre surface with various desirable surface properties by choosing the appropriate chemical reactants and experimental parameters. This process is considered as "green" technology since the plasma is a solvent-free process (Gaiolas, 2009) and produces little waste and by-products and does not demand energy consuming drying (Pykonen, 2010).

2.5 Surface Modification of Fillers

As mentioned before, mineral fillers are used in papermaking to enhance the physical properties of paper (Neimo, 1999). The papermaking fillers can be used for surface filling and

surface coating applications (Shen et al., 2012). Many studies have been done for the synthesis and fabrication of hydrophobic and superhydrophobic mineral fillers surfaces (Hu et al., 2009, Huang et al, 2011, Mesic et al, 2010, Ogihara et al., 2012).

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 (Gill 2000, Shen et al. 2009). 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 furnish (Shen et al., 2009). This will result in lower effectiveness of the sizing agent 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. Gill (1995) developed a way to achieve hydrophobicity of the filler surfaces with C12-C22 fatty acid. Kurrle (1996) patented a process to modify CaCO₃ fillers with a starch-soap complex. Other approaches include the use of polymers to render fillers hydrophobic (Gill, 2000; Niinikoshi et al., 2007).

Huang et al. (2011) reported the preparation of hydrophobically modified titanium dioxide with a coupling agent (3-(trimethoxysilyl) propyl methacrylate). They added the modified filler to the pulp slurry for sheet formation. The resulting paper contact angle ranges from 126.5° to 154.2° with the sliding contact angle less than 3° . Mesic et al. (2010) reported that the hydrophobic clay that is used in the plastic industry can be employed as filler in the water base dispersion coatings for linerboard (Shen et al., 2012). They mixed the hydrophobic clay with a low dose of wax and coated the cellulose substrate with it. The coating resulted in a contact angle of 150° but no hysteresis value was reported.

2.6 Janus Particles and Films

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 (Perro et al., 2005). For example, one side is hydrophilic, while the other is hydrophobic. This property can be used for particular assemblies like dual functionality devices (Perro et al. 2005). 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 (Perro et al. 2005).

Hong et al. (2006) were able to fabricate Janus particles of silica in large quantities by a chemical modification method. They froze the untreated particles of silica at the liquid-liquid interface of emulsified molten wax and water. Then the outer surfaces of the immobilized particles were treated chemically. Jiang et al. (2009) also fabricated trivalent patchy colloidal particles by a two step μ -contact (micro contact) printing method. In this method the polydimethylsiloxane (PDMS) stamp lifts the outermost particles from a solid surface, and then a second PDMS stamp lifts the opposing pole of the particle from the first stamp. Therefore, they first modified one pole of the particles, then the other pole, leaving other portions of the particle intact. Figure 2.6 shows the SEM images of Janus particles and Janus films.



Figure 2.6: (a, d) Janus films (d: Stamboulides, 2010) (b, c) Janus particles (b: adapted from Perro et al., 2005; c) Reprinted with permission from Jiang and Granick, "A Simple Method to Produce Trivalent Colloidal Particles, Langmuir, Copyright 2009 American Chemical Society)

2.7 Plasma Processing

Plasma is a state of ionized gas containing reactive components such as electrons, ions, photons, radicals, and variety of neutral species (Balu et al. 2009, Pykonen et al., 2010). This

phenomenon was first observed by Irving Langmuir when he tried to strike an electrical discharge in a gas. He offered the term "plasma", as the way electric discharge carries ions, electrons, neutrals and gas impurities; the blood plasma carries red corpuscles, white corpuscles and germs (Balu, 2009, Mott et al., 1971).

Plasma is usually referred to as the forth state of matter. When energy is applied to a material in a solid state, the motion of molecules and atoms increase and the transition to the liquid state and the gas state will occur. If more energy being applied to the system, some of the molecules and atoms will disintegrate and form charged sub-particles, electrons, and ions (Pykonen, 2010). Other reactive particles are generated such as radicals and excited species because of the collisions. Generally, plasma applies radio frequency (RF) or microwave energy to gas (Vaswani, 2005). The pressure of the plasma chamber is in the range of 0.01-10torr, electron densities between 108 and 1012 cm⁻³, and electron energies between 1 and 10ev (Vaswani, 2005). These types of plasma are non-equilibrium plasma because the electron temperatures are much higher than the temperature of ions and neutral species (Vaswani, 2005).

In plasma processing, organic gases are partially ionized via an electric discharge which causes the creation of highly activated species and radicals. The generation of the reactive species can be done at room temperature which is one of the considerable advantages for treatment of wood fibres since fibres are easily decomposed at higher temperatures.

The plasma-solid interaction consists of three main categories: etching or ablation, plasma activation, and plasma coating (Pykonen et al., 2010). During the etching or ablation process the outermost layer of the surface is removed and a degree of roughness is created depending on the substrate. In the plasma activation the surface will be modified chemically or physically by the species in the plasma. 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) (Pykonen et al, 2010). The functional layers such as hydrocarbons, hydrocarbons with polar groups, organosilicons, halocarbons (e.g. fluorocarbons) and organometallics can be deposited by PCVD (Pykonen et al, 2010).

The reactive species in the plasma may participate in different reactions with the surface as shown in Figure 2.8, which are crosslinking (bonding a polymer chain to another), etching, deposition, and functionalization. Also crosslinking of the gas species may occur which results in

the formation of species in vapor phase. The reactions can be controlled by using a set of appropriate conditions such as type of gas or vapor, reactor design, and operation conditions (flowrate, power, pressure, and substrate temperature) (Balu et al., 2008, Balu, 2009).



Figure 2.7: Reaction mechanism for plasma surface modification (adapted from Mukhopadhyay,

2009)

Plasma enhanced chemical vapor deposition (PECVD) is an alternative for depositing a variety of thin films at low temperatures. Since the formation of the reactive species in the gas phase take place by collision in the gas phase, the substrate can be maintained at low temperature. Some of the desirable features of PECVD films are good adhesion, low pinhole density, good step coverage, and uniformity.

2.8 Plasma Treatment of Paper Surfaces

The first application of plasma treatment on a cellulosic surface was performed in the 1970s by using microwave plasma for the modification of the bonding properties of cellulose (Balu et al., 2009, Wertheim et al., 1972). Since then the plasma processing of a cellulosic surface was

reported using a variety of precursor gases such as: nitrogen, argon, oxygen, hydrogen, ammonia, sulfur dioxide, hydrocarbons, fluorocarbons, halogens, and organosilanes depending on the desired properties (Balu et al., 2009). Pure cellulose is hydrophilic in nature with the water contact angle of around 20°. However, depending on the pulping technique, the wood fibre may contain different amounts of cellulose, lignin, hemicelluloses and extractives and this will affect the final wettability of the handsheet. One of the critical issues in the paper industry is the control of paper hydrophilicity since this property influences the dye uptake and printability efficiency.

The effect of oxygen plasma treatment on three Kraft pulps was investigated by Carlsson et al. (1991). The results indicate the increase in hydrophilicity and water absorption properties due to the oxidation of lignin and extractives of the fibre.

Among the mentioned precursors, hydrocarbon, organosilicon, and fluorocarbon plasma coatings have been used for making hydrophobic paper surfaces (Pykonen, 2010). One of the desired properties of plasma deposition is the individual coverage of fibres by polymer thin film which does not block the interfibre pores (Balu, 2009).

The first fluorocarbon treatment of paper surface was done by Sapieha et al. (1988, 1990) which rendered paper hydrophobic. In their work, different ratios of CF_4 and O_2 gases were tested and the hydrophobicity was measured in terms of water absorption time through the paper. By increasing the CF_4 flow rate of the feed the water absorption time increases.

The surface property of paper differs in terms of roughness and chemical concentrations on its two sides: felt or wire side during the paper making process. This characteristic that is referred to as "two-sidedness" was studied by Sahin et.al (2007) by deposition of CF_4 film on the paper. He reported the felt side is more prone to fluorination than the wire side due to the concentration of coarse fibrous materials on the felt side.

Vaswani et al. (2005) studied the effect of pentafluoroethane (CF_3CHF_2) and octafluorocyclobutane (C_4F_8) thin film on the paper which results into a hydrophobic surface. However, the water vapor diffusion through the paper substrate and the film occurs readily.

CHAPTER 3: MATERIALS AND METHODS

In the following section the experimental set up, equipment, and methods are described.

3.1 Experimental Set-up, Equipment and Materials

A variety of equipment was used in this study. They include a custom designed Former for preparing the handsheets, a Fibre Classifier for obtaining different fibre length of pulp, a Plasma Enhanced Chemical Vapor Deposition (PECVD) apparatus for surface treatment of the fillers and paper samples, a high resolution camera, a micropipette, a COM-TEN universal tester for performing tensile strength measurements, a water vapor transmission rate analyzer for determining the vapor permeability of the handsheets, and the equipment to perform the Cobb test for the water permeability analysis of the handsheets. In addition, scanning electron microscopy (SEM) for surface morphology, X-ray photoelectron spectroscopy (XPS) and a FTIR-ATR (Attenuated Total Reflectance) for surface elemental composition and chemical bonds analysis were additionally employed.

3.2 Experimental Methods

3.2.1 Handsheet Preparation

All handsheets were prepared using a modified former that works similar to a standard handsheet former (Montgomery, 2010). In order to simulate the paper making process a vacuum was used. The schematic in Figure 3.1 shows the handsheet former. The former is constructed of two 3" diameter clear acrylic circular cylinders which are located above and below the forming fabric. A flush mounted gauge pressure transducer (GP: 50 Model 218-C-SZ-10-SG) is located in the wall of the test chamber below the forming fabric. A vacuum chamber which is made of a 13mm thick PVC sheet is connected to the bottom of the test chamber by a 20mm diameter PVC pipe and electrically actuated solenoid valve. A vacuum pump is attached to the vacuum chamber in order to adjust the pressure to the desired value. All handsheets were made at the vacuum pressure of -34 KPa (10 inHg). The selection of suction pressure is based on the pressure range that is encountered in industrial processes.



Figure 3.1: Schematic of the Handsheet former (adapted from Montgomery, 2010)

The Peroxide-bleached TMP (thermo mechanical pulp) with the pH of 6.9 ± 0.2 was used in this study. The pulp was supplied by a leading pulp and paper mill in British Columbia with 4.28% consistency and it was a mixture of spruce, fir, and pine fibres. The handsheets were prepared using three different fillers, namely precipitated calcium carbonate, kaolin clay (39% Al₂O₃, 46% SiO₂, 13% H₂O), and talc (63% SiO₂, 32% MgO, 5% H₂O). The PCC (precipitated Calcium Carbonate) filler was obtained from Specialty Minerals Inc (Bethlehem, Pennsylvania, USA) with the particle shape of rosette, average particle size of $10.22\mu m$ (measured by Scircco 2000 Mastersizer, the provider technical data sheet reported the median particle size of $1.3\mu m$), dry brightness of 98%, and a zeta potential value of -17.8 ± 0.3 mV (measured by Zetasizer 2000) at a concentration of 0.002 wt% in distilled deionized water (DDW). The kaolin clay filler was available at the Pulp and Paper Center in UBC and has an average particle size of 13.5µm and a zeta potential value of -15.1 ± 0.7 mV at a concentration of 0.002 wt% in distilled deionized water (DDW). Also, the talc filler (available at the rheology lab in the Department of Chemical and Biological Engineering at UBC) had the average particle size of 34.72 µm and zeta potential value of -12.5 ± 2.5 mV at a concentration of 0.002 wt% in DDW. The SEM images of the fillers are shown in Figure 3.2.



Figure 3.2: SEM Images of fillers (a) PCC (b) Talc (c) Clay

The following chemicals were used in the preparation of handsheets:

- Cationic tapioca starch S880 supplied by National Starch ULC (Surrey, BC, Canada) with the nitrogen content of 0.9-1.10%N and an average molecular mass of 3 million Da.
- Cationic flocculent (acrylamide copolymer) supplied by Eka Chemicals (Magog, QC, Canada) with the average molecular mass of 10 million Da.
- Silica as a 8.1 wt% suspension supplied by Eka Chemicals (Magog, QC, Canada) with the mean size of 5 nm.
- Distilled deionized water (DDW) was used for the preparation of filler and polymer solutions

A suspension of 1.67 wt% starch was prepared and cooked according to the procedure provided by National Starch ULC (Sang et al., 2011). The pulp suspension was prepared with

concentrations shown in Table 3.1. The formed handsheets were dried and kept in the condition room prior to surface treatment.

Concentration%									
1.02	%	4.28%		0.167%	6	0.0119	%	0.006%	6
Filler (%)	V(ml)	Pulp(g)	Water(g)	Starch(kg/t)	V(ml)	Floc(kg/t)	V(ml)	Silica(kg/t)	V(ml)
25	8.58	6.1	485	10	2.10	0.3	0.95	0.4	2.33
35	12.01	5.3	483	10	2.10	0.3	0.95	0.4	2.33
45	15.44	4.5	480	10	2.10	0.3	0.95	0.4	2.33

Table 3.1: Pulp suspension (Sang et al., 2011)

Fibre Classification. One set of experiment was performed by making handsheets with three different sized fibre lengths. The pulp was classified into five different fibre lengths using the Bauer-McNett classifier. The TAPPI standard of T233 cm-95 was followed. The fibres were collected from the screen openings of 1.19 mm, 0.595 mm, 0.297 mm, 0.149 mm, and 0.074 mm. The Tyler series numbers for these openings are 14, 28, 48, 100, and 200. Different handsheets were prepared by mixing 50% of the unclassified pulp with 50% of the classified pulp from openings 48, 100, and 200. Therefore three different handsheets were prepared in which the dominant fibre length was 0.297mm, 0.149mm, and 0.074mm. These experiments were carried out in order to investigate the effect of roughness on hydrophobicity. It is believed that coarse, stiff, long fibres fractions cause surface roughness in a dry sheet (Norgren S., 2008). However, the hair-like nano scale roughness is dominant on the surface of handsheets made with fines which can affect the hydrophobicity.

3.2.2 Preparation of Fillers for PECVD

PECVD is a high vacuum chamber and due to this high vacuum, treatment of the fillers as powder is not possible since the vacuuming process will remove the powder from the surface. Therefore, the PCC and kaolin clay fillers were prepared in the form of pellets and as a thin film on microscope glasses (Figure 3.3).

The thin films were prepared by dispensing 1mL of 1.02% PCC and clay solution on microscope slides. The pellets were formed using aluminum mold and the Carver laboratory press (model no. 2518).



Figure 3.3: (a) Film of PCC on microscope slide (b) Pellet of PCC

3.2.3 Surface Plasma Treatment

The plasma treatment of the samples was performed using Trion/RIE (reactive ion etch) plasma enhanced chemical vapor deposition (PECVD) (model: ACD) with a vacuum loadlock, 250V AC, and a frequency of 60Hz.

Handsheets Treatment. The oxygen plasma for etching the handsheets and CF₄ precursor plasma for thin film deposition were used. The PECVD operation parameters are summarized in Table 3.2.

Precursor Gas	Pressure (mTorr)	Power (W)	$T(^{\bullet}C)$
O_2	100	300	20
CF ₄	1000	200	20

Table 3.2: PECVD operation parameters

The handsheets were treated at two different etching times of 15min and 20min with the oxygen gas flow rate of $10 \text{ cm}^3/\text{min}$. The CF₄ deposition was performed for 20min at three levels of flow rates, $40 \text{ cm}^3/\text{min}$, $30 \text{ cm}^3/\text{min}$, and $10 \text{ cm}^3/\text{min}$.

Fillers Treatment. Fillers were treated by PECVD using CF_4 flow rates of $10cm^3/min$ and $40cm^3/min$ at the same plasma operating parameters used for handsheets.

3.2.4 Contact Angle Measurements

The contact angle of water droplets were measured by the goniometry method by capturing images with a high resolution camera under a light source. A 2μ L distilled deionized water droplet with a typical resistivity of less than 18.2 M Ω .cm at 25 °C, a total organic carbon content of less than 10 ppb, and a neutral pH value of 7 was used. The droplets of water were dispensed on the respective surfaces with a piston-driven air displacement pipette. Digital images of the
water droplet on the surfaces were taken with a Nikon D90 digital camera. The contact angles were determined by analyzing droplet images with the software FTA32 Version 2.0. Advancing and receding contact angles were determined by monitoring the growing and shrinking droplet. The camera was set to capture three images per second for advancing and receding contact angle analysis.

3.2.5 Surface Analysis

Scanning Electron Microscope (SEM). The surface structures of the handsheets before and after plasma etching and deposition were analyzed with a Hitachi S-3000N-VP scanning electron microscope. The operating voltage of 5KV and 10KV was adjusted in order to prevent damaging of the papers. The variable pressure mode was selected since the paper and the CF_4 films are insulators.

Energy Dispersive X-ray spectroscopy (EDX). The EDX analysis in Z-direction was performed using the same equipment (Hitachi S-3000N-VP scanning electron microscope). The aim of the EDX analysis was to understand the distribution of the filler at the top side, wire side, and the thickness (cross section) of the handsheets (Modgi et al, 2006, Modgi et al., 2006). For the EDX analysis 3 areas over the handsheet surface were selected for analysis shown in Figure 3.4 (a). The top side and the wire side of the handsheets were analyzed by EDX. Then the thickness of the sheets was divided into 4 areas and each area was analyzed for mineral content (Figure 3.4 (b)).



Figure 3.4: EDX analysis sampling procedure

In order to obtain the elemental composition of the material surface the X-ray photoelectron spectroscopy (XPS) was used. This equipment is capable of scanning the first 10nm of the surface. The spectra were collected using Leybold model MAX200 XPS with Al K- α X-rays, and 15kV, 20MA emission current. The base pressure was kept at 2×10⁻⁹ Torr.

FTIR-ATR. Fourier transform infrared spectrometers (FTIR) with attenuated total reflectance (ATR) were obtained with a Thermo Niccolet AVATAAR 360 FTIR Spectrometer. The samples were cut (0.5×0.5 cm) and pressed against the ATR crystal using a flat metal with a controlled pressure. The level of the pressure was kept constant for all samples.

3.2.6 Handsheets Property Measurements

Tensile Strength. The TAPPI standard method of T494 om-96 is used in the pulp and paper industry to determine the tensile strength of paper. According to this standard the sample length of 100mm is required. However, the handsheets that were made by the modified former in this study have a diameter of 78mm which restricts the use of the TAPPI standard tensile test. Generally, the L&W Tensile Tester is used which is based on the TAPPI standard, i.e. the samples are 100mm in length and it is not possible to test lower length samples. Another laboratory tensile strength measurement apparatus is the COM-TEN Universal Tester which is flexible for using different sample lengths. In order to understand the discrepancy between the COM-TEN universal tester and L&W Tensile tester (that follow the TAPPI standard) and get a validation for our results, the tensile test was carried out on both pieces of equipment using two different industrial copy paper samples. The tensile strength and the standard error of the mean for both samples are shown in Table 3.3. Since the discrepancies between the results were not high the COM-TEN tester was used for tensile measurement of the handsheets.

Sample	Paper Sa	ample 1	Paper Sa	mple 2
Test Method	L&W Tensile Tester	COM-TEN Tester	L&W Tensile Tester	COM-TEN Tester
Tensile Strength (MPa)	23.02	25.35	41.21	39.58
Standard Error of the Mean (MPa)	0.43	0.79	0.63	0.89

Table 3.3: Tensile strength values for L&W Tensile Tester and COM-TEN Tester

WVTR (Water Vapor Transmission Rate). In order to understand the water vapor absorption of the paper the WVTR tests were performed based on the TAPPI standard method of T448 (water vapor absorption rate of paper and paperboard at 23°C and 50% relative humidity). The IGA-003 Multicomponent Analyser (Hiden-Isochema, Warrington, UK) was used for measuring the water vapor transmission rate of the handsheets.

Cobb Test. The water absorption to the paper was measured using the TAPPI standard of T441 om-04. The samples were put in contact with water for 60s and the weight of the samples was measured by analytical balance before and after the test.

Air Resistance (Gurley Method). The air resistance test was performed in order to estimate the permeability of handsheets. This method measures the time that is required for a certain volume of air to pass through the handsheet. The TAPPI standard method of T460 om-02 was followed.

3.3 Limitations of the study

The limitations of the study were as follows:

- Due to the lack of a goniometer, the contact angles were measured manually by a micropipette, a high resolution camera, and a light source. The speed at which the dynamic contact angles are performed, the increase of water droplet within certain intervals, as well as the applied pressure could not be quantified.
- The plasma enhanced chemical vapor deposition (PECVD) that is used for the deposition of fluorocarbon films is a vacuum chamber. Due to the vacuum pressure having the fillers in a powder form in the chamber is not possible. Therefore, the filler powders were treated in two ways. First, they were treated as a thin film on microscope slides which limits the amounts that can be treated each time since the films are thin. Second, they were treated as pellets of fillers. It is believed that the plasma affects only the outermost surface. However, removing only this layer from the pellets to obtain only fully plasma treated filler particles is not possible.

3.4 Experimental Approach

Two types of experiments were carried out. First, handsheets were prepared using untreated fillers. Then the handsheets were treated by PECVD and consequently their wetting behavior as

well as their other properties was studied. In the second approach fillers were treated using PECVD to make them partially hydrophobic. Figures 3.5 and 3.6 show the experimental approach in a flowchart format.



Figure 3.5: Handsheets treatment approach



Figure 3.6: Fillers treatment approach

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Handsheet Treatment

4.1.1 "Roll off" and "Sticky" Water Droplet, Roughness Effect

As mentioned before there are two important parameters that are required for the fabrication of superhydrophobic surfaces, namely, surface roughness and low surface energy. Some microscale roughness on the surface of paper due to the shape and position of fibres and fines in the network does exist. However, for superhydrophobic surfaces dual scale roughness, micro and nano-scale, is an important factor as well.

Plasma treatment on handsheets was performed in two steps. First, the samples were etched using O_2 plasma which is believed to create the nano-scale roughness on the paper. Then, the CF₄ was deposited on the surface of handsheet to provide the low surface energy required. Vaswani (2005) reported that the oxygen plasma treatment oxidizes the surface due to hydroperoxide formation as well as reduces the surface by creation of carbon-oxygen double bonds in cellulose. However, the plasma processing conditions that are reported in these studies were aggressive, since their focus were on the interfibre bonding, internal structure of fibres and the coating distribution within the paper (Sapieha et al., 1988). In this work, the oxygen etching plasma was applied in order to alter the top layers of the handsheets and maintain the bulk properties. Therefore, mild etching conditions were applied for etching the amorphous portions of the cellulose.

Table 4.1 shows the water contact angle results for handsheets with PCC and clay fillers. These handsheets were prepared without any other chemical additives, i.e containing only filler (25% loading) and fibre. In order to understand the effect of etching on hydrophobicity, some of the handsheets were treated only by plasma CF_4 deposition on the surface without the prior O_2 etching step. The results show increase in contact angle for the handsheets that were first etched and then were subjected to CF_4 deposition.

When the water droplet was dragged on the surface, the rolling off superhydrophobicity behavior was observed on the handsheets that were subjected to oxygen etching plus plasma CF_4 deposition. This rolling off superhydrophobicity is similar to the lotus leaf behavior. However, on the handsheets that were only treated by CF_4 deposition, the water droplet was a sticky

hydrophobic droplet. Figure 4.1 shows the contact angle on the surface of O_2 etched plus CF_4 deposited (a), and only CF_4 deposited (b) handsheets. Although there is a small difference between the contact angles of these droplets, a droplet exhibits rolling off behavior on the O_2 etched plus CF_4 deposited handsheet and sticky behavior for CF_4 deposited handsheet.

	Static Contact Angles			
Paper	Untreated	Oxygen Etched	CF ₄ Deposited	<i>O</i> ₂ Etched & CF ₄ Deposited
Fibre only	Hydrophilic	Hydrophilic	145°± 3	162°± 2
PCC	Hydrophilic	Hydrophilic	$146^{\circ} \pm 6$	152°±4
Clay	Hydrophilic	Hydrophilic	144°± 7	$160^{\circ} \pm 6$

Table 4.1: Contact angle results before and after plasma treatment



Figure 4.1: (a) Rolling off droplet (b) sticky droplet when the droplet is dragged on the surface

Figure 4.2 shows the SEM results for samples before and after plasma treatment. As seen, the effect of O_2 etching on the surface of the handsheet is obvious in comparison with the handsheets that were only treated with CF₄. The surfaces of untreated handsheets and CF₄ deposited ones have some micro-scale roughness. The etching caused creation of nano-scale roughness on fibre surface and is accompanied by an increase on hydrophobicity. Figure 4.2b shows the effect of O_2 etching on a single fibre surface at higher magnification.



Figure 4.2: SEM results on plasma treated handsheet

In order to confirm the effect of roughness on hydrophobicty, oxygen etching was performed for 15min and 20min on the surface followed by CF_4 deposition. Figure 4.3 shows how the static contact angle changes for handsheet samples prepared at the two levels of etching time, 15min and 20min and with different filler levels. As seen the static contact angles for handsheets that were subjected to 20min etching is higher.



Figure 4.3: Effect of plasma etching time on hydrophobicity

As previously mentioned the fibre network provides the micro scale roughness. However, each cellulose fibre consists of microfibril bundles with the diameter ranging from 3-30nm which can provide the nano-scale roughness that is required for superhydrophobicity (Balu et al., 2008). The microfibrils contain the crystalline cellulose moieties and the matrix around the microfirils is naturally amorphous (Balu et al., 2008). The oxygen plasma etched the surface of cellulose to a point that the microfibrils will be exposed and therefore the roughness will be created. It is believed that the amorphous regions of cellulose fibre are more susceptible to changes due to the low level of order in these regions. Also, most of the reactants penetrate the amorphous regions of cellulose and leave the intra-crystalline regions unaffected (Ciolacu et al., 2011). Balu (2008) reported that in the etching process the oxygen species (O[°] and O^{*}) will react with cellulose (P) and form OH, CO, and CO₂ and remove material from the surface according to the following reaction:

$$P+O^* \rightarrow P^*+OH$$

 $P^*+O \rightarrow P^*+CO+CO_2$

Fibre size effect. The Bauer-McNett classifier was used for classifying the fibres. The handsheets were prepared by mixing 50% of the classified fibres from mesh opening 48, 100,

and 200 and 50% of unclassified fibres. The fraction of pulp that passes through the 200 Bauer-McNett mesh is considered as fines fraction (Vaino, 2007). Therefore, for example, the amount of fines on handsheet that is made with 50% of the classified fibre with screen opening of 0.074mm is dominant. Also the handsheets were filled with PCC at 25% loading. The plasma treatment on these handsheets was performed with 20min oxygen etching and CF_4 deposition flowrate of $40 \text{cm}^3/\text{min}$. The contact angle results on the felt side and wire side of the handsheets are given in Table 4.2.

Tylor Series No.	Screen Openings (mm)	Contact angle on Felt side	Contact angle on Wire side
48	0.297	118.2 ± 2.6	140.8 ± 2.9
100	0.149	120.3 ± 2.8	142.2 ± 1.8
200	0.074	132 ± 1.1	154 ± 2.3

Table 4.2: Contact angles on handsheets prepared with classified fibres after plasma treatment

As seen from the Table the contact angle increases as the fibre length decreases. The difference in contact angle between the handsheets with fibre lengths of 48 and 100 Bauer-McNett mesh is relatively low. However, the contact angle is significantly higher on a handsheet with fines (200 mesh). It is believed (Vaino, 2007) that the properties of fines are different than fibres due to fines small size (length) and larger surface area. It is also known that the amount of extractives and hydrophobic lignin is higher in fine fraction than the fibre fraction and this can be the reason for the higher contact angle of a handsheet that is made predominantly with fines. Moreover, handsheets made with fines possess a more hairlike roughness that is dominant on these handsheets compared to those handsheets that made with longer fibres.

4.1.2 Plasma Processing on Filled Handsheet, Filler Type and Concentration Effect

As mentioned in the methodology part, handsheets with three different fillers, namely PCC, clay, and talc, with three wt% loading, 25, 35, and 45 were prepared. The handsheet samples were subjected to oxygen etching followed by CF_4 deposition on the surface. All the plasma treatment was performed on the felt side of the handsheets. The static contact angle was measured on both sides of the treated handsheets (felt side and wire side). Figure 4.4 shows the felt side contact angle results for all handsheets that were treated with CF_4 flowrate of $40 \text{cm}^3/\text{min}$. The summary of all contact angle results are listed in Table A.1-A.7 of Appendix A.



Figure 4.4: Felt side contact angle of handsheets after plasma treatment (CF_4 flowrate of $40 \text{ cm}^3/\text{min}$, Left Plot: 15min O₂ etching, Right Plot: 20min O₂ etching)

Before the treatment the static contact angle of all handsheets were found to be ~10°. As the results show, the contact angle of all samples increased significantly after plasma treatment. However, the results show that the contact angle decreases as the concentration of the filler increases in the handsheet and this is consistent for all three fillers. It can be concluded that the effect of plasma treatment on fibre is dominant as the amount of fibre decreases (or the concentration of filler increases). However, different fillers behave differently in terms of wettability. Some of the handsheets with clay fillers are still hydrophilic after the treatment. The different behaviour in the wettability of handsheets can be attributed to the different surface energies of the fillers. The reported surface energy in literature for PCC, talc, and kaolin clay are 75-80 J/cm², 35-40 J/cm², and 550-600 J/cm² respectively (Sharma et al., 1998), with talc having the lowest surface energy and kaolin clay having the highest surface energy. Therefore, the reason for hydrophilicity of clay filled handsheets is due to the highly polar surface of kaolin as well as its high surface energy (Salmah et al., 2009).

By considering the surface energies, the handsheets filled with talc should result in higher contact angles than the handsheets filled with PCC. However, the PCC filled handsheets have the highest contact angles (Figure 4.4). This can be due to different z-direction distribution on the handsheet. In order to confirm our hypothesis, the distribution of fillers in the felt (top), wire side and z-direction (thickness) of the handsheets was examined by using SEM/EDX analysis.

In Fordrinier papermaking machines, the water is removed from one side of the sheet. This mechanism causes significant differences on the composition and microstructure of both sides of the sheet. This property, the difference on both sides of the same sheet, is referred as "two sidedness" of paper (Sahin, 2007). The side that is in contact with forming fabric or the paper making machine wire during the process is referred to as the wire side (bottom side) while the other side is referred to as the felt side (top side). It is believed that the concentration of fines and fillers are lower on the wire side than the felt side due to the asymmetric water drainage on the wire section of the papermaking machine (Sahin, 2007).

Figures 4.5 shows the amount of filler on the felt and wire side by determining the percent of a key element (Ca and Si). As seen there is no significant difference in handsheets filled with talc and clay compared to the handsheets filled with PCC. For handsheets filled with PCC the calcium concentration on wire side is higher than the concentration on the felt side. This reveals the different behaviour of PCC filled handsheets. Since the PCC filled handsheets have less filler on the top side and the effect of plasma on fibre is dominant, the contact angle for PCC filled handsheets is higher than those filled with talc and clay.

The z-direction filler distribution is shown in Figure 4.6. As seen the handsheets with talc and clay have similar filler concentrations along the z-direction whereas the calcium content of the handsheets filled with PCC has a different distribution with more Ca on the wire side.



Figure 4.5: Filler distribution on top and wire side of handsheets with filler loading wt% of 35



Figure 4.6: Filler distribution on z-direction of handsheets with filler loading wt% of 35

4.1.3 Effect of CF₄ Plasma Flowrate on Hydrophobicity

In order to study the effect of plasma flowrate on the wetting behaviour of the handsheets, the treatment experiments with CF_4 deposition flowrates of 40 cm³/min, 30 cm³/min, and 10 cm/min³ were conducted. Prior to CF_4 deposition all the handsheets were subjected to O_2 etching. Summary of all static contact angles on felt and wire side of the handsheets are presented in Appendix (Table A.1-A.7). Figure 4.7 shows the contact angle on the wire side of PCC filled handsheets at different plasma flowrates.



Contact Angles on Wire Side for PCC Filled Handsheets at Different Plasma Flowrate

Figure 4.7: Effect of plasma flowrate on wire side contact angle of handsheets filled with PCC

Although the treatment was performed on the felt side of the handsheets, the wire side also became hydrophobic. According to the results (Figure 4.7), as the flowrate increases the hydrophobicity of the handssheets on the wire side also increases. It is mentioned in the literature that plasma treatment only affects the outermost surface (Sahin et al., 2002, and Navarro, 2003). However, for porous surfaces the plasma treatment is also effective in the bulk when the material is porous and the depth of permeation can be controlled by plasma processing parameters (Mukhopadhyay, 2002 and Tu, 1994). Thus, this study shows that one plasma processing parameter can be the flowrate of the precursor gas.

The results shown in Figure 4.8 indicate that at the flowrates of 30 and 10 cm³/min the felt side contact angle is higher than the wire side but for a flowrate of 40 cm³/min the contact angles on the wire side is higher than the felt side.







Figure 4.8: Comparison of contact angle on felt side and wire side for PCC filled handsheets (20 min O_2 etching and CF_4 deposition with Flowrate of 10, 20, and $40 \text{cm}^3/\text{min}$)

As it was mentioned above, this is due to the fact that ions, radicals, and the highly excited CF_x molecules are very small and can easily penetrate through the pore structure of the handsheet and make the wire side hydrophobic as well. The higher contact angle of the wire side at the 40cm³/min flowrate may be attributed to the rougher structure of the forming fabric on the wire side of the handsheet (see image in Figure 4.9).



Figure 4.9: The roughness that is created on wire side due to the forming fabric

4.1.4 Advancing and Receding (Dynamic) Contact Angles, Wenzel vs. Cassie Regimes

The contact angle hysteresis was obtained by measuring the advancing and receding contact angles. The difference between the advancing and receding contact angles is defined as hysteresis and for a surface to be characterised as superhydrophobic, it should be less than 10°. After settling the water droplet gently on the surface, by growing and then shrinking the volume of the water droplet on the surface the advancing and receding contact angle was obtained (Figure 4.10a).



Figure 4.10: Advancing and receding contact angles for handsheet filled with PCC.

For superhydrophobic handsheets, or the "rolling-off" superhydrophobicity, dispensing of water droplet on the surface was difficult and the droplet was not detached from the pipette tip. This behaviour is shown in Figure 4.10a. As the volume of the droplet increases, the three phase contact line as well as the contact diameter suddenly extends. This sudden increase is associated with maximum contact angle or the advancing contact angle (Yeh, 2007). As the droplet shrinks, the receding contact angle is identified when it reaches a minimum, right before the contraction of the three phase contact line. The purple image on Figure 4.10a is the advancing contact angle

and the pink image is the receding contact angle. The last image on the right shows that after growing and shrinking of the water droplet no water remained on the surface. Therefore, the surface is superhydrophobic and the droplet has no affinity for it. Also, the water droplet does not detach from the pipette tip and is lifted with it.

Figure 4.10b shows the advancing and receding contact angle values for handsheets filled with 25% PCC loading. The values of the advancing and receding contact angles of handsheets that were subjected to 15min and 20min oxygen plasma followed by CF_4 deposition at flowrate of $40 \text{cm}^3/\text{min}$ are shown in Appendix A Table A.8 and A.9. The errors associated with advancing and receding contact angles are within $\pm 2^\circ$ to $\pm 4^\circ$ for all samples.

It is known that the static contact angle value should be between the advancing and receding contact angles (summary of static contact angle for all sample are shown in Appendix A Tables A.1-A.7). Kietzig et al., (2011) reported that the contact angle values vary depending on how the water droplet is being dispensed from pipette tip onto the metallic surfaces. As mentioned, due to the high water repellency of some the handsheets, the water droplet prefers to be attached to pipette tip. However, in order to obtain the static contact angle, the droplet was forced on to the surface by applying pressure to the dispensing pipette (Figure 4.11).



Figure 4.11: Static contact angle

The pressure was applied manually to the pipette to have the droplet detached from the tip. The results show that due to the applied pressure the static contact angles are not within the advancing and receding contact angles. In fact the values are considerably lower. It was proved by Kietzig et al., (2011), that the applied pressure causes homogeneous wetting regime or Wenzel state since the water droplet fills the surface valleys. However, during the dynamic contact angle measurements (Figure 4.10a), the air pocket forms and therefore the heterogeneous composite or Cassie-Baxter state is obtained.

4.1.5 Handsheet Properties Tests, Tensile, WVTR, and Cobb Values

Tensile Strength. The tensile strength of all handsheets was measured by the COM-TEN universal tester. The results are shown in Figure 4.12 (and Figure B.1 in Appendix B) for samples treated with CF_4 deposition of $40 \text{ cm}^3/\text{min}$. It is known that fillers enhance some of the paper properties such as smoothness and brightness; however they negatively affect the tensile strength. As the filler content in paper increases, the tensile strength of paper decreases. The same trend was observed in our study. It was also seen that the plasma treatment causes a decrease in the tensile strength of handsheets. As the oxygen etching time increases the tensile strength decreases. This is due to the reduction of mechanical properties in the thin surface layer of handsheets. Sahin et al. (2002) reported that the cellulose bonds, at "intra and inter- fibre crossings", have been influenced by plasma treatment. However, they reported that at a very harsh plasma environment the tensile strength reduces only by 22% compared to the untreated paper.

By comparing the effect of filler type on tensile strength of handsheets (Figure 4.13), at low concentration of filler (25%) the PCC filled handsheets have higher tensile strength, however as the concentration of filler increase (35% and 45%) the handsheets filled with clay and talc resulted to higher tensile comparing to PCC filled handsheets at the same concentration. It is reported (IMERYS technical guide) that the platy structure of kaolin clay and talc have less negative effect on fibre-fibre bonding and they can be used at higher concentrations. Thus, the shape of the filler particle has an impact on the tensile strength of the handsheet.



Figure 4.12: Tensile Index of handsheets before and after plasma treatments



Figure 4.13: Effect of filler type on Tensile strength after plasma treatment

Water Vapor Transmission Rate (WVTR). Water vapor transmission rate was measured at 23°C and 50% relative humidity according to TAPPI standard method of T448. Figure 4.14 shows WVTR results for untreated and plasma treated handsheets.



Figure 4.14: WVTR of handsheets before and after plasma treatment

It was observed that although the handsheets are hydro and superhydrophobic and exhibit very good water repellency, their WVTR values are high and thus they are not a good water vapour barrier. The flexible packaging market requires WVTR values that are two orders of magnitude lower than 40 g/m²/day.

As seen from the data the WVTRs of the plasma treated filled handsheets follow the same trend at the two different oxygen etching time, with PCC filled handsheets having the highest WVTR values and talc filled handsheets having the lowest WVTR values. However, the trend for untreated handsheets is totally different and clay filled handsheets has the lowest WVTR values. This may be attributed to the platy structure of kaolin clay which causes a higher tortuosity in the handsheet. This property accounts for the low WVTR values as it provides a longer path for the water vapour molecules to transfer (Figure 4.15). Mesic (2010) observed the same behaviour for their uncoated kaolin clay filled linerboard and a significant higher WVTR values after the hydrophobic treatment. Sahin et al. (2007) reported that the shape and size of pores in paper as well as fibre wettability and swelling properties affect the water absorption and water uptake.



Figure 4.15: water vapour path in handsheets filled with platy fillers and spherical fillers

The porosity of the substrate is a significant factor for the water vapour transmission rate. It is known that mineral pigments fill the pores in fibre networks. According to the results the WVTR of the untreated handsheet that is made with 100% fibre is higher that the WVTR value of the filled handsheets. Also, after the plasma treatment the WVTR values increase compared to untreated handsheets, which can be due to the etching process.

The air permeability of the handsheets at 35% filler loading was obtained using the Gurley method. The time that takes to displace 100ml of air for PCC, clay, and talc filled handsheets before and after plasma treatment are shown in table 4.3. The results are in accordance with the size of fillers (PCC 1.22µm, clay 13.5µm, and talc 34.72µm). Therefore, based on filler size

(larger fillers fill more pores in the paper) and the air resistance results, the WVTR trend for handsheets after plasma treatment can be explained.

Filler Type (35% Loading)	Untreated	Treated (15 min O_2 + 20 min CF_4)
		Time (s)
PCC	11.8±0.14	11.53±0.84
Clay	15.5±1.5	14.02 ± 0.98
Talc	24.05±0.2	20.3±1.2

Table 4.3: Air permeability results for handsheets before and after plasma treatment

Cobb Values. The Cobb values were obtained following TAPPI standard T441 om-04. The Cobb value is an expression of the water absorption capacity of a handsheet. The units of the absorption capacity are gram water absorbed per m^2 . The results are shown in Table 4.4. The Cobb values are in agreement with the contact angle results with PCC filled handsheets having the lowest water absorption and clay filled handsheets having the highest water absorption. Also, as the etching increases the Cobb values decrease.

Comple		Cobb Value (g/m ²)		
581	npie	15min. O_2 Etching+ CF_4	20min. O_2 Etching+ CF_4	
	25%	5.40	1.80	
PCC	35%	5.40	5.40	
	45%	5.40	5.40	
	25%	5.40	3.60	
Talc	35%	7.20	5.40	
	45%	9.00	7.20	
	25%	7.20	7.20	
Clay	35%	14.40	21.59	
·	45%	26.99	25.19	

Table 4.4: Cobb values for handsheets after plasma treatment

The Cobb values show minor absorption of water in handsheet. This may raise the question if there is absorption of water droplets on the surface of handsheets during contact angle measurements. In order to study this effect the contact angle of water droplet was measured by dispensing 1 μ L of water droplet on the surface of handsheets and taking the image of the same droplet every 10 seconds over 1 min (the same time that Cobb values were measured). After analysing the contact angles it was found there is no significant change in the contact angle

values which show there is no detectable absorption of water droplet in the handsheet. The results are shown in Table 4.4.

Time (a)	Contact Angles			
Time (s)	PCC (35%)	Clay (35%)	Talc (35%)	Fiber Only
0	141	141	142	145
10	141	142	143	144
20	140	143	142	144
30	141	140	142	146
40	141	141	143	145
50	141	143	142	146
60	142	142	143	145

Table 4.5: Contact angles of droplets over 1min

ATR-FTIR. ATR-FTIR was used to identify the chemical linkages and chemical properties of the bulk cellulose structure after plasma treatment. The IR techniques identify the changes in functional group distribution. Sahin et al. (2007) reported that CF_x molecules covalently bond to paper surface. Figure 4.16 shows the FTIR spectra for untreated, 15min O₂ etched and CF_4 deposited, and 20min O₂ etched and CF_4 deposited fibre only handsheets. The spectrum of the handsheets from untreated fibre correlates well with the FTIR spectra for cellulose surfaces that are reported in literature (Sahin et al., 2007, Balu, 2009, Ferrero et al. 2006). The presence of the absorption band in the 1100-1500 cm⁻¹ region confirms the presence of fluorocarbon film on the surface. The FTIR spectra for all handsheets are provided in Figure D.1 in Appendix D.



Figure 4.16: FTIR spectra for Handsheets made with 100% fibre

4.2 **Filler Treatment with PECVD**

The pellets and thin films of precipitated calcium carbonate and kaolin clay were treated by PECVD CF₄ deposition at flow rate of 40cm³/min for 20 minutes. The wettability test was performed on the samples before and after the treatment. The hydrophilic PCC sample remained hydrophilic after CF₄ deposition and no detectable change in the contact angle was observed. The hypothesis was that the porosity of the PCC fillers, i.e., the powder form of PCC, may not reveal the increase of contact angle since the water droplet passes through the pores immediately. Therefore, in order to investigate the presence of fluorine on the surface of PCC fillers XPS analysis were performed on the PCC thin film sample before doing any wettability tests. The results show the deposition of fluorine on the PCC samples. However, in order to understand the existence of chemical bonds between the PCC and the deposited CF_x, the samples were washed by distilled deionized water and the XPS test was performed again. The results are shown in Figure 4.17 and Table 4.5.



PCC plasma treated before and after washing

Figure 4.17: XPS Analysis for PCC thin films before and after washing

Element	Before Washing	After Washing
Liement	At%	At%
Si	2.57	7.51
С	23.02	41.51
0	12.61	34.23
Na	2.63	1.21
Mg	1.23	1.07
F	38.78	7.06
Ca	16.9	7.4
Al	2.26	-

Table 4.6: XPS analysis, At% of elements after CF₄ deposition

According to the results the amount of fluorine on the surface was decreased by about 82% after washing the samples. This shows that the binding between fluorine and calcium is weak and there may be minor formation of CaF_2 salt with ionic bonds. It is noted that the solubility of CaF_2 is very low in cold water, 0.0015g in 100 mL water at 18°C.

The same experiment was performed for kaolin clay fillers. The thin films of clay fillers were treated by CF_4 deposition on the samples. The contact angle was increased by about 70°. Figure 4.18 show the dynamic contact angle on the clay sample before and after the treatment.



Figure 4.18: The kaolin clay samples (a) before and (b) after plasma treatment

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

In this work it was shown that dual scale roughness is a key property for fabrication of superhydrophobic paper which confirms previous findings. The manufactured handsheets that were subjected to oxygen plasma etching prior to fluorocarbon deposition show superhydrophobicity with low hysteresis. However, those that were only treated by fluorocarbon plasma resulted in "sticky" hydrophobicity behavior (high hysteresis). Another important factor was the effect of filler type and concentration in the handsheets. After the plasma treatment although the contact angles on all of the handsheets filled with PCC, talc, and clay increase, the handhsheets with kaolin clay remained hydrophilic for high concentrations of filler (35% and 45%). This was justified due to the polarity of kaolin clay as well as its high surface energy. Although the plasma treated handsheets show excellent water repellency, they are not a good water vapor barrier. This is good for applications were breathable but water repellent paper is required. It was confirmed that the two important factors that affect WVTR values are permeability of paper as well as fillers shape and size. Furthermore, it was shown that plasma processing has a negative effect on tensile strength of handsheets. Comparing the tensile index values, it is seen that as the etching time increases the tensile strength of handsheets decreases.

It was observed that the fluorination of kaolin clay filler increased its contact angle immediately after the treatment. However, the contact angle on PCC fillers remained unchanged after the treatment. The XPS analysis shows that there are no permanent bonds between the PCC fillers and fluorine molecules after plasma treatment.

Further investigation on fabrication of partial hydro/superhydrophobic filler (Janus fillers) is recommended. More specifically the emphasis will be towards understanding and improving WVTR and also the inclusion of Janus particles in the manufactured handsheets. Finally, understanding and quantifying the fluorine penetration depth into the paper after plasma treatment is recommended.

BIBLIOGRAPHY

- 1. Baker, C.F. (2005). Emerging Technol. For Fillers and Pigments, Pira Intl, Surrey, UK.
- Balu, B., Breedveld, V., Hess, D.W. (2008). Fabrication of "Roll-off" and "Sticky" Superhydrophobic Cellulose Surfaces via Plasma Processing, *Langmuir*, 24, 4785-4790.
- Balu, B., Kim J.S., Breedveld, V., Hess, D.W. (2009). Design of Superhydrophobic Paper/Cellulose Surfaces via Plasma Enhanced Etching and Deposition, *Contact Angle, Wettability and Adhesion*, 6, 235-249.
- Balu, B., Kim, J. S., Breedveld, V., Hess, D. W. (2009), Tunability of the adhesion of water Drops on a superhydrophobic Paper Surface via Selective Plasma Etching, *J. of Adhesion Science and Technology*, 23, 361-380.
- Balu, B. (2009). Plasma Processing of Cellulose Surfaces and Their Interactions with Fluids, Georgia Institute of Technology, USA.
- Bittoun, E., Marmur, A. (2009). Optimizing Super-Hydrophobic Surfaces: Criteria for Comparison of Surface Topographies. *Journal of Adhesion Science and Technology*, 23, 401-411.
- Carlsson, C.M.G., Strom, G. (1991). Reduction and Oxidation of Cellulose Surfaces by Means of Cold-Plasma. *Langmuir*, 7(11), 2492-2497.
- 8. Cassie, A.B.D., Baxter, S. (1944), Wettability of Porous Surfaces, *Transactions of the Faraday Society*, 40, 546-551.
- Cheng, Y.T., Rodak, D.E., Wong, C.A., Hayden, C.A. (2006). Effects of Micro- and Nano-Structures on the Self-Cleaning Behaviour of Lotus Leaves. *Nanotechnology*, 17, 1359– 1362.
- Cho, S.C., Hong, Y.C., Cho, S.G., Ji, Y.Y., Han, C.S., Uhm, H.S. (2009), Surface Modification of Polyimide Films, Filter Papers, and Cotton Clothes by HMDSO/Toluene Plasma at Low Pressure and Its Wettability, *Current Applied Physics*, 9, 1223-1226.
- 11. Ciolacu, D., Ciolacu, F., Popa, V.I. (2011). Amorphous Cellulose-Structure and Characterization. *Cellulose Chem. Technol.*, 45(1-2), 13-21.
- 12. Courbin, L., Stone, H.A. (2007). Your Wetting Day. Physics Today, 84-85.

- Feng, L., Li, S., Li, Y., Li, H., Zhang, L., Zhai, J., Song, Y., Liu, B., Jiang, L., Zhu, D. (2002). Super-Hydrophobic Surfaces: From Natural to Artificial. *Advanced Materials*, 14 (24), 1857-1860.
- Ferrero, F., Bongiovanni, R. (2006), Improving the Surface Properties of Cellophane by Air Plasma Treatment. *Surface & Coatings Technology*, 200 (16-17), 4770-4776.
- Gaiolas, C., Belgacem, M.N., Silva, L., Thielemans, W., Costa, A.P., Nunes, M., Silva, M.J.S. (2009). Green Chemicals and Process to Graft Cellulose Fibres, *Journal of Colloid* and Interface Science, 330(2), 298-302.
- Gao, L., McCarthy, T.J. (2006). Contact Angle Hysteresis Explained. *Langmuir*, 22 (14), 6234-6237.
- Gao, L.C., McCarthy, T.J. (2006). The "Lotus Effect" Explained: Two Reasons Why Two Length Scales of Topography Are Important. *Langmuir*, 22 (7), 2966-2967.
- Gao, L.C., McCarthy, T.J. (2006). "Artificial Lotus Leaf" Prepared Using a 1945 Patent and Commercial Textile. *Langmuir*, 22 (14), 5998-6000.
- Gao, L., McCarthy, T.J. (2007). How Wenzel and Cassie Were Wrong. *Langmuir*, 23 (7), 3762-3765.
- Gill, R. A. (1995). Modified filler material for alkaline paper and method of use thereof in alkaline paper making, U.S. Patent 5,380,361, Jan.10th.
- 21. Gill, R. A. (2000), Surface modified fillers for sizing paper, U.S. Patent 6,126,783, Oct.3rd.
- Goncalves, G., Marques, P.A.A.P., Trinadade, T., Neto, C.P., Gandini, A. (2008). Superhydrophobic Cellulose Nanocomposites. *Journal of Colloid and Interface Science*, 324 , 42-46.
- Groenendijk, M. (2008). Fabrication of Super Hydrophobic Surfaces by fs Laser Pulses. Macro Material Processing, 44-48.
- Hong, L., Jiang, S., Granick, S. (2006). *Simple* Method to Produce Janus Colloidal Particles in Large Quantity. *Langmuir*, 22, 9495-9499.
- Hu, Z., Zen, X., Gong, J., Deng, Y. (2009). Water Resistance Improvement of Paper by Superhydrophobic Modification with microsized CaCO₃ and Fatty Acid Coating. *Colloids and Surface A: Physicochem. Eng. Aspects*, 351, 65-70.

- Hu, Z., Deng, Y. (2010), Superhydrophobic Surface Fabricated from Fatty Acid-Modified Precipitated Calcium Carbonate. *Ind. Eng. Chem. Res.* 49, 5625-5630.
- Huang, L., Chen, K., Lin, C. Yang, R., Gerhardt, R.A. (2011). Fabrication and Characterization of Superhydrophobic high opacity paper with titanium dioxide nanoparticles. *J. Mater Sci.*, 46, 2600-2605.
- Im, M., Im, H., Lee, J.H., Yoon, J.B., Choi, Y.K. (2010). Analytical Modeling and Thermodynamic Analysis of Robust Superhydrophobic Surfaces with Inverse-Trapezoidal Microstructures. *Langmuir*, 26(22), 17389-17397.
- Jiang, S., Granick, S. (2009). A simple Method to produce Trivalent Colloidal Particles. Langmuir, 25(16), 8915-8918.
- 30. Johnson, R.E., Dettre, J.R., Dettre, R.H. (1969). Wettability and Contact Angles. *Surface and Colloidc Science*, 2.
- Johnson, Jr., Dettre, R.E., Dettre R.H. (1964). Contact Angle Hysteresis. 3. Study of an Idealized Heterogeneous Surface. *Journal of Physical Chemistry*, 68 (7),1744-1750.
- Johnson, Jr., Dettre, R.E., Dettre R.H. (1964). Contact Angle Hysteresis. I. Study of an Idealized Rough surface, in *Contact Angle, Wettability and Adhesion. Adv. Chem. Ser.*, R.F. Gould, Editor. Amer. Chem. Soc., Washington D.C.,112-135.
- Kietzig, A.M., Hatzikirakos, S.G., Englezos P. (2009). Patterned Superhydrophobic Metallic Surfaces. *Langmuir*, 25 (8), 4821-4827.
- Kietzig, A.M., Mirvakili M.N., Kamal, S., Englezos, P., Hatzikiriakos, S.G. (2011). Laser Patterned Super-Hydrophobic Pure Metallic Substrates: Cassie to Wenzel Wetting Transitions. *Journal of Adhesion Science and Technology*, 25, 2789-2809.
- 35. Kurrle, F.L. (1996). Process for enhancing sizing efficiency in filled papers, U.S. Patent 5,514,212, May. 7th.
- Lai, S. (2003). Mimicking Nature: Physical Basis and Artificial Synthesis of the Lotus-Effect.
- Larsson P.A., Wagberg L. (2009). Highly Hydrophobic Paper Surfaces by Wax Adsorption onto Polyelectrolyte Multilayer Treated Fibres. 7th International Paper and Coating Chemistry Symposium, 299-300.

- Liu, B., He, Y., Fan, Y., Wang ,X. (2006). Fabricating Super-Hydrophobic Lotus-Leaf-Like Surfaces through Soft-Lithographic Imprinting. *Macromolecular Rapid Communication*, 27 , 1859-1864.
- Ma,M., Hill,R.M. (2006). Superhydrophobic Surfaces. Colloid & Interface Science, 193-202.
- 40. Marmur, A. (2006). Soft Contact: Measurment and Interpretation of Contact Angles. *The Royal Society of Chemistry, Soft Matter*, 2, 12-17.
- Mesic, B., Kugge, C., Jarnstrom, L. (2010). Superhydrophobic Paper Coating Containing Non-Conventional Clay. *TAPPI 11th Advanced Coating Fundamentals Symposium*, Oct. 11-13, Munich, Germany.
- Modgi, S., McQuaid, M., Englezos, P. (2006). SEM/EDX analysis of Z-direction distribution of mineral content in paper along the cross-direction. *Pulp & Paper Canada*, 107 (5), 48-51.
- Modgi, S., McQuaid, M.E., Englezos, P. (2006). SEM/EDX Analysis: A Technique for Z-Direction Mineral Topography in Paper, *Nordic Pulp and Paper Research Journal*, 21(5), 132-137.
- Montgomery, J. (2010). The Role of Suction Boxes on Forming Section Retention and Filler Migration, University of British Columbia, Vancouver, B.C.
- 45. Mott- Smith, H.M. (1971), History of "Plasma". Nature, 233, 219-219.
- Mukhopadhyay, S.M., Joshi, P., Datta, S., Macdaniel, J. (2002). Plasma Assisted Surface Coating of Porous Solids. *Applied Surface Science*, 201 (1-4), 219-226.
- Mukhopadhyay, S., Fangueiro, R. (2009). Physical Modification of Natural Fibres and Thermoplastic Films for Composites- a Review. *Journal of Thermoplastic Composite Materials*, 22(2), 135-162.
- Navarro, F., Davalos, F., Denes, F., Cruz, L.E., Young, R.A., Ramos, J. (2003). Highly Hydrophobic Sisal Chemithermomechanical Pulp (Ctmp) Paper by Fluorotrimethylsilane Plasma Treatment. *Cellulose*, 10 (4), 411-424.
- 49. Neimo, L. (1999). "Papermaking Chemistry (Book 4)," In: Papermaking Science and Technology, Gullichsen, J., and Paulapuro, H. (Ed.s), Finish Paper Engineers' Association and Tappi, Helsinki.

- 50. Neinhuis, C., Barthlott, W. (1997). Characterization and Distribution of Water-Repellent, Self-Cleaning Plant Surfaces, *Annals of Botany*, 79, 667-677.
- Niinikoshi, M., Malmstrom, O., Nurminen, M., Sundberg, K., Zetter, C. (2007). Method for Pretreatment of Filler, Modified Filler with a Hydrophobic Polymer and Use of the Hydrophobic Polymer, U.S. Patent 7, 211, 608, May.1st.
- 52. Norgren S., Hans, H. (2008). Moisture-induced surface roughness in TMP sheets. *Journal of Pulp and Paper Science (JPPS)*, 34 (3), 139-146.
- Ogihara, H., Xie, J., Okagaki, J., Saji, T. (2012). Simple method for preparing superhydrophobic paper: spray-deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency. *Langmuir*, 28(10), 4605-4608.
- 54. Otten, A., Heminghaus, S. (2004). How Plants Keep Dry: A Physicist's Point of View. Langmuir, 20 (6), 2405-2408.
- 55. Perro, A., Reculusa, S., Ravaine, S., Bourgeat-Lami, E. Duguet, E. (2005). Design and synthesis of Janus micro- and nanoparticles, *J. Mater. Chem.*, 15, 3745–3760.
- 56. Pykonen, M., Johansson, K., Dubreuil, M., Vangeneugden, D., Strom, G., Fardim, P., Toivakka M. (2010). "Evaluation of Plasma-Deposited Hydrophobic Coatings on Pigment-Coated Paper for Reduced Dampening Water Absorption", *J. of Adhesion Science and Technology*, 2010, 24, 511-537.
- Quan, C., Werner, O., Wagberg, L., Turner, C. (2009). Generation of Superhydrophobic Paper Surfaces by a Rapidly Expanding Supercritical Carbon Dioxide-Alkyl Ketene Dimer Solution. *Journal of Supercritical Fluids*, 49 (1), 117-124.
- 58. Quere, D., Lafuma, A., Bico, J. (2003). Slippy and Sticky Microtextured Solids. *Nanotechnology*, 14, 1109-1112.
- Rankin, P., Luukkonen, K., Lindstrom, M. (2000). Options for Soft Sizing of Mechanical Papers. *TAPPI Papermakers Conference*, Vancouver, BC, Canada, Apr. 16th-19th.
- Roberts, J. C. (1996), Neural and alkaline sizing. *In: Paper Chemistry*. Roberts J. C. (ed.), Glasgow, Blackie Academic & Professional, ISBN 0 7514 0236 2, pp. 140-160.
- Sahin, H.T., Manolache, S., Young, R.A., Denes, F. (2002). Surface Fluorination of Paper in CF₄-RF Plasma Environments. *Cellulose*, 9(2), 171-181.

- 62. Sahin H. T. (2007). RF-CF4 Plasma Surface modification of paper: chemical evaluation of two sidedness with XPS/ATR-FTIR, *J. of Applied surface science*, 2007, 253, 4367-4373.
- Salmah, H., Ruzaidi, C.M., Supri, A.G. (2009). Compatibilisation of Polypropylene/ Ethylene Propylene Diene Terpolymer/Kaolin Composites: The Effect of Maleic Anahydride-Grafted-Polypropylene. *Journal of Physics Sciences*, 20(1), 99-107.
- Sang, Y., McQuaid, M., Englezos, P. (2011). Optimization of Chemical Use for Highly Filled Mechanical Grade Papers with Precipitated Calcium Carbonate. *BioResources*, 6(1), 656-671.
- 65. Sapieha, S., Wrobel, A.M., Wertheimer, M.R. (1988). Plasma-Assisted Etching of Paper. *Plasma Chemistry and Plasma Processing*, 8(3): p. 331-346.
- Sapieha, S., Verreault, M., Klemberg-Sapieha, J.E., Sacher, E., Wertheimer, M.R. (1990), X-Ray Photoelectron Study of the Plasma Fluorination of Lignocellulose. *Applied Surface Science*, 44(2), 165-169.
- 67. Sharma, S., Bash, W. (1998). Talc as a Dye-Extender in Colored Papers. *TAPPI Coating Conference Proceedings*. Atlanta, GA: TAPPI Press.
- Shen, J., Song, Z., Qian, X., Liu, W. (2009). Modification of Papermaking Grade Fillers: A Brief Review. *BioResources* 4(3), 1190-1209.
- 69. Shen, J., Qian, X. (2012). Use of Mineral Pigments in Fabrication of Superhydrophobically Engineered Cellulosic Paper. *BioResources*, 7(4), 4495-4498.
- 70. Smook, G.A., *Handbook for Pulp & Paper Technologists*. 3rd ed. 2002, Vancouver. B.C.: Angus Wilde Publications Inc.
- 71. Stamboulides C. (2010). Microscopic Ice Friction of Polymeric Substrates, University of British Columbia, Vancouver, B.C.
- Swerin A., Wahlander M., Fundamental and Applied Aspects of Superhydrophobicity in Papermaking and Packaging, 7th International Paper and Coating Chemistry Symposium, 301-304 (2009).
- Tejado A., De Ven, T.,G.M.V., Effect of Fibre Hydrophobicity on the Wet Web Strength of Paper, 7th International Paper and Coating Chemistry Symposium, 83-90 (2009).
- Tischer, P.C., Sierakowski, M.R., Westfahl, H. Jr., Tischer, C.A. (2010). Nanostructural Reorganization of Bacterial Cellulose by Ultrasonic Treatment. *Biomacromolecules*, 11(5), 1217-24.
- 75. Tu, X., Young, R.A., Denes, F., Improvement of Bonding between Cellulose and Polypropylene by Plasma Treatment. *Cellulose*, 1994. 1(1), 87-106.
- Tuteja, A., Choi, W., McKinley, G. H., Cohen, R. E., Rubner, M. F., Design parameters for superhydrophobicity and superoleophobicity, *MRS Bulletin*, 33, 752-758 (2008).
- 77. Vaino, A.K., Paulapuro, H. (2007). Interfibre Bonding and Fibre Segment Activation in Paper. *BioResources*, 2(3), 442-458.
- Vaswani, S., Koskinen, J., Hess, D.W. (2005). Surface Modification of Paper and Cellulose by Plasma-Assisted Deposition of Fluorocarbon Films. *Surface & Coatings Technolog*, 195(2-3), 121-129.
- Wagterveld, R.M., Berendsen, C.W.J., Bouaidat, S., Jonsmann, J. (2006). Ultralow Hysteresis Superhydrophobic Surfaces by Excimer Laser Modification of SU-8. *Langmuir*, 22, 10904-10908.
- Wang, F., Tanaka, H. (2000). Aminated Poly-N-Vinylformamide as a Modern Retention Aid of Alkaline Paper Sizing with Acid Rosin Sizes. *Journal of Applied Polymer Science*, 78(10), 1805-1810.
- Wang, R. K. (2006). in Science. Technology and Education of Microscopy: an overview, 1, 10.
- Wenzel, R.N. (1936), Resistance of Solid Surface to Wetting by Water. *Ind. Eng. Chem.*, 28, 988-994.
- 83. Wertheim.Mr, Suranyi, G., Goring, D.A.I. (1972). Improvement in Bonding Properties of Cellulose and Polyethylene by Treatment in a Microwave Discharge. *Tappi*, 55(12), 1707.
- 84. Wilson, I. (2006), Industrial Minerals & Rock Commodities, Markets, & Uses. 7th Edition, Kogel J.E., Trivedi N.C., Barker J.M., Krukowski S. T. (Ed.s); *Society for Mining and Exploration, Inc.*
- Wolansky, G., Marmur, A. (1999). Apparrent Contact Angles on Rough Surfaces: the Wenzel Equation Revisited. *Colloids and surfaces*, 156, 381-388.

- 86. Yang, H., Deng, Y. (2008). Preparation and Physical Properties of Superhydrophobic Papers. *Journal of Colloid and Interface Science*, 325 (2), 588-593.
- Yeh, K.Y., Chen, L.J. (2008). Contact Angle Hysteresis on Regular Pillar-like Hydrophobic Surfaces. *Langmuir*, 24, 245-251.
- 88. Yoon, S.Y., Deng Y. (2006). Starch-fatty complex modified filler for papermaking. *TAPPI Journal*, 5 (9), 3-9.

APPENDIX A: ADVANCING AND RECEDING CAS, AND STATIC CAS

Filler		Felt Side		Wire Side				
Concentration	on PCC Talc		Clay	PCC Talc		Clay		
25	139 ± 2.1	129 ±4.6	99 ± 12.7	145 ± 2.1	141 ± 2.2	140 ± 3.6		
35	137 ± 2.7	127 ± 2.4	80 ± 19.5	142 ± 1.1	139 ± 3.2	117 ± 8.4		
45	133 ± 2.3	123 ± 3.9	77 ± 16	132 ± 4.1	138 ± 3	124 ± 7.2		

Table A.1: Static CAs on handsheets: Containing starch, O2 treatment of 20min, CF4 flowrate of 40cm3/min

Table A.2: Static CAs on handsheets: Containing starch, O₂ treatment of 15min, CF₄ flowrate of 40cm³/min

Filler		Felt Side		Wire Side			
Concentration	Concentration PCC Talc		Clay	РСС	Talc	Clay	
25	135 ± 7.7	112 ± 4.4	81 ± 18	148 ± 5.2	140 ± 8	118 ± 11.2	
35	124 ± 5.1	102 ± 5.4	65 ± 34.5	144 ± 7.8	127 ± 5	113 ± 7.1	
45	120 ± 8.8	94 ± 14.3	57 ± 45.16	140 ± 5.1	117 ± 10.8	100 ± 14	

Table A.3: Static CAs on handsheets: Without starch, O₂ treatment of 20min, CF₄ flowrate of 40cm³/min

Filler		Felt Side		Wire Side			
Concentration PCC		Talc	Clay	РСС	Talc	Clay	
25	138 ± 2.6	133 ± 3.7	125 ± 5.3	148 ± 3.1	147 ± 1.8	132 ± 9.7	
35	136 ± 2	129 ± 4.2	63 ± 13	144 ± 1.8	144 ± 3.6	130 ± 6.4	
45	132 ± 3.3	124 ± 2.1	121 ± 6.4	143 ± 1.5	143 ± 2.9	99 ± 17.9	

Table A.4: Static CAs on handsheets: Without starch, O2 treatment of 15min, CF4 flowrate of 40cm3/min

Filler		Felt Side		Wire Side			
Concentration	РСС	Talc	Clay	РСС	Talc	Clay	
25	145 ± 3.1	141 ± 3.2	126 ± 3.8	146 ± 4.1	142 ± 2.9	131 ± 1.8	
35	143 ± 2.3	137 ± 2.7	116 ± 9.7	141 ± 3.2	140 ± 0.8	128 ± 2.8	
45	140 ± 5.5	132 ± 2.5	112 ± 12.9	137 ± 3.7	139 ± 2.7	126 ± 2.6	

Filler		Felt Side		Wire Side			
Concentration	ntration PCC Talc		Clay	РСС	Talc	Clay	
25	148.5 ± 2	145.1 ± 2.04	145.2 ± 1.96	139.4 ± 4.58	140.5 ± 3.03	116.04 ± 14.89	
35	143.9 ± 2.06	141.2 ± 2.88	101.2 ± 13.84	133.5 ± 1.24	137.2 ± 4.83	100.2 ± 12.81	
45	141.6 ± 2	134 ± 3.57	66.6 ± 12.54	114.6 ± 18.53	134.2 ± 7.58	90.6 ± 14.07	

Table A.5: Static CAs on handsheets: With starch, O2 treatment of 15min, CF4 flowrate of 30cm³/min

Table A.6: Static CAs on handsheets: With starch, O2 treatment of 20min, CF4 flowrate of 30cm3/min

Filler		Felt Side		Wire Side				
Concentration	РСС	Talc	Clay	PCC	Talc	Clay		
25	148.3 ± 1.79	139.9 ± 4.2	104.67 ± 14.45	139.4 ± 3.11	141 ± 2.36	103.5 ± 16.02		
35	146.7 ± 1.39	135.4 ± 4.02	87 ± 13.23	136 ± 1.82	140.6 ± 2.32	99.38 ± 7.14		
45	144.8 ± 2.33	132.5 ± 3.07	82.67 ± 13.82	121.3 ± 5.47	129.2 ± 4.33	86.38 ± 18.2		

Table A.7: Static CAs on handsheets: With starch, O₂ treatment of 20min, CF₄ flowrate of 10cm³/min

РСС		Felt side		Wire side			
	25	35	45	25	35	45	
10sccm/min	141.1	135.7	132.7	127.5	122.3	120.8	

	Dynamic Contact Angles, Felt Side												
Contact angle	РСС			Talc			Clay			E'lan			
	25	35	45	25	35	45	25	35	45	Fibre			
θ _{Adv}	168	159	158	164	164	149	152	125	67	158			
θ _{Rec}	158	153	157	157	154	143	131	99	55	153			
Hysteresis	10	6	1	7	10	6	21	26	12	5			

Table A.8: Dynamic CAs on handsheets: Containing starch, O₂ treatment of 15 min, CF₄ flowrate of 40 cm³/min

	Dynamic Contact Angles, Wire Side												
Contact angle	PCC			Talc			Clay			E'lan			
	25	35	45	25	35	45	25	35	45	Fibre			
θ_{Adv}	144	142	153	165	162	161	161	154	94	158			
θ _{Rec}	135	130	149	158	152	158	151	142	74	155			
Hysteresis	9	12	4	7	10	3	10	12	20	3			

Table A.9: Dynamic CAs on handsheets: Containing starch, O₂ treatment of 20 min, CF₄ flowrate of 40 cm³/min

Dynamic Contact Angles, Felt Side											
Contact angle	РСС			Talc				Ethan			
	25	35	45	25	35	45	25	35	45	<i>F lbre</i>	
θ_{Adv}	163	157	156	157	167	151	134	122	87	151	
θ _{Rec}	157	153	149	144	153	139	114	95	75	150	
Hysteresis	6	4	7	13	14	12	20	27	12	1	

Dynamic Contact Angles, Wire Side											
Contact angle	РСС			Talc			Clay			Ethan	
	25	35	45	25	35	45	25	35	45	F lbre	
θ_{Adv}	163	156	141	158	155	150	168	132	118	162	
$\theta_{\rm Rec}$	159	144	120	151	148	133	158	110	80	160	
Hysteresis	4	12	21	7	7	17	10	20	38	2	

APPENDIX B: TENSILE INDEX FIGURES



Figure B.1: Tensile Index values for all fillers

APPENDIX C: WATER VAPOR TRANSMISION RATES



68



Figure C.1: WVTR values for all handsheets

APPENDIX D: ATR-FTIR SPECTRA



Wavenumber, cm⁻¹



wavenumber, cm-1



Figure D.1: FTIR spectra for all handsheets