Enhanced Barrier Performance of Cellulosic Wood
Fiber/Filler Network

by

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ABSTRACT

Cellulose is an abundant material, which is widely used in papermaking. It is both a biodegradable and sustainable material. However, its hydrophilic nature may limit its applications in specific and novel areas such as waterproof packaging and paper based microfluidics. In this thesis, three different routes are followed to render the surface of the paper superhydrophobic. First, chemical vapor-phase silanization is done on handsheets made from wood pulp with untreated kaolin clay and precipitated calcium carbonate (PCC) as fillers. The effect of fiber length, filler’s type, size, and concentration on the barrier performance of handsheets is shown. Secondly, microfibrillated cellulose (MFC), which serves as reinforcement agent in paper, is employed as an additive to change the hydrophilic property of paper. MFC is silanized to obtain hydrophobicity before being dispersed into the pulp suspension. Then the resulting paper undergoes an additional silanization (post-treatment). The third approach involves depositing Janus clay particles on untreated paper. A Janus particle has a hydrophobic and a hydrophilic surface. Because clay particles are hydrophilic, they are treated to obtain hydrophobicity on one side, while the other side remains hydrophilic. An efficient method to obtain these types of particles is the formation of a Pickering emulsion. The study here, focuses on the determining the barrier properties of the prepared superhydrophobic or hydrophobic papers: wettability, water vapor transmission rate (WVTR), and air permeability. The handsheets with shorter fiber length, precipitated calcium carbonate, smaller filler size and lower filler content, were found to exhibit lower WVTR values. The water contact angle of handsheets loaded with fillers, Janus clay particles and hydrophobic MFC, was found to be 120~130°, 141° and 134~144° respectively.
PREFACE

This dissertation is original, unpublished, independent work by the author, Xianzhong Feng.
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CHAPTER 1. INTRODUCTION

In this chapter the motivation of the study is presented as well as a brief introduction to the main materials used in this work.

1.1 Motivation of the Study

The interest on cellulose-based materials research is growing due to the fact that these materials exhibit biodegradation and renewability and thus are environment-friendly. There is a growing demand for such sustainable industrial and consumer products (Ljungberg, 2007). Cellulose may be obtained from plants, food crops and even bacteria. Cellulose is a fundamental material for paper manufacture. Its application is limited to tissue, printing, food containers and packaging, in part because of the hydrophilic nature of cellulose. This research aims at rendering the cellulose paper hydrophobic and or superhydrophobic through functionalization of filler/additives, such as kaolin clay, precipitated calcium carbonate and microfibrillated cellulose (MFC), with the aid of chemical vapor-phase silanization. The addition of these filler/additives makes a remarkable difference on the microstructure and surface properties of paper, such as porosity, density, and roughness. Combined with the effect of low-surface-energy chemical, dichlorodimethylsilane (DCDMS), the barrier performance can be improved by affecting wettability and permeability of water and air molecules. The effects of fiber size and filler’s type, particle size, content on the barrier properties of paper are also investigated in this study. The papers with improved barrier property have a strong potential in special applications such as waterproof and self-cleaning packages, microfluidic devices and detection of gas and liquid.

1.2 Cellulosic Wood Fiber and Paper

Cellulose is one of the most important natural materials in the world, which derives from wood, plants and bacteria. Wood consisting of cellulose, hemicellulose, lignin and extractives, is the major source of cellulose. The repeating molecular unit of cellulose is \( \beta \)-D-glucopyranose, which forms a linear chain through acetal function between C-1 and C-4 carbon atoms (Figure 1.1) (Figueiredo et al. 2010). There are a large amount of hydroxyl groups existing along the polymeric chain. Thus, cellulose is hydrophilic in nature and capable for chemical modification. Cellulosic molecular chains bound
together through intermolecular hydrogen bonding. Cellulose fibers have crystallographic and amorphous domains. In the crystalline domain, the cellulose chains orient in a parallel form, and behave impermeable to water (Figueiredo et al. 2010). In contrast, the cellulose molecules in the amorphous domain are more dispersible in water and have higher reactivity.

![Chemical structure of cellulose](image)

**Figure 1.1:** Structure of cellulose (Adapted from Figueiredo, 2010)

Cellulose plays an essential role in both people’s daily life and in manufacturing. In comparison with fossil derivative materials, cellulose-based materials are biodegradable, renewable and recyclable. It is the main component in paper, textile, membranes, etc. (Cerruti et al. 2008). Paper and paperboard products consume most of cellulose-based materials all over the world.

It is widely recognized that the original papermaking process was developed in China by Cai Lun around 105 AD. In the modern papermaking industry (Figure 1.2), wood is transformed into pulp after chemical (e.g. Kraft process, sulfite process) and mechanical (e.g. thermomechanical process (TMP), groundwood process (GW)) pulping. Then, the pulp is fed into a papermaking machine and undergoes pressing and drying to form paper sheets. In finishing processes, the obtained paper is modified to alter its chemical and or physical properties to meet the demand of applications. Paper is made into packaging and food containers, printing and writing papers, and sanitary and household papers (McCarthy & Urmanbetova 2011).
Figure 1.2: A schematic of the modern papermaking process (Adapted from www.paperonline.org)

1.3 Fillers and Additives

Except for cellulosic fibers, mineral fillers constitute the second largest component in paper. The most widely used fillers include kaolin clay, calcium carbonate, titanium dioxides, and Talc (Figure 1.3). Conventionally, fillers are added into pulp suspension in the wet end. The addition of fillers lowers the cost of paper manufacturing. The regular price of pulp is around $400-800/ton, while the filler cost of clay and PCC is around $100-200/ton. Besides the cost, the fillers can also help improve the optical properties of paper, such as brightness and printing quality by providing ink adsorption. The water drainage rate will increase as well. However, there are several adverse effects accompanying the addition of fillers. First of all, the paper suffers a loss in strength, since the fillers interfere with the intermolecular hydrogen bonding between fibers. During the wet-end operation, fillers may cause abrasive problems to the machines, and dust hazardous in factory as well.
Although it is cost effective to use more fillers in paper, usually the filler content is up to 50% in paper. In order to retain the fillers when draining water, some polymers are used as additives, such as cationic polyacrylamide (cPAM), and starch (Shen et al. 2009b). With the aid of these polymers, preflocculation of fillers and polymer coating on the surface of fillers happen (Chauhan & Bhardwaj 2014). Thus, the fillers are fixed onto the fibers.

Applying fillers only at the surface of paper via a size press is an alternative to conventional wet-end addition (Shen & Qian 2012). In this process, the fillers are placed onto paper surface and inserted into the existing pores of matrix. Since fillers don’t penetrate into the bulk, the decrease of paper strength is alleviated.

In recent years, there is interest on biodegradable, environmental friendly and recyclable materials, which points to a new demand for filler development. Also, fillers play an essential role in the creation of papers with unique properties. How to efficiently modify the fillers is an ongoing research topic (Shen et al. 2009b). Filler modification brings important properties, such as hydrophobic, magnetic, photocatalytic, flame retardant and deodorizing ability to paper (Shen et al. 2011).

Figure 1.3: Filler used in paper products by grade in 2008 (Adapted from Finnish Forest Industries, 2009)

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<tr>
<th>Filler Description</th>
<th>Percentage</th>
<th>Amount</th>
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<tbody>
<tr>
<td>Kaolin</td>
<td>38%</td>
<td>11.4Mt</td>
</tr>
<tr>
<td>Talc, TiO2 and others</td>
<td>7%</td>
<td>2.1Mt</td>
</tr>
<tr>
<td>Ground Calcium carbonate (GCC)</td>
<td>38.5%</td>
<td>11.5Mt</td>
</tr>
<tr>
<td>Precipitated Calcium Carbonate (PCC)</td>
<td>16.5%</td>
<td>11.5Mt</td>
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<td>16.5%</td>
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1.3.1 Kaolin Clay

Clay is the second largest filler used in paper (after calcium carbonate). It consists of sodium and potassium silicates with metal oxides (e.g. alumina, magnesium oxide) and hydroxide. Tetrahedral and octahedral sheets are two basic crystal structures of clay. Different ratio of these two crystal structures constitutes various types of clay minerals, such as kaolinite (1:1), montmorillonite and illite.

The term “Kaolin” is derived from a hill, named as “Kauling” in China, meaning high ridge. The clay at that location has been mined for ceramics centuries ago (Prasad et al. 1991). The chemical formula of Kaolin clay can be represented as Al₂O₃·2SiO₂·2H₂O. Kaolin clay has a plate-like shape (Figure 1.4) with positive charge at the edge and negative charge on the surface.

**Figure 1.4:** Delamination of kaolin stacks (Adapted from Murray & Kogel, 2005)

Kaolin clay is one of the most versatile raw materials, and can be used in numerous applications, such as paper, coatings, fire proof-materials, ceramics and rubber (Liu et al. 2013). The papermaking industry consumes the largest amount of Kaolin clay for paper coating and filling in US (Prasad et al. 1991). With the aid of Kaolin clay, the smoothness, brightness, printability, fire resistance are improved as well as significant cost savings are realized in the operation (filler is cheaper than fibres).

1.3.2 Calcium Carbonate

Calcium carbonate is considered as dominant mineral filler in the papermaking industry. With the addition of CaCO₃, the paper exhibits enhanced brightness, opacity, and printability. There are two main types of CaCO₃: ground calcium carbonate (GCC)
and precipitated calcium carbonate (PCC). GCC is generally obtained by grinding limestone and chalk from shells of marine life. Its most common crystal structure is rhombohedral. PCC is manufactured by chemical reaction of calcium quicklime slurry and carbon dioxides (as shown below), and performs higher brightness. By controlling the reaction conditions, the characteristics of PCC, such as particle size, particle shape, surface area, and crystal structure can be well designed to meet the demand of a specific application.

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (1-1)
\]
\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (1-2)
\]

PCCs with different crystal structures perform different behavior in paper. When colloidal PCC is applied into pulp suspension, it agglomerates into an ellipsoidal shape and mostly deposits at the end of fibers. In contrast, rhombohedral and scalenohedral type of PCC forms a spider-web structure with fibers (Subramaniana et al. 2007). Thus, the papers loaded with different type of PCCs exhibit significant differences on filler retention, dewatering, density and tensile strength.

However, the chemical nature of PCC limits its use under acidic conditions. Calcium carbonate dissolves in an acidic environment. Precipitated calcium carbonate fillers become acid-resistant, when modified by a treatment with phosphoric acid and sodium hexametaphosphate (Shen et al. 2009a). Compared with unmodified filler, these acid-tolerant fillers can considerably increase the brightness, air permeability of paper, and the retention of filler.

Calcium carbonate is hydrophilic in nature, with a water contact angle close to 0, which results to its poor compatibility with polymer matrix. In order to make hydrophobic CaCO\textsubscript{3} and broaden its applications, surface modification is needed. Generally, polymer grafting, surfactant, and stearic acid are adopted to modify the hydrophilic character of CaCO\textsubscript{3}.

In a modification process, polymer grafting is performed on calcium carbonate particles surface (Wu & Lu 2003). During this process, mechanical energy, provided by stirring, is applied to promote the reaction by producing active sites on the particle surface, the carbonate ions. As a result, the polymer grafting needs less initiating
reactants and the overall reaction time is decreased. In addition, multi-layered grafted polymer on calcium carbonate is achieved. So it offers a fascinating view upon surface modification.

Cationic and anionic surfactants are common chemicals to change the surface charge of fillers. CTAB (hexadecyltetramethylammonium bromide) and sodium oleate can be used to modify calcium carbonate nanoparticles (NPCC) via the wet carbonation technique (Dufresne et al. 2014). After the paper is coated with these cationic or anionic NPCC, several key properties of paper change. The water contact angle increases to 112° for CTAB-NPCC coated paper, while that of ground calcium carbonate-coated paper and oleate-NPCC paper is 104° and 42°, respectively.

Calcium carbonate nanoparticles (NPCC) are hydrophilic in nature. In order to render the surface of these particles hydrophobic, dodecanoic acid (DA) is employed. Ca\(^{2+}\) reacts with DA and forms hydrophobic Ca(C\(_{12}\)H\(_{23}\)O\(_2\))\(_2\), which covers the surface of hydrophilic CaCO\(_3\). By increasing the dosage of DA, the water contact angle of NPCC dramatically increased to 120° (complete coverage) (Chen et al. 2010).

1.3.3 Microfibrillated Cellulose

Microfibrillated cellulose (MFC) is a branch of the cellulose family, described as micro or nano level fibers. MFC may serve as reinforcement additive in papermaking. MFC has a large surface area with hydroxyl groups and can be well dispersed into a pulp suspension. The hydroxyl groups provide possibilities for modification of MFC. If it is reacted with some polymers or organic molecules by proper methods, the hydrophilic property of MFC can be changed to hydrophobicity.

A literature gave a comprehensive review of microfibrillated cellulose (MFC) and provided the definition of microfibrillated cellulose, such that distinguish it from cellulose and nanocellulose (Lavoine et al. 2012). MFC consists of aggregates of 10-50 cellulose microfibrils with a diameter in the range 20-60 nm and a length of several micrometers. This paper also discussed the mechanical and chemical treatment for MFC. The intrinsic properties of MFC are also reported, including morphology, crystallinity and surface chemistry. And the barrier properties, such as water vapor transfer, oxygen...
barrier and hydrophilicity, are emphasized in certain applications, like MFC nanocomposites.

Figure 1.5: Structure of microfibrillated cellulose (Adapted from Lavoine et al. 2012)

Due to the MFC’s hydrophilic nature, a number of nanocomposites can be made through dispersing MFC into hydrophilic matrices uniformly. To extend its application in fabrication of new nanocomposites, various chemical modifications have been explored to change the hydrophilicity of MFC to hydrophobicity (Siro & Plackett 2010). The resulting materials can be well applied into hydrophobic polymers serving as a reinforcement agent. This article also presented many types of cellulose-based nanocomposites and the corresponding fabrication methods.

Cellulose nanocrystals and microfibrillated cellulose have great potential applications in four areas: aerogels, emulsions, templated materials, and stimuli-responsive nanodevices (Tingaut et al. 2012). The characteristics of cellulose-based materials in these fields are also demonstrated. Furthermore, based on the microstructure and performance of the nanocellulose, many functionalization methods are developed to modify its surface, in order to open up new possibilities for application.

1.4 Janus Particles

A Janus particle has two sides of different chemistry or polarity. It is named after a god of the Roman religion. Janus particles of various shapes are divided into three categories: polymeric, inorganic, and polymeric-inorganic. Fabrication methods for these particles include Pickering emulsion interfacial synthesis, self-assembly of block copolymer and phase separation (Liang et al. 2014; Walther et al., 2008). The special structure of Janus particles opens up a door to the applications in fields such as water-

According to the Pickering emulsion route to fabricate Janus particles, untreated particles adsorb at a wax/water interface, and their exposed surfaces towards a continuous phase are chemically modified. Subsequently, the prepared particles are detached from the wax droplets and the inner surfaces undergo further chemical treatment. The chemical modification is done in either liquid or vapor phase (Hong 2006; Jiang et al. 2008). The geometry (Janus balance) of the particles can be controlled by adjustment of the surfactant concentration (Jiang & Granick 2008).

Kalia et al. (2014) studied the surface modification of nanofibrillated cellulose, which shares similar structure with microfibrillated cellulose, despite the difference in length. After modification, the hydrophilic character of nanofibrillated cellulose is changed to hydrophobicity and the compatibility with polymer is enhanced (Kalia et al. 2014). The study demonstrated that nanofibrillated cellulose could be used as reinforcement additive in polymer matrices.

Amphiphilic Janus particles can be applied onto a textile with the hydrophobic side pointing outwards. Larger particles of micrometer size fill in the space between fibers, and smaller particles (submicrometer size) deposit right on the surface of a fiber bundle. The synergistic effect of hydrophobicity and dual roughness contributes to the water-repellent textile (Synytska et al. 2011).

1.5 Pickering Emulsion

Pickering emulsion was first proposed by Pickering in 1907 (Pickering, 1907). By employing mechanical forces, such as agitation, oil can be dispersed into water but without stabilizers, the dispersed oil phase (oil droplets) will soon coalesce and phase separation occurs. However, if solid particles (e.g. silica) are added into the emulsions, a thermodynamically stable emulsion can be obtained. The mechanism behind this phenomenon is that, the oil droplets are covered by solid particles, which play a similar role as a surfactant. The optimum condition to form a Pickering emulsion is that the contact angle of particles is approximately 90°. The energy equation for stabilization is given below:
\[ \Delta E = \pi r^2 \gamma_{ow} (1 - |\cos \theta_{ow}|)^2 \] (1-3)

where \( \Delta E \) is the change of energy when particles adsorb at the oil/water interface, \( r \) is the particle radius, \( \gamma_{ow} \) is the interfacial tension between water and oil, and \( \theta_{ow} \) is the contact angle (Aveyard et al. 2003).

The wetting behavior of solid particles at the oil/water interface is governed by the surface energies of all components in the emulsion system (Binks & Clint 2002). For example, the three phase contact angles of calcium carbonate and hydrophilic silica at the interface of dodecane/water are around 40° (Aveyard et al. 2003).

Many types of fillers have potential to stabilize a Pickering emulsion. These fillers can be organic or inorganic, such as block polymers, clay, silica, and calcium carbonate, with particle size of micrometer to nanometer (Chevalier & Bolzinger 2013). When the water contact angle of the filler is close to 90°, the stability of the resulting Pickering emulsion is the best. Polymer grafting is an option to change the contact angle of inorganic fillers, switching its hydrophilicity to slight hydrophobicity.

Laponite RD, which is synthetic clay, is used to prepare Pickering emulsion. And in a next step, polymerization of styrene can be proceeded in the dispersed oil phase (Cauvin et al. 2005). These disc-like clay particles with negative surface charge can stabilize an oil-in-water emulsion (Guillot et al. 2009). And the three-phase contact angle is slightly lower than 90°, which serves as a requisite of Pickering emulsion stability. The addition of salt favors the flocculation of clay and contributes to the stability of Pickering emulsion (Ashby & Binks 2000). The diameter of oil droplet is submicron.

In addition to inorganic fillers, some carbohydrate-based particles, such as cellulose nanocrystals and hydrophobically modified starch microparticles can stabilize Pickering emulsions (Dickinson 2012). Several researchers investigated improved stabilization of Pickering emulsions by using hydrophobic microfibrillated cellulose (MFC) (Lif et al. 2010; Andresen & Stenius 2007; Rein et al. 2012), nanofibrils (Klodian Xhanari et al. 2011), starch-based nanosphere (Tan et al. 2012), and polymer grafted cellulose nanocrystals (Zoppe et al. 2012). Their studies also covered the influence of particle concentration, oil/water ratio, and degree of hydrophobization of cellulose/starch on the stability of the Pickering emulsion (K. Xhanari et al. 2011). In recent years, cellulose
nanocrystals derived from plant, and bacterial sources are found to stabilize Pickering emulsions without hydrophobization, since the crystalline region of cellulose is amphiphilic in comparison with the amorphous one (Kalashnikova et al. 2011; Wen et al. 2014). In further study, it is shown that surface charge density (SCD) of cellulose nanocrystals plays a significant role in the stabilization. Cellulose nanocrystals with SCD below 0.03 e/nm$^2$ are able to act as stabilizers (Kalashnikova 2012).

In a Pickering emulsion, many literatures assume that the solid particles uniformly distribute at the interface of oil/water and form monolayer coverage. However, based on a study on the morphology of microparticles at Pickering emulsion interface, it is shown that aggregated structure exist as well (Dai et al. 2008). The extent of agglomeration depends on the concentration and chemistry of particles.

The properties of Pickering emulsion are function of factors, such as surface energy of components, oil-to-water volume ratio, physical properties, and the concentration of particles, surfactant, and electrolyte (Aveyard et al. 2003).

As mentioned at the beginning of this section, in a Pickering emulsion, the oil droplets are encapsulated by solid particles. However, this may not be sufficient to form a long-term stable emulsion system. If the particles self-assemble a framework (like a gel) in the continuous phase (water), driven by the surface charge, the viscosity of emulsion will be enhanced and the network can protect the dispersed phase (oil) from coalescence (Thieme et al. 1999). This phenomenon is observed in Pickering emulsion stabilized by clay (Chen et al. 2011). The disc-like clay forms a card-house-like structure in water phase and favors the stability of emulsion.

At the beginning of the preparation of a Pickering emulsion, mixing is essential to disperse oil in water well. However, after the emulsion is stable, simple shear flow may destabilize the system, due to the disruption of the droplet-particle network (Whitby et al. 2011). Thus, it is better not to apply mixing after the emulsifying stage.

Different oil-to-water ratio results in different state, such as O/W emulsion, W/O emulsion and powdery state (Nonomura & Kobayashi 2009). Phase inversion occurs when the oil-to-water ratio changes (e.g. the addition of extra water). Among these states, O/W emulsion without separation of excess oil and water is regarded as the optimum
state in this study. Caifu Li et al. (2009) used Laponite clay to stabilize a paraffin wax/water Pickering emulsion. It is reported that, the proper oil/water ratio ranges from 3:7 to 7:3, which is a relatively wide range (Li et al. 2009).

The optimum oil-to-water ratio to prepare stable Pickering emulsion depends on the nature of particle solids. Hydrophilic particles favor the formation of an oil/water (O/W) emulsion, while hydrophobic particles favor the formation of a water/oil (W/O) emulsion (Aveyard et al. 2003). Partially hydrophobic particles are able to stabilize both O/W and W/O emulsions. The selection of oil affects the type of emulsion as well.

It is common that the size of oil droplet reduces when increasing the concentration of solid particles. However, there is no obvious relation between the extent of particle adsorption at the interface and the stability of the emulsion. Even at very low surface coverage of droplet, stable emulsion can be formed (Vignati & Piazza 2003).

Surfactant, like Tween 60 and Sodium Caseinate, can be added into a Pickering emulsion, serving as co-emulsifier. The surfactant decreases the surface tension of water, and promotes the break and dispersion of oil droplets. Thus, the O/W emulsion has higher long-term stability and smaller size of droplets. More hydrophilic silica particles are adsorbed at the interface between oil and water, due to higher surface area of oil droplets. However, much too high concentration of surfactant may lead to the displacement of particles at the interface (Pichot et al. 2010). The interaction between particles and surfactant also influences the structure and the stability of Pickering emulsion (Whitby et al. 2008; Whitby et al. 2009; Wang et al. 2010).

The addition of salt, such as sodium chloride, also affects the stability of Pickering emulsion. When increasing the salt concentration, the zeta potential of particles decreases, and the flocculation of particles both at the interface and in the suspension are favored (Yang et al. 2006). But the three phase contact angle of particles barely changes.

1.6 Silanization

The silane agent involved in this research refers to the compounds containing silicone, fatty groups and chloride/ethoxyl. It has a relatively low surface energy and can be used to functionalize cellulose and fillers, in order reduce their hydrophilic character. The process of performing chemical modification with a silane agent on hydrophilic
substrates is defined as silanization. After silanization, the treated samples obtain higher water contact angle and lower moisture adsorption.

The grafted quantity of a silane agent on a cellulosic fiber surfaces depends on the chemical structure and the initial concentration of silane (Rachini et al. 2012). It is shown that higher concentration results to higher grafted quantity. A silane agent with amino group may cause higher grafted quantity, due to the hydrogen bonding between the –NH₂ and the hydroxyl groups on the fiber (Rachini et al. 2012; Ifuku & Yano 2015).

In a recent study, three different types of silanes (PFDTES, MODDCS, and DCDMS) were used to treat filter paper through a solution-immersion process and chemical vapor deposition (Oh et al. 2011). Reaction time and silane concentration are considered as the two experimental factors. After sufficient reaction with dichloro-dimethylsilane (DCDMS), the filter paper has a water contact angle ranging from 120° to 130°.

Compared with doing silanization in liquid-solid system, a solvent-free process is remarkably simple and efficient. Chlorosilanes with low boiling point provide the possibility of vapor-phase silanization. Especially, trichloromethylsilane (TCMS) and dichloro-dimethylsilane (DCDMS) are volatile and capable in modifying the fiber/filler surface at modest conditions, such as room temperature and atmospheric pressure (Cunha et al. 2010; Jiang et al. 2008). In this study, DCDMS is adopted as the silane agent.

![Figure 1.6: Schematic of silanization on hydrophilic surface by DCDMS](image)

**1.7 Criteria for Superhydrophobic Surface**

The idea of a superhydrophobic surface comes from the Lotus leaf surface, which exhibits extreme water-repellency and self-cleaning properties (Barthlott & Neinhuis 1997; Neinhuis 1997). Superhydrophobicity refers to a water contact angle larger than 150°, with a contact angle hysteresis less than 10° (Yan et al. 2011; Latthe et al. 2014).
The wettability of a surface depends on the chemical nature of material and the surface roughness. To establish a superhydrophobic surface, low surface energy and dual sale roughness are both required. Generally, the approach to fabricate a superhydrophobic surface is either enhancing the surface roughness of a hydrophobic surface, or coating low-surface-energy chemicals on a rough surface (Li et al. 2007). The water barrier property of the surface is assessed through the measurement of the water contact angle, water vapor transmission rate, and oxygen transmission rate.

In the paper manufacturing industry, surface treatment is mainly referred to as sizing, generally including internal and external sizing. In an external sizing process, polymer-based hydrophobic particles are dispersed in starch solution. Then the hydrophobic particles deposit onto untreated papers through a dip-coating process. The loading of particles on paper is highly dependent on the type of surface charge, which is responsible for the interactions between hydrophobic particles and negatively charged starch (Iselau et al. 2015).

Stanssens et al. (2011) utilized a coating material to fabricate hydrophobic papers. They synthesized an organic nanoparticle, partially imidized poly(styrene-co-maleimide), under pure conditions and in palm oil solvent. Then the nanoparticle is deposited onto paper, followed by further thermal curing, to achieve outstanding hydrophobic performance (Stanssens et al. 2011). The nanoparticles formed in oil provide better water repellency. The water static contact angle reaches 148°. The water droplets can roll off the surface giving rise to the self-cleaning property.

Gao et al. (2015) developed a superhydrophobic film on the surface of filter paper. In their work, TiO₂ is adhered onto paper, and provides both micro and nano structures. Then the paper is coated by octadecyltrichlorosilane, which serves as a low surface energy agent (Gao et al. 2015). The resulting paper has a water contact angle of 153° and the oil contact angle of 135°.

Mirvakili et al. (2013) applied plasma enhanced chemical vapor deposition (PECVD) to make superhydrophobic handsheet consisting of cellulose and filler (Mirvakili et al. 2013). The results show that the wettability of a handsheet is highly affected by oxygen plasma etching, which increases the roughness before fluorocarbon deposition. Moreover,
the contact angle is also a function of the fiber length and the filler properties. Although oxygen etching resulted in high water repellency of handsheets, it adversely affects its strength properties.

Glavan et al. (2014) reported an omniphobic paper prepared by fluoroalkyltrichlorosilanes. The water contact angle of this paper is higher than 140°. In addition, it resists to a variety of liquids, such as organic liquids, aqueous solutions, and even blood (Glavan et al. 2014). Based on their work, the molecular length and fluorination degree of organosilane have a large effect on the liquid-resistant property of the paper. After silanization, the mechanical flexibility of the paper is retained and thus the papers can be folded into any desired shapes for certain application, such as gas sensor. Interestingly, this technology is much less expensive than the advanced hydrophobic treatment of Gore-Tex and Nafion.

1.8 Wettability

Wettability of smooth surface

Consider a liquid droplet is placed on a smooth solid surface statically. The contact angle \( \theta \) is defined as the angle between the solid-liquid interface and the tangent line of the droplet contour curve at the three-phase interface, as shown in Figure 1.7. This angle depends on the adhesion between the liquid and solid. The higher the adhesion, the lower the contact angle. If the contact angle is larger than 90°, the surface is non-wetting. And if the liquid is water, the surface of solid is known as hydrophobic. In extreme case, when the water contact angle approaches 180°, superhydrophobic or perfectly dewetting performance exists.

The contact angle \( \theta_Y \) can be expressed by Young-Laplace equation as shown below. The interfacial surface tension between solid-vapor, liquid-vapor and solid-liquid are represented as \( \gamma_{sv}, \gamma_{vl}, \) and \( \gamma_{sl} \) respectively (Groenendijk, 2008).

\[
\cos \theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{vl}}
\]
Wettability of rough surface

If the solid surface is rough, the Young-Laplace equation is not applicable any more. Here the surface roughness factor $\omega_r$ is introduced to correct the above equation. It is defined as the ratio of effective, non-linear length of the surface profile and the linear length between two points. For a flat surface, the roughness term equals to 1.

\[
\omega_r = \frac{l_{eff}}{l} \tag{1-5}
\]

**Wenzel model** (Wenzel, 1936): there is no air trapped between the liquid and the rough solid face, which means that the liquid droplet fills up all the grooves on solid surface. Then the corrected contact angle $\theta^*$ is shown as:

\[
\cos \theta^* = \omega_r \times \cos \theta_Y \tag{1-6}
\]

**Cassie-Baxter model** (Cassie, 1944): some air is trapped in the grooves between the liquid and solid surface, due to very high roughness. Then the contact angle $\theta_{CB}^*$ is as follows:

\[
\cos \theta_{CB}^* = -1 + f_s \times (\cos \theta_Y + 1) \tag{1-7}
\]

where $f_s$ is the fraction of the solid surface in contact with liquid.

To decide whether the Wenzel or the Cassie-Baxter model is applicable, the critical roughness $\omega_{r,cr}$ is needed. If $\omega_r > \omega_{r,cr}$, Cassie-Baxter model applies. In the following equation, the contact angle is given by eq. (1-4).

\[
\omega_{r,cr} = 1 + \frac{\tan^2 \theta_Y}{4} \tag{1-8}
\]
1.9 Applications in Packaging and Fundamental Device

Cellulose based materials are widely used in packaging, as they are both environmentally friendly and cost-efficient. In some specific cases, such as packaging, the barrier properties of the cellulosic materials are always under concern. The packaging materials are required with low water vapor and air permeability as well as water repellency. These properties highly depend on the chemistry and microstructure of the papers.

Besides traditional use in packaging, hydrophobic paper can be designed as microfluidic device (Renault et al. 2013) and for oil/water separations (Gao et al. 2015). By selectively modifying the surface properties of paper (hydrophilic or hydrophobic), the patterned paper can be used to trap chemical and biological liquid for analysis (Chitnis et al. 2011).
CHAPTER 2: THESIS OBJECTIVES

Packaging is an important application that paper is used. In some specific applications, water repellent packaging materials are needed and the traditional way is to use wax to create a hydrophobic surface. Despite its low cost, wax hampers the recyclability of paper used in these applications. As a result, there is a need for fabrication methods of hydrophobic/superhydrophobic papers driven by sustainability considerations.

Rendering paper hydrophobic is expected to broaden its applications. In this research, the main goal is to prepare hydrophobic paper through three different routes engaging fillers, MFC and silanization. One of the challenges here is how to obtain Janus hydrophobic/hydrophilic particles.

So the key point of this research is to apply hydrophilic fillers, hydrophobic MFC and Janus particles into pulp/paper. During the process, silane, which serves as low surface energy agent, is used to modify the fillers, MFC and paper. After that, the study will explore the barrier properties of the resulting papers. The water contact angle, water vapor, and air permeability, will be measured to assess the barrier properties of the paper.

The objectives of the present study are:

1. Prepare handsheets loaded with mineral fillers and then apply a silanization treatment of the handsheets. Determine the effect of fiber size, filler properties (filler type, size, content) and silanization on the barrier performance of the handsheets (wettability, water vapor resistance and air permeability).

2. Prepare hydrophobic MFC and deposit it onto the surface of paper and then apply silanization. Determine how the loading of hydrophobic MFC affects the wettability of paper.

CHAPTER 3: MATERIALS AND METHODS

This following section presents the experimental setups, chemicals used for handsheet preparation and the related measuring equipment. Along with that, the methodology and the characterization technologies will be described as well.

3.1 Materials and Experimental Apparatus

Materials:

Softwood Kraft pulp with different fiber sizes was used to prepare handsheets. The pulp is supplied by a leading pulp mill in British Columbia, Canada. The average fiber size in the pulp suspension is measured using Scircco 2000 Malvern Mastersizer (Malvern Instrument, Malvern, UK). The results of fiber size are reported as a mean diameter of a volume equivalent sphere, and the associated errors are within ±4µm to ±10µm. The specifications of pulp are given in Table 3.1.

Table 3.1: Pulp and fiber specifications

<table>
<thead>
<tr>
<th>Pulp type</th>
<th>Fiber size/µm</th>
<th>Wet pulp consistency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft Unrefined (KU)</td>
<td>927</td>
<td>2.9%</td>
</tr>
<tr>
<td>Kraft Refined-1 (KR₁)</td>
<td>807</td>
<td>2.3%</td>
</tr>
<tr>
<td>Kraft Refined-2 (KR₂)</td>
<td>724</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

The fillers used in preparation of handsheets include kaolin clay and precipitated calcium carbonate particles in micrometer and nanometer.

Table 3.2: The specifications of fillers

<table>
<thead>
<tr>
<th>Filler type</th>
<th>Particle size</th>
<th>Zeta potential/mV</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin clay</td>
<td>13.5µm</td>
<td>-15.1±0.7</td>
<td>Pulp&amp;Paper center, UBC, CA</td>
</tr>
<tr>
<td>Calcined clay</td>
<td>6.92µm</td>
<td>-17.9±0.8</td>
<td>Dry Branch, GA, USA</td>
</tr>
<tr>
<td>Nanoclay</td>
<td>12-20nm*</td>
<td>-12.1±0.4</td>
<td>Sigma-Aldrich, ON, CA</td>
</tr>
<tr>
<td>PCC</td>
<td>10.22 µm</td>
<td>-17.8±0.3</td>
<td>Specialty Minerals, PA, USA</td>
</tr>
<tr>
<td>NPCC</td>
<td>15-40nm*</td>
<td>-14.4±1.1</td>
<td>Nanotech, Xiamen, CN</td>
</tr>
</tbody>
</table>
Note: * The information is provided by the company. The particle size is measured by Scircco 2000 Mastersizer, and the zeta potential is determined by Zetasizer 2000 at a concentration of 0.002 wt% in distilled deionized water (DDW). Clay consists of Al₂O₃, SiO₂, and crystal (bound) water with different ratio.

Except for pulp and fillers, the following chemicals were used in the preparation of handsheets, among which cPAM and silica served as the filler retention system.

- Cationic polyacrylamide (cPAM) supplied by Eka Chemicals (Magog, QC, Canada) with the average molecular mass of 10 million Da.
- 8.1 wt% Silica suspension supplied by Eka Chemicals (Magog, QC, Canada) with the mean size of 5 nm.
- Distilled deionized water (DDW) with a typical resistivity of less than 18.2 MΩ.cm at 25 °C, a total organic carbon content of less than 10 ppb, and a neutral pH value of 7.
- Dichlorodimethylsilane (DCDMS) with a boiling point of 70°, supplied by Sigma-Aldrich Canada Co. (Oakville, ON, Canada).
- Compressed nitrogen gas.
- Anhydrous calcium chloride powder (desiccant, 20mesh and finer, >96%) supplied by Fisher Scientific.
- Microfibrillated cellulose with average particle size of 8µm, supplied by J. Rettenmaier USA LP.

The chemicals used to fabricate Pickering emulsions and Janus particles are as follows:

- Paraffin wax chunks with melting point of 53-57°C, supplied Sigma-Aldrich Canada Co. (Oakville, ON, Canada).
- Didodecyldimethylammonium bromide (DDAB), serving as a cationic surfactant, supplied Sigma-Aldrich Canada Co. (Oakville, ON, Canada).
- Chloroform (≥99.5%) supplied Sigma-Aldrich Canada Co. (Oakville, ON, Canada).
- Kaolin clay, calcined clay, nanoclay, precipitated calcium carbonate (PCC) and NPCC, as shown in Table 3.2.
Experimental apparatus:

The equipment employed for making handsheets includes a customized handsheet former, and a vapor-phase silanization setup.

The equipment engaged in the preparation of Pickering emulsion and Janus particles includes conical flask, magnetic stirrer, plate heater, funnel, screenings, and centrifugal machine.

Characterization:

A high-resolution camera and a micropipette for contact angle measurement, Gurley machine for determining air permeability, an analytical balance and a Hitachi S-3000N-VP Scanning electron microscope.

3.2 Preparation of Handsheets Loaded with Fillers

All handsheets are prepared by the apparatus originally fabricated by Montgomery (2010). It consists of two blocks, the filtration part and vacuum system. A 76-mm diameter forming fabric is immobilized between two acrylic cylinders with flanges. In the middle of the flange plate, a circular gum gasket is placed to provide an airtight seal. A flush-mounted gauge pressure transducer (GP:50 Model 218-C-SZ-10-GS) is attached to the inner wall of cylinder below the forming fabric. The prepared pulp/filler suspension is added above the forming fabric. To simulate the papermaking process, a vacuum pump is employed. The vacuum chamber, with a 20mm PVC pipe on top, is constructed by 13mm thick PVC plated. During operation, the pressure is controlled between -5 to -10 in Hg. And the electrically actuated solenoid valve is controlled by software. Before starting the drainage of a pulp suspension, the cylinder between the valve (closed) and the forming fabric is filled with deionized water. The dewatering step can be finished in several filtration cycles.
Figure 3.1: Schematic of customized handsheet former (Montgomery 2010)

The types of pulp used to prepare handsheets are KU, KR₁ and 50%-50% mixed pulp (KU+KR₁, KU+KR₂).

The fillers applied in preparation of the handsheets include micro or nano clay and precipitated calcium carbonate, with the filler loading concentrations of 0%, 20% and 40% in the handsheet. Before the addition of filler into pulp, the fillers are dispersed in deionized water at a concentration of 1.02%.

To help retain the fillers, chemical retention aids are used. The loading of cationic polyacrylamide (cPAM) is 0.3kg per ton of pulp, which suggests 0.72ml cPAM solution (0.011wt%) per sheet. And the loading of silica is 0.4kg per ton of pulp, which suggests 1.82ml silica solution (0.006wt%) per sheet.

Table 3.3: Pulp Suspension Concentrations

<table>
<thead>
<tr>
<th>Filler/%</th>
<th>V/ml</th>
<th>Pulp/%</th>
<th>W/g</th>
<th>cPAM(kg/t)</th>
<th>V/ml</th>
<th>Silica(kg/t)</th>
<th>V/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0.27</td>
<td>0.3</td>
<td>0.72</td>
<td>0.4</td>
<td>1.82</td>
</tr>
<tr>
<td>20</td>
<td>5.34</td>
<td>80</td>
<td>0.22</td>
<td>0.3</td>
<td>0.72</td>
<td>0.4</td>
<td>1.82</td>
</tr>
<tr>
<td>40</td>
<td>10.68</td>
<td>60</td>
<td>0.16</td>
<td>0.3</td>
<td>0.72</td>
<td>0.4</td>
<td>1.82</td>
</tr>
</tbody>
</table>
The pulp suspension concentrations are given in Table 3.3. A certain weight of wet pulp was diluted into total weight of 300 g with deionized water, followed by the additions of filler solution, cPAM solution, and silica solution. The suspension was mixed and poured into the handsheet former. After filtration, the wet handsheet was removed from the forming fabric and placed onto a blotter and pressed by a roller the handsheet samples were dried in the condition room (50% relative humidity, 25 °C) for 24 hours prior to further property tests.

The total grammage/basis weight (fibers and fillers) of paper is 60g/m². The diameter of handsheet is 76 mm, and the area is 45.4 cm². Thus, the target weight per dried handsheet is 0.2724 g. And the tolerant range of weight is within 30%.

### 3.3 Silanization on Handsheets

The prepared handsheets are hydrophilic due to the existence of hydroxyl groups. A vapor phase silanization process is done over these handsheets to make the surface hydrophobic. The schematic of the apparatus is shown below.

---

**Figure 3.2:** Schematic of silanization equipment (Adapted from Jiang et al. 2008)

The boiling point of silane agent (DCDMS) is 70°C, thus, it is easy to be vaporized at room temperature (Oh et al. 2011). The compressed nitrogen gas is plugged into the
bubbler to vaporize the silane. The sand-core frit, which serves as the chamber for vapor phase silanization, is filled with silane and nitrogen gas in few minutes. Then the handsheets cut in “2x2 cm” is put into the frit for 1 min to be silanized.

3.4 Preparation of Handsheets with Hydrophobic MFC

Preparation of hydrophobic microfibrillated cellulose

1. Stoichiometry of silanization

The chemical formula of MFC powder can be described as \((C_6H_{10}O_5)n\), same as cellulose fibers. In each hexose structural unit, there are three hydroxyl groups, which are responsible for the hydrophilic nature of MFC. In order to render MFC hydrophobic, these hydroxyl groups are functionalized by a low surface-energy chemical (DMDCS). Assume that the hydroxyl groups existing at the surface and inside the bulk of MFC powder are thoroughly reacted with the silane agent. The calculation of stoichiometry is performed below.

\[
(C_6H_{10}O_5) \sim \frac{3}{2}Si(CH_3)_2Cl_2
\]

The purity of MFC is 99.5%. The molecular weights of cellulosic unit and silane are 162 and 129.06, respectively. The density of silane is 1.07g/cm^3 at 25ºC. For 1g of sample, the volume of required silane equals to

\[
1g \times 99.5\% \div 162g/\text{mole} \times \frac{3}{2} \times 129.06g/\text{mol} \div 1.07g/cm^3
\]

which is 1.11ml. Alternatively, this can be written as 0.9g-MFC/ml-silane.

2. Solvent-free silanization of MFC

Different volumes of DMDCS are used to modify a certain mass of MFC powder, which is 0.9g. The volume of DMDCS varies from 0.4ml, 0.7ml to 1.0ml. This is designed to show how the hydrophobic performance of MFC depends on the quantity of silane changes. The silanization setup is the same as shown in Figure 3.2. The MFC is placed in the frit, while the silane agent is in the bubbler. Dry nitrogen released from a gas container flows through the setup at a rate of 2-3 bubbles per second. Silane agent with low boiling point then vaporizes and mixes with nitrogen. Finally, silane agent reaches the frit and reacts with MFC. During this procedure, shake the frit every five minutes to ensure the adequate contact between silane and MFC.
Deposition of hydrophobic microfibrillated cellulose on handsheets

Prepare KU handsheets without any filler using filtration equipment, which consists of Buchner funnel and suction flask. Hydrophobic MFC is dispersed in deionized water with the aid of sonication lasting 30min. Then the suspension is added onto KU handsheet surface. After the water drains away and drying at room temperature, a thin film of hydrophobic MFC is established at the handsheet surface. The loadings of hydrophobic MFC on handsheets are 10%, 30% and 50%, based on the dry mass of pulp.

After the deposition of hydrophobic MFC, another silanization treatment is performed on the resulted handsheets to render the surface totally hydrophobic.

3.5 Pickering Emulsion Stabilized by Fillers

In this process, solid particles are added into an oil/water mixture to stabilize the emulsion. The solid particles employed here include kaolin clay, calcined clay, nano-clay, and micro/nano precipitated calcium carbonate. Paraffin wax with melting point of 53-57°C is preheated to 85°C to be in its liquid oil phase. And solid particles are dispersed into DI water under magnetic stirring, followed by heating up to the same temperature as wax. Then the melt wax is added into water. Keep stirring for 5-10 min, and the oil breaks into small droplets. Driven by the thermodynamic force, solid particles are immobilized at the surface of oil droplets. Ideally, the emulsified oil phase ends up at the top without coalescence, while the water phase remains at the bottom. After cooling down to the room temperature, the wax solidifies and the solid particles are locked into the position.

The wax pellets are filtered from the prepared Pickering emulsion and undergo a washing step. Wax pellets in large size are screened away. The excessive fillers remaining in water are discarded. The rest are collected and dried at room condition for further treatment.

3.6 Fabrication of Janus Kaolin Clay Particles

Many approaches have been proposed to fabricate Janus particles in liquid or gas phase. Generally, precipitated calcium carbonate is rendered hydrophobic by reaction with stearic acid in a solvent. Clay has hydroxyl groups, which provides the possibility of reacting with a silane agent. Silane with low boiling point, such as DCDMS, is easily
vaporizing at room temperature. Then a vapor phase silanization process can be conducted. Compared with reaction in solvent, vapor phase silanization is free of post-treatment, such as liquid separation. The method adopted here is vapor phase silanization, using the same setup as doing silanization on handsheets. The wax pellets with kaolin clay are transferred into the frit. At room temperature, silane (DCDMS) is vaporized with nitrogen blowing by and reaches the frit to modify the solid particles. To sufficiently modify clay, the reaction time is kept at 1 hr, with three bubbles per second. During the process, the outer face of clay particles is functionalized with hydrophobic methylsilane groups.

Transfer the obtained wax pellets into centrifugal tubes, and add chloroform to 20ml scale line. Shake the tube up and down several times. Then the paraffin wax is dissolved and Janus clay particles are released. After centrifuging, the insoluble Janus clay particles precipitate and the rest solution is decanted away. Repeat the centrifuging step with chloroform and ethanol three times each. Keep the Janus clay particles in ethanol for further use. Finally, the geometry of the Janus particles is confirmed by the distributive behavior at toluene/water interface.

The obtained wax/filler colloidosome was transferred into centrifugal tubes, and 20 ml chloroform was added to the tube. Shake the tube up and down several times. Then the paraffin wax was dissolved and Janus clay particles were released. After centrifuging, the insoluble Janus clay particles precipitated at the bottom, and the rest of the solution was decanted away. The centrifuging step was repeated with chloroform and ethanol three times each. The Janus clay particles were kept in ethanol for further use. Finally, the geometry of the Janus particles is confirmed by the distributive behavior at toluene/water interface.

3.7 Incorporation of Janus Clay Particle Coating on Handsheet

A KU pulp suspension was used to prepared handsheets with basis weight of 60g/m². The pulp suspension was transferred into a funnel, followed by the addition of aqueous Janus clay particles solution on top. Due to the hydrophobic/hydrophilic geometry, Janus particles evenly distributed on the surface of water automatically with their hydrophobic sides facing the air. The amount of Janus clay particles applied on each trial should guarantee a full coverage over the handsheet surface. After the water is totally drained,
Janus clay particles deposit at the surface of handsheets and a hydrophobic film is established. More than one deposition cycles are essential to achieve a dense hydrophobic coating.

3.8 Handsheet Properties Characterization

3.8.1 Weight of Handsheets

After the paper specimen is kept in condition room for more than 24hrs. The weight of paper is determined by analytical balance. Generally, the moisture content takes 10% over the total mass.

3.8.2 Thickness (L&W Micrometer)

The thickness of dried paper is determined by L&W Micrometer. For each specimen, the reported thickness is the average at five spots on handsheets surface.

3.8.3 Air Resistance (Gurley Method)

According to TAPPI standard of T460 om-02, the air resistance of paper is measured by Gurley machine. The time required for 100ml air to pass through a certain circular area (6.45 sq.cm.) of paper at a pressure differential of 1.22kPa, is considered as indicator of the air resistance.

Both the internal structure and the surface finish of paper have a main effect on the air permeability. The type, length, and also the alignment of fibers influence the structure of paper, as well as the fillers.

3.8.4 Water Vapor Transmission Rate (WVTR)

WVTR test can be performed by cup method similar as the TAPPI standard method of T-448. All the handsheets are preconditioned at 23°C and 50% relative humidity for 24hrs prior to measurements. Then the handsheets are cut into discs with a diameter of 1.6cm. These paper specimens are sandwiched between two rubber gaskets, and tightly mounted on a glass analyzer with a hollow cap to secure well sealing. The actual diameter of paper exposed to the environment is 0.9cm. Inside the analyzer, there is anhydrous calcium chlorides powder serving as desiccant. During the measurement, water vapor transports through the paper and adsorbed by the desiccant. The change of the total weight of the analyzer is recorded for a week and an average value is reported.
The water vapor transmission rate (WVTR) result is calculated as the equation below, in the unit of g/(m²·day).

\[
WVTR(g \cdot m^{-2} \cdot day^{-1}) = \frac{\Delta m (g \cdot day^{-1})}{\text{Area}(m^2)}
\]  

(3-3)

3.8.5 Water Contact Angle Measurement

The static contact angle of a water droplet can be measured with capturing images by a high-resolution camera, Nikon D90 digital camera. The prepared paper sample is horizontally placed before a light source, and then a 3µL deionized water droplet is loaded on the surface by pipette. For each sample, the images are taken on five spots. Then the software FTA32 Version 2.0 is used to analyze the contact angle.
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Thickness and Density of Handsheets

The results of thickness (mm) and density (kg/m³) of handsheets are shown in Table 4.1 to 4.4. The density of handsheet is calculated as eq. (4-1).

\[
Density = \frac{Weight}{Thickness \times Area}
\]  

(4-1)

Table 4.1: The thickness and density of handsheets with KU

<table>
<thead>
<tr>
<th>Loading</th>
<th>Test</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Load</td>
<td>Thickness</td>
<td>0.3657</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>Thickness</td>
<td>0.2853</td>
<td>0.2823</td>
<td>0.2947</td>
<td>0.3075</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>203</td>
<td>200</td>
<td>209</td>
<td>191</td>
</tr>
<tr>
<td>40%</td>
<td>Thickness</td>
<td>0.2025</td>
<td>0.2298</td>
<td>0.2239</td>
<td>0.2876</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>194</td>
<td>190</td>
<td>213</td>
<td>228</td>
</tr>
</tbody>
</table>

Table 4.2: The thickness and density of handsheets with KR₁

<table>
<thead>
<tr>
<th>Loading</th>
<th>Test</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Load</td>
<td>Thickness</td>
<td>0.2836</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>595</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>Thickness</td>
<td>0.2585</td>
<td>0.2164</td>
<td>0.2592</td>
<td>0.2523</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>601</td>
<td>566</td>
<td>450</td>
<td>559</td>
</tr>
<tr>
<td>40%</td>
<td>Thickness</td>
<td>0.2304</td>
<td>0.2254</td>
<td>0.2933</td>
<td>0.2385</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>511</td>
<td>608</td>
<td>433</td>
<td>571</td>
</tr>
</tbody>
</table>
Table 4.3: The thickness and density of handsheets with KU+KR<sub>1</sub>

<table>
<thead>
<tr>
<th>Loading</th>
<th>Test</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Load</td>
<td>Thickness</td>
<td>0.3315</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>372</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>Thickness</td>
<td>0.2705</td>
<td>0.2645</td>
<td>0.2966</td>
<td>0.2821</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>425</td>
<td>401</td>
<td>383</td>
<td>466</td>
</tr>
<tr>
<td>40%</td>
<td>Thickness</td>
<td>0.2499</td>
<td>0.1933</td>
<td>0.2731</td>
<td>0.2427</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>381</td>
<td>419</td>
<td>316</td>
<td>480</td>
</tr>
</tbody>
</table>

Table 4.4: The thickness and density of handsheets with KU+KR<sub>2</sub>

<table>
<thead>
<tr>
<th>Loading</th>
<th>Test</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Load</td>
<td>Thickness</td>
<td>0.3284</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>497</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>Thickness</td>
<td>0.2937</td>
<td>0.2796</td>
<td>0.3007</td>
<td>0.2834</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>486</td>
<td>559</td>
<td>431</td>
<td>547</td>
</tr>
<tr>
<td>40%</td>
<td>Thickness</td>
<td>0.2683</td>
<td>0.2163</td>
<td>0.2620</td>
<td>0.2839</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>462</td>
<td>490</td>
<td>371</td>
<td>543</td>
</tr>
</tbody>
</table>

From the tables above, it is concluded that the density of handsheet mainly depends on the fiber size. As the fiber size decreases, the handsheets become denser.
4.2 Water Vapor Transmission Rate (WVTR) of Handsheet

The results for the WVTR in g(water vapor)/(m²·day) at 23°C and 50% RH are shown in Tables 4.5 to 4.9.

**Table 4.5:** The WVTR values of handsheets with KU (g/(m²·day))

<table>
<thead>
<tr>
<th></th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>807</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>801</td>
<td>789</td>
<td>840</td>
<td>819</td>
</tr>
<tr>
<td>40%</td>
<td>831</td>
<td>824</td>
<td>844</td>
<td>840</td>
</tr>
</tbody>
</table>

**Table 4.6:** The WVTR values of handsheets with KR₁ (g/(m²·day))

<table>
<thead>
<tr>
<th></th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>303</td>
<td>272</td>
<td>478</td>
<td>380</td>
</tr>
<tr>
<td>40%</td>
<td>474</td>
<td>307</td>
<td>665</td>
<td>633</td>
</tr>
</tbody>
</table>

**Table 4.7:** The WVTR values of handsheets with 50%-50% KU + KR₁ (g/(m²·day))

<table>
<thead>
<tr>
<th></th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>430</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>508</td>
<td>487</td>
<td>714</td>
<td>639</td>
</tr>
<tr>
<td>40%</td>
<td>654</td>
<td>517</td>
<td>759</td>
<td>732</td>
</tr>
</tbody>
</table>

**Table 4.8:** The WVTR values of handsheets with 50%-50% KU + KR₂ (g/(m²·day))

<table>
<thead>
<tr>
<th></th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>273</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>438</td>
<td>327</td>
<td>670</td>
<td>496</td>
</tr>
<tr>
<td>40%</td>
<td>608</td>
<td>412</td>
<td>706</td>
<td>659</td>
</tr>
</tbody>
</table>
Table 4.9: The WVTR values of handsheets before and after silanization

<table>
<thead>
<tr>
<th></th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#1 CC</th>
<th>#1-2 PCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>807</td>
<td>123</td>
<td>430</td>
<td>273</td>
<td>801</td>
<td>840</td>
</tr>
<tr>
<td>Treated</td>
<td>813</td>
<td>95</td>
<td>334</td>
<td>148</td>
<td>825</td>
<td>850</td>
</tr>
</tbody>
</table>

Index statement: #1 stands for KU. #2 stands for KR1. #3 stands for 50%-50% KU + KR1. #4 stands for 50%-50% KU + KR2. #1 CC stands for KU with 20% loading of calcined clay. #1 PCC stands for KU with 20% loading of precipitated calcium carbonate.

The errors of WVTR tests are shown in the following Table 4.10.

Table 4.10: The errors of WVTR values of handsheets

<table>
<thead>
<tr>
<th>Handsheets</th>
<th>WVTR</th>
<th>ST. DEV.</th>
<th>Error%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KR1</td>
<td>123</td>
<td>32</td>
<td>26</td>
</tr>
<tr>
<td>KU+KR1</td>
<td>431</td>
<td>71</td>
<td>16</td>
</tr>
<tr>
<td>KU+KR1+20%MC</td>
<td>508</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>KU+KR1+40%MC</td>
<td>654</td>
<td>55</td>
<td>8</td>
</tr>
<tr>
<td>KU+KR1+20%NC</td>
<td>487</td>
<td>85</td>
<td>17</td>
</tr>
<tr>
<td>KU+KR1+20%MP</td>
<td>714</td>
<td>47</td>
<td>7</td>
</tr>
<tr>
<td>KU+KR1+20%NP</td>
<td>638</td>
<td>48</td>
<td>8</td>
</tr>
</tbody>
</table>
4.2.1 Effect of Fiber Size on WVTR of Paper

Figure 4.1: The WVTR values of handsheets with different fiber sizes

KU, KR₁ and KR₂ have the longest, medium and shortest fiber size, respectively. It is observed that as fiber size decreases, the WVTR value decreases significantly. Especially, the KU handsheet has a WVTR value of 807 g/(m²·day), while KR₁ handsheet has a WVTR value of 123 g/(m²·day). And when half of KU pulp is replaced by KR₁ or KR₂, the WVTR values drop to 1/2 and 1/3 levels. The reason is that, refined pulp fiber has larger surface area and more exposed hydroxyl groups, compared with that of unrefined pulp (Mirvakili et al. 2016). Therefore, more hydrogen bonding between fibers can be formed. This results to the formation of denser handsheets and the decrease of porosity. Finally, the water vapor resistance increases.
4.2.2 Effect of Filler Type on WVTR of Paper

Figure 4.2: The WVTR values of handsheets loaded with different fillers

As shown in the figure above, filler type has an obvious effect on WVTR values. Except for the case of KU, the handsheets loaded with PCC has a highest WVTR value.

The hypothesis to explain the above observations is that clay has a disc-like shape (Murray & Kogel 2005) and blocks the diffusion path for water vapor molecules to pass through the handsheets (Mirvakili, 2012). In another word, the tortuosity in handsheet with clay fillers is higher than the one with rosette PCC.

In the figure, it is also clear that WVTR values of KU are barely affected by filler type. It is due to the high porosity in handsheets. There is low resistance for water vapor to pass through the Z-direction. Thus the effect of filler type on WVTR is concealed. The hypothesis can also be confirmed by the high air permeability of less than 5 seconds for KU handsheets.
4.2.3 Effect of Filler Content on WVTR of Paper

Figure 4.3: The WVTR values of handsheets loaded with Calcined clay (upper) and PCC (below) at different filler content.
As is explained above, the filler effect on WVTR of KU handsheets can be ignored. For the rest of the handsheets, it is concluded that, higher filler content results in larger WVTR values. It happens in both the cases of calcined clay and precipitated calcium carbonate on handsheets made of refined fibers. As we know, cellulosic fibers form strong networks due to hydrogen bonding. The occurrence of filler between fibers may disrupt the inter-fiber attraction force, which results in the loss of handsheet’s density and increase of the porosity. This would lead to the decreases of water vapor resistance in bulk. The same trend is observed on the handsheets with nanosized fillers as well.

### 4.2.4 Effect of Filler Size on WVTR of Paper

![WVTR values of KR₁ handsheets with different filler size](image)

**Figure 4.4:** The WVTR values of KR₁ handsheets with different filler size

By comparing the WVTR values of handsheets loaded with microsized and nanosized fillers, it is obvious that nanosized fillers have less negative effect on the water vapor barrier properties of handsheets. The hypothesis is that, the paper with nanosized fillers is denser in bulk and less porous, compared with the paper with microsized fillers. Also, the reason might be that the retention of nanosized fillers in the handsheets is less than that of microsized fillers. Thus, the hydrogen bonding between fibers is less disrupted in handsheets with nanosized fillers.
4.2.5 Effect of Silanization on WVTR of Paper

Figure 4.5: The WVTR values of handsheets without filler before and after silanization

Except for the KU handsheet, the WVTR values reduced by 23%, 22% and 46% for “KR1”, “KU+KR1”, and “KU+KR2” handsheets, respectively. After silanization, the hydrophobic methylsilane group chemically bonded on the surface of fibers, stenches towards the interspace between fibers. This may reduce the transmission rate of water vapor molecules through the bulk.

4.3 Air Permeability of Handsheets

The air permeability values are less than 5 seconds for KU handsheets, which is beyond the applicable condition of Gurley machine.

Table 4.11: Air Permeability of KU+KR2 handsheets (s/100cc)

<table>
<thead>
<tr>
<th></th>
<th>Calcined clay</th>
<th>PCC</th>
<th>NPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>2171</td>
<td>454</td>
<td>2875</td>
</tr>
<tr>
<td>40%</td>
<td>1370</td>
<td>94</td>
<td>1118</td>
</tr>
</tbody>
</table>

From the data above, it can be concluded that the air permeability value is a function of porosity and tortuosity in the handsheets:
1. As the fiber size decreases, more hydroxyl groups exist at the surface of a fiber. Thus, more intermolecular hydrogen bonding occurs and the fiber-fiber network becomes stronger and denser. The porosity of handsheet decreases and its air permeability increases.

2. The more fillers loaded into the handsheets, the more intermolecular hydrogen bonding is disrupted. As a result, the tensile strength of handsheet suffers a loss, and the handsheet becomes less dense. Thus, the air permeability values increase.

3. Compared with handsheet with microsized fillers, the handsheet loaded with nanosized fillers are less porous, due to the small size of filler. So their air permeability is lower.

4. The handsheets with clay have larger air permeability values, compared with handsheets with PCC. The clay has a disc-like shape, while PCC is rosette, so the tortuosity is higher and the path for air to pass through the bulk of handsheet is more complicated in the case of handsheets with clay.

4.4 Wettability of Handsheets after Silanization

Tables 4.12 to 4.15 show WCA results of the handsheets with different fiber sizes, filler types, and concentrations. Wire side refers to the side of handsheet facing the forming fabric, while felt side is the top side.

<table>
<thead>
<tr>
<th>Wire side</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>134.7±4.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>130.3±7.1</td>
<td>128.1±5.0</td>
<td>123.5±4.1</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>132.0±1.8</td>
<td>125.5±6.5</td>
<td>125.4±6.7</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Felt side</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No load</td>
<td>130.8±3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>130.3±4.5</td>
<td>132.9±5.0</td>
<td>122.3±3.3</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>130.4±3.1</td>
<td>130.9±4.0</td>
<td>118.3±5.4</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>
**Table 4.13:** Water contact angle (WCA) of KR₁ handsheets

<table>
<thead>
<tr>
<th>Wire side</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>128.0±4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>124.1±6.0</td>
<td>129.0±4.1</td>
<td>116.7±7.4</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>121.2±7.9</td>
<td>121.3±5.7</td>
<td>124.4±3.1</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Felt side</td>
<td>Calcined clay</td>
<td>Nanoclay</td>
<td>PCC</td>
<td>NanoPCC</td>
</tr>
<tr>
<td>No load</td>
<td>126.6±6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>129.8±9.3</td>
<td>131.1±5.2</td>
<td>135.0±1.4</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>118.3±10.4</td>
<td>127.9±3.9</td>
<td>129.4±3.7</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

**Table 4.14:** Water contact angle (WCA) of KU+KR₁ handsheets

<table>
<thead>
<tr>
<th>Wire side</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>128.6±5.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>123.9±3.3</td>
<td>123.7±9.4</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>129.1±2.8</td>
<td>127.4±2.5</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Felt side</td>
<td>Calcined clay</td>
<td>Nanoclay</td>
<td>PCC</td>
<td>NanoPCC</td>
</tr>
<tr>
<td>No load</td>
<td>127.8±5.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>134.7±2.5</td>
<td>131.4±1.5</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>126.4±3.7</td>
<td>131.6±6.8</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

**Table 4.15:** Water contact angle (WCA) of KU+KR₂ handsheets

<table>
<thead>
<tr>
<th>Wire side</th>
<th>Calcined clay</th>
<th>Nanoclay</th>
<th>PCC</th>
<th>NanoPCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No load</td>
<td>128.5±3.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>131.4±4.1</td>
<td>134.7±5.7</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>127.2±3.7</td>
<td>123.5±3.1</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Felt side</td>
<td>Calcined clay</td>
<td>Nanoclay</td>
<td>PCC</td>
<td>NanoPCC</td>
</tr>
<tr>
<td>No load</td>
<td>128.5±3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>128.5±4.9</td>
<td>125.3±4.5</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>40%</td>
<td>134.0±8.4</td>
<td>132.1±4.6</td>
<td>Hydrophilic</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>
The water contact angle on filter paper after silanization of DCDMS is between 120º and 130º, based on literature reports (Oh et al. 2011). Most of the data fall into this range, except for the handsheets with PCC and NPCC cases.

### 4.4.1 Effect of Fiber Size on Water Contact Angle

![Figure 4.6: The water contact angle of handsheets without filler](image_url)

It is observed that KU hansheets have the highest water contact angle on both sides. And KR₁ handsheets have the lowest water contact angle. This is attributed to the highest surface roughness of unrefined handsheets (Mirvakili et al. 2016). In addition, it is found that wire side has higher water contact angle than felt side. As wire side faces the forming fabric, thus, it copied the morphology of the fabric and became rougher than the felt side (Mirvakili, 2012).

### 4.4.2 Effect of Filler Type on Water Contact Angle

From the data in the tables above, handsheets with clay are more hydrophobic than the ones with PCC (except the felt side of KR₁ handsheets with PCC). The reason is that, clay can be rendered hydrophobic by silanization due to the existence of hydroxyl groups on its surface. By contrast, CaCO₃ is inert during silanization, and keeps it hydrophilic.
property after treatment. As a result, the hydrophobicity of handsheets with CaCO₃ exposed towards the environment is lowered.

**4.4.3 The Influence of Other Factors on Water Contact Angle**

The effects of filler size, and filler content on surface wettability of handsheets are not obvious. Low surface energy, along with high roughness, is required to fabricate superhydrophobic handsheets. And the smoothness of surface may be the limit to further improve the water contact angle value.

**4.5 Wettability of Handsheets Loaded with Hydrophobic MFC**

*The effect of silane concentration on wettability of MFC*

In the experimental part 3.4, different volume of silane agent (DCDMS) (i.e. 0.4ml, 0.7ml, 1.0ml) is used to modify 0.9g MFC. After silanization, all the treated MFCs perform hydrophobic. The hypothesis is that, the wettability of MFC is only related to its surface hydrophilic/hydrophobic character. More silane agent used in the treatment may result to a thorough modification of both the bulk and the surface of MFC fiber bundles. But a small amount of silane agent (0.4ml) is able to sufficiently replace the –OH groups on fiber surface by –O-Si(CH₃)₂. And the internal –OH groups of fibers remain hydrophilic.

*Water contact angle of handsheets with hydrophobic MFC*

After hydrophobic MFC is prepared, it is deposited onto the surface of KU handsheets. The designed loading of hydrophobic MFC ranges from 10%, 30% to 50%. The actual loading is shown in Table 4.16, along with the corresponding water contact angle value.
Blank experiment result: The water contact angle of KU handsheet after silanization is 133.9±1.6º.

From the table above, it is observed that the water contact angle (WCA) is between 134º and 144º, which is higher than that of silanized KU handsheet without hydrophobic MFC. The chemical nature of MFC and fiber in KU pulp is similar. However, the deposition of hydrophobic MFC onto KU handsheet may introduce micro and nano scale roughness somehow, since MFC has a fiber length in micrometer and a fiber diameter in nanometer. Thus, the roughness of KU handsheet increases after the loading of hydrophobic MFC, and finally the surface hydrophobic performance is enhanced.

### 4.6 The Stability of Pickering Emulsions

Pickering emulsion is defined as an oil/water emulsion stabilized by solid particles. And it has been reported that many types of solid particles (e.g. colloidal silica) are able to adsorb at the oil/water interface, thus a stable Pickering emulsion can be established. The stability of Pickering emulsion highly depends on the surface energy of oil, water and solid particles, the oil/water ratio, the concentration and size of solid particles, the surfactant concentration, pH and salt, and the force applied on the system (e.g. agitation, sonication).

In this study, melted paraffin wax is used as oil phase, several types of filler are considered to stabilize the Pickering emulsion, including Kaolin clay, calcined clay, nano-clay, PCC and nano-PCC. Didodecyldimethylammonium bromide (DDAB) serves
as a co-emulsifier. The stability results of these Pickering emulsions are given in the following table.

Table 4.17: The stability of Pickering emulsion stabilized by Kaolin clay

<table>
<thead>
<tr>
<th>No.</th>
<th>Wax/g</th>
<th>Water/g</th>
<th>DDAB(mg/ml)</th>
<th>Filler/g</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>14</td>
<td>0</td>
<td>0.28</td>
<td>Coalescence</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>14</td>
<td>0.0001</td>
<td>0.28</td>
<td>Coalescence</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>14</td>
<td>0.0011</td>
<td>0.28</td>
<td>Large droplet</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>14</td>
<td>0.014</td>
<td>0.28</td>
<td>Small droplet</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>14</td>
<td>0.1</td>
<td>0.28</td>
<td>Stable</td>
</tr>
</tbody>
</table>

From this table, the effect of DDAB (cationic surfactant) concentration on the stability of Pickering emulsion is obvious. When the concentration of DDAB is at a relatively low level (Case 1&2), the oil droplets coalesce right after stopping the agitation. It means that the adsorption of Kaolin clay at the interface is very weak and Kaolin clay cannot solely stabilize Pickering emulsion. As the concentration of DDAB increases, the size of oil droplet decreases. At DDAB concentration of 0.1mg/ml, a stable Pickering emulsion is formed, and there is no excess oil existing in the mixture. There are two mechanisms of how surfactant favors the stability of Pickering emulsion. First, DDAB can help stabilize emulsions by lowering interfacial tension between oil and water. Besides, DDAB adsorbs on the surface of Kaolin clay and modifies hydrophilic Kaolin clay into intermediate hydrophobic. Thus, the capability of Kaolin clay as emulsifier is improved.

Table 4.18: The formula of Pickering emulsion stabilized by other fillers

<table>
<thead>
<tr>
<th>Filler type</th>
<th>Wax/g</th>
<th>Water/g</th>
<th>DDAB(mg/ml)</th>
<th>Filler/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined Clay</td>
<td>6</td>
<td>14</td>
<td>0.05</td>
<td>0.28</td>
</tr>
<tr>
<td>Nano-clay</td>
<td>6</td>
<td>14</td>
<td>0.1</td>
<td>0.28</td>
</tr>
<tr>
<td>PCC</td>
<td>6</td>
<td>14</td>
<td>0.1</td>
<td>0.28</td>
</tr>
<tr>
<td>Nano-PCC</td>
<td>7</td>
<td>35</td>
<td>0.005</td>
<td>0.5</td>
</tr>
</tbody>
</table>
In summary, based on the observations in preparing stable Pickering emulsion, the following phenomena are observed.

- The oil-to-water ratio is important, and the ideal range is from 0.2:1 to 0.45:1 in this study.
- The proper concentration of DDAB ranges from 0.005mg/ml to 0.1mg/ml. If its concentration is too high (e.g. 0.2mg/ml), the oil phase is stabilized by DDAB without filler, and does not form in Pickering emulsion.
- There should be sufficient amount of fillers to cover the whole surface of the oil droplet, otherwise, the stability of Pickering emulsion is poor. And it is inefficient to add excessive fillers into the mixture.
- The agitation should last for about 5-10min. The stability of Pickering emulsion decreases after 10min, as the formed structure of emulsion is destroyed again.
After the preparation of a Pickering emulsion, the colloidosomes are filtered from the suspension. The SEM images in Figure 4.7 confirm the successful fabrication of a stable Pickering emulsion. The surface of wax colloidosomes is covered by fillers. The aggregation of fillers is observed as well. Meanwhile, at some spots, the wax is exposed to the environment without fillers. This uneven coverage of filler does not hamper the
stability of Pickering emulsion. However, it is not favorable for the surface modification of filler, such as preparation of Janus particles. Only the very outmost layer of fillers can be modified.

4.7 Wettability of Handsheets Coated with Janus Clay Particle

Janus Kaolin clay is prepared through Pickering emulsion route. Hydrophilic kaolin clay adsorbs at the interface of wax/water. In vapor-phase silanization treatment, one side of kaolin clay particle is modified as hydrophobic. After releasing the clay fillers from the wax, Janus kaolin clay is obtained and then deposited onto KU handsheets. Several cycles of deposition of Janus particles on handsheets are performed to ensure a sufficient coating. After that, the resulting handsheets undergo silanization for 1 min as post-treatment, in order to ensure that there is no hydrophilic spot exposed at the paper surface.

![Figure 4.8: Static water contact angle on handsheets coated with Janus clay particle](image)

The resulting handsheet exhibits an excellent hydrophobic performance, with static water contact angle of 141°, which is much higher than the hydrophobic handsheets with fillers (120°~130°). This is mainly attributed to its higher surface roughness with Janus Kaolin clay in micrometer.
CHAPTER 5: CONCLUSION AND RECOMMENDATION

In this study, hydrophobic handsheets with different types of fillers or MFC were prepared. The effects of fiber size, filler characters (filler type, size, loading) and silanization on the barrier performance of the handsheets (wettability, water vapor transmission rare (WVTR) and air permeability) were determined. As fiber size decreases, the surface area increases and more hydroxyl groups are exposed at the fiber surface. More hydrogen bonding between fibers may form. As a result, the WVTR values of handsheets with short fibers are significantly lower than those with long fibers. Compared with PCC, clay has less negative effect on the water vapor resistance of handsheets. This is attributed to the disc-like shape of clay, which blocks the path of water vapor/air molecules to pass through the bulk of paper. Also, it is shown that handsheets with higher filler loading suffer a loss of water vapor resistance. The reason is that fillers hamper the intermolecular hydrogen bonding and the density of paper decreases. In addition, the WVTR values of handsheets with micrometer size fillers are higher than that with nanometer fillers. Silanization treatment can render the surface of handsheets from hydrophilic to hydrophobic, and enhance the water vapor resistance. Correspondingly, high WVTR values always come with high air permeability, since these barrier properties are highly depends on the porosity and density of the paper.

The water contact angle of handsheets loaded with fillers, Janus clay particles and hydrophobic MFC, was found to be 120~130°, 141° and 134~144° respectively. Wire side of paper exhibits better hydrophobic performance, compared with felt side. Handsheets with clay have higher water contact angle than that with PCC, since PCC is inert (not responsive) to silanization and remains hydrophilic. The effects of filler size, and filler content on surface wettability of handsheets are not obvious. As the silanization treatment is performed in all cases, the surface energy of these hydrophobic handsheets is the same. Thus, the difference of the water contact angle on hydrophobic handsheets prepared in three approaches is attributed to the surface roughness of paper.
BIBLIOGRAPHY


56. Shen, J. et al., 2009a. A preliminary investigation into the use of acid-tolerant precipitated calcium carbonate fillers in papermaking of deinked pulp derived


