Microparticle Retention Aid Systems in Mechanical Pulp Suspensions

by

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ABSTRACT

In this thesis, the effectiveness of microparticle retention aid systems comprising of different cationic starches (tapioca and waxy maize), cationic flocculants (flocculant 1, linear with low charge density and flocculant 2, branched with medium charge density polyacrylamides) and anionic colloidal silica in improving retention and drainage of thermomechanical pulp (TMP) suspensions loaded with precipitated calcium carbonate (PCC) is studied.

While starch is primarily added as dry strength agent in PCC-filled TMP suspensions, it also has a significant role in improving retention and drainage. Tapioca starch, which has both amylose and amylopectin, is found to be a better retention and drainage aid than waxy maize starch, which only contains amylopectin.

In the absence of starch, both flocculants are ineffective in improving retention and drainage. With starch, both flocculant and silica are significant in enhancing retention and drainage further. Increasing the dosage of either flocculant or silica generally increases retention as well as drainage.

Flocculant 2 is found to give slightly worse total and filler retention but better drainage compared to flocculant 1. The dosage of flocculant 2 is only half that of flocculant 1 though – for this reason overall flocculant 2 is deemed more effective in improving retention and drainage than flocculant 1.

Split starch addition, where a portion of the starch is premixed with PCC and the rest added to the pulp, causes a slight decrease in both retention and drainage. Therefore, should the papermaker decide to use this approach, the starch should be split in a 25:75 ratio between PCC and the pulp to minimize the negative effects.

Due to the cost benefits of using increased amounts of PCC, it is desirable to increase PCC content beyond the standard currently used (250 kg/t OD pulp for communications-
grade paper). However, at very high dosages of PCC (500 kg/t OD pulp), the best combination identified in this work (tapioca starch, flocculant 2 and silica) is unable to maintain good retention and drainage. Increasing retention aid dosages may help retain more PCC, however this tactic can rapidly become uneconomical. A new approach is thus needed to achieve such highly-filled papers.
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CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Challenges in papermaking
Retention aid technology is constantly evolving with the changes underway in papermaking. Some of the current trends include greater use of cheaper raw materials e.g. using mechanical rather than chemical pulp; using increasing amounts of mineral fillers rather than fibers; increased degree of whitewater closure and faster machine speeds. While these strategies allow papermakers to minimize cost and remain competitive, it makes wet end conditions more challenging. Use of the aforementioned cheaper raw materials, for instance, introduces large amounts of fines, fillers and various dissolved and colloidal substances (DCS) in the wet end. These substances have been found to be detrimental to the papermaking process and to paper properties [1,2]. Additionally, excessive accumulation of such substances in the whitewater system can reduce paper machine runnability due to wet end breaks and deposit formations [3]. Faster machine speeds, which have been indicated as the main avenue to achieve future productivity growth in the paper industry [4], increase turbulence at the forming zone, which can result in poor fines and filler retention. High machine speeds also require increased drainage in order to limit the amount of energy required to remove water from the formed sheet.

The main consequence of these trends is that papermakers need to simultaneously obtain a high level of retention, drainage and formation in order to achieve an efficient papermaking process. Microparticle retention aid systems have been developed to help overcome these new challenges because the classical single or dual retention aid systems are often inadequate to deal with them [5]. Single polymer retention aids, for instance, are less likely to perform well in an environment with high levels of fines, filler and other interfering substances. Dual polymer retention aid systems resolve this issue, but they often require a compromise between process efficiency dictated by retention and drainage and product quality determined by formation. Microparticle retention aid systems, on the
other hand, can achieve increased retention and drainage with no sacrifice in formation [6,7,8].

Improved retention of fines and fillers can provide numerous benefits to a mill. For instance, it can lead to better sheet formation. Formation of the paper web begins with the retention of the suspended materials in the furnish onto the machine wire. If no retention aid chemicals were present, most of the fibers would be mechanically retained on the wire while most of the fiber fines and filler would build up in the white water system and eventually lost through the effluent. Moreover, the concentration of fines and fillers will be significantly higher on the top side, compared to the wire side of the sheet, resulting in a sheet defect known as ‘two-sidedness’ [5,7]. Due to lack of fines and fillers, the wire side will be relatively rough and exhibits poor print quality. On the other hand, the top side can be susceptible to linting problems because of excessive amounts of fines and fillers. Improved retention will improve the distribution of fillers within the sheet, which will improve the opacity and printing properties of the paper.

Improved retention also leads to better productivity. A cleaner whitewater system reduces the rate at which deposits is formed, which in turn improves runnability by reducing break frequency. With microparticle retention aid systems, improved retention also brings about improved drainage, which allows for higher machine speeds and thus increased production rates or a corresponding reduction in steam consumption in the dryer section. Finally, good retention reduces the loss of fillers and other additives to the mill effluent. All of these benefits often translate to the bottom line as reduced costs or increased production [9].

1.2 Retention and drainage
1.2.1 Overall vs. first pass retention
A paper machine’s wet end starts at the point where the thick stock is diluted to form the thin stock. Various additives e.g. mineral fillers, strength-enhancing chemicals and retention aids are added to the thin stock, which then flows out of the slice in the headbox onto a moving fine mesh fabric. The fabric goes over several drainage units and water is
extracted from the forming stock. This white water is circulated back to the fan pump to dilute the incoming thick stock. A portion of the white water is also sent to the saveall where the solids are recovered and the clarified water is sent to upstream operations for dilution or cleaning purposes.

There are only two outputs from a paper machine: the final paper product and the effluent stream. If any material is not converted into the final product, it will enter the white water stream and accumulate in the system. This can cause quality as well as operational problems e.g. two-sidedness and drainage issues. Retention aids are added to the system to prevent the loss of such materials, especially the fines, fillers and other additives which are too small to be retained on the wire by mechanical filtration.

Retention is defined as the relative ability to hold the various components of the papermaking furnish in the sheet as it forms on the forming fabric. Two parameters, namely overall and first pass retentions, are used to characterize the retention of fibers and additives during papermaking. Overall retention is defined as the ratio of the amount of materials retained in the final product coming off the reel at the dry end to the amount of materials going into the process at the wet end. For a process to be economical the overall retention needs to be above 90% [10]. In contrast, first pass retention is a measure of how efficiently a given furnish component in the headbox stock is retained on the sheet in a single pass through the forming section. First pass retention can be obtained for any component in the papermaking furnish and it has been found that it affects the final paper quality as well as paper machine operations more than overall retention [10]. From this point on, the term ‘retention’ will be used interchangeably with ‘first pass retention’. Two parameters, total and filler retentions, are of particular interest.

\[
\text{Total retention} = \frac{\text{amount of fibers retained in the sheet}}{\text{amount of fibers added at the headbox}} \quad \text{(Eq. 1.1)}
\]

\[
\text{Filler retention} = \frac{\text{amount of filler retained in the sheet}}{\text{amount of filler added at the headbox}} \quad \text{(Eq. 1.2)}
\]
1.2.2 Retention of fillers in mechanical pulp suspensions

Retention is controlled by two factors: mechanical and chemical. Mechanical filtration involves entrapment of materials on the wire mesh and is responsible for most long fiber retention. However, this factor cannot be relied upon for retention of fines and fillers because their particle size is too small. For example, PCC particles have an average size of 500 to 3000 nm compared to $10^6$ nm for fibers [11]. Hence, it is necessary to resort to chemical means to retain these particles in the sheet. In fact, over 90% of filler retention is controlled by the usage of retention aid chemicals [11].

The retention characteristics of a papermaking furnish depends on a variety of factors, including the pulp type, fiber length distribution, pulping and bleaching process, pulp washing conditions, fines and filler content, filler type, pH, degree of whitewater closure, conductivity, anionic trash level and the hydrodynamic shear imposed at the headbox [5,12,13,14]. The degree of variability in these factors can be much higher in the production of mechanical grades than in fine paper applications [12]. Bleaching with no washing and varying dosages of brightening chemicals, for example, can cause large swings in the cationic demand of the furnish. Some of the anionic trash generated during the pulping and bleaching of mechanical pulps include lipophilic extractives, lignins, polysaccharides, other inorganic materials and organic products of oxidation of wood components [15,16]. Regardless of their organic or inorganic nature, the anionic character of these substances makes them reactive towards retention polymers and reduces their effectiveness. Conductivity, which is a measure of concentration and mobility of ionic species in solution, may also vary significantly. Variation in salt concentration not only affects the electrical double layer of the colloidal materials, it also changes the conformation of polymeric retention aids and affects their adsorption. In fact, changes in salt concentration are one of the sources of instability in paper machine retention and drainage [13,17]. All of these factors make mechanical pulp furnishes some of the more difficult furnishes with respect to achieving good fines and filler retention [7,18,19,20].
1.2.3 Drainage (dewatering)

Drainage or dewatering is the process of removing the water associated with the headbox furnish so that the solids content of the paper web increases from approximately 1 to 95%. Water removal processes are very important because they impact paper quality and paper machine productivity.

Three types of water-fiber relationships have been described: free water, sorbed water and water of constitution. Free water is water held within the capillaries of the paper web and it can flow freely from the sheet when gravitational and hydraulic pressures are applied. Sorbed water is held on fiber surfaces by hydrogen bonding interactions between water, cellulose and hemicellulose. It is generally considered to include water within fiber walls but not within fiber lumens. Sorbed water can be determined using the water retention value test. Water of constitution is bound into the crystalline packing structure of fibers and is essentially inaccessible to papermaking dewatering processes.

Water removal occurs in four distinct zones on the paper machine: forming or free drainage, vacuum, pressing and dryer zones. Much of the free water in a paper web can be removed in the first three zones, whereas free water held in the smallest capillaries and sorbed water are removed in the dryer zone. Wet end chemistry has the greatest impact in the forming and vacuum zones, less impact on pressing zone and very little effect in the drying zone [21].

Two different dewatering processes occur in the free drainage zone: filtration and thickening. Filtration occurs when fibers and fillers are able to move freely in a suspension and a sharp boundary exists between the suspended particles and the forming mat. Consistency in the suspension remains constant throughout this process. Thickening, on the other hand, occurs when the particles in suspension are immobilized in a network whose structure collapses as drainage proceeds. There is no sharp boundary between the formed mat and the suspension. Filtration is the predominant dewatering mechanism in the free drainage zone.
Some factors that affect drainage include filler content, fiber fines content and the degree and type of aggregation of furnish particles. Filler has two competing effects: they do not interact with water as strongly as fibers, thus promoting drainage. However, they can become lodged in the fiber mat pores where they block the flow of water through the network. Fiber fines interact strongly with water and may swell as a result of this interaction, which leads to reduced drainage rate. Mechanical pulps not only contain a large amount of fiber fines, they are also often highly filled. As a result, without any retention/drainage aid it is difficult to obtain good drainage with mechanical pulps.

To achieve good drainage in the free drainage, vacuum and pressing zones, it is important that any retention/drainage aids flocculate fiber fines and fillers but not flocculate fibers. It is also crucial that these flocs are uniformly distributed for good vacuum and pressing response.

1.3 Microparticle retention aid systems
Dual retention aid systems based on microparticles have been introduced to the papermaking industry since early 1980s. These retention aid systems are usually based on negatively charged anionic colloids and positively charged synthetic or natural polymers. Some of the early microparticle retention aid systems include colloidal silica in conjunction with cationic starch [22], sodium montmorillonite together with cationic polyacrylamide [23] and colloidal aluminum hydroxide combined with cationic starch [24]. These initial systems, applied mainly in wood-free furnishes e.g. in fine paper and board manufacturing, were successful because they provided higher retention level and better drainage. This resulted in better formation and a more homogeneous sheet, providing a clear advantage over the single or dual polymer retention aid systems in use at the time.

Out of all the paper machines utilizing microparticle retention aid systems worldwide, about half use some form of colloidal silica [18,19] while the other half uses bentonite [19]. Most customers are in the fine paper or virgin board segments, however, in recent years a broader range of papermaking segments are starting to benefit from the
microparticle retention aid system. Advanced developments in both the microparticles and the polymers have made it possible for microparticle retention aid systems to be effective in more difficult, wood-containing furnishes such as newsprint, light weight coated (LWC) and supercalendered (SC) papers. In this work, the focus will be on the applications of microparticle retention aid systems in wood-containing grades of paper.

1.3.1 Microparticles

Many different types of microparticles have been developed. They have different charges (cationic or anionic), physical structure (dispersed single particles or structured aggregates) and chemical compositions (silica-based, clay-based, organic micropolymers). The major types of microparticles are described.

1.3.1.1 Colloidal silica

Colloidal silica has the same chemical formula as quartz sand, SiO₂. What makes colloidal silica unique is its very small size. The conventional colloidal silica used as retention aid in papermaking are generally composed of discrete spheres of silica about 3 to 5 nm in diameter and have a specific surface area of about 500 to 600 m²/g [19,25].

Colloidal silica solutions are typically prepared by acidification of a sodium silicate (water glass) solution to produce silicic acid. In commercial applications, sulphuric acid is commonly used for this purpose. The silicic acid is then condensed to form particles 1 to 2 nm in diameter before it is grown under specific conditions, e.g. pH between 7 and 10 and in the absence of salts, to produce the desired diameter colloids. When the desired particle size has been reached, the colloidal silica solution is stabilized by diluting the solution to prevent further growth.

The surface of colloidal silica is covered with hydroxyl groups. These hydroxyl groups can ionize in aqueous solutions with a pH above 2 such that the silica particles become anionic. The degree of ionization of the hydroxyl groups is pH dependent. It is this anionic surface charge that allows the colloidal silica to flocculate a paper furnish which
has been made cationic by the prior addition of other chemicals. Clearly, smaller particles will have greater specific surface area and thus will have greater anionic charge density.

In late 1980s and early 1990s, a number of patents such as [26] were issued which claim silica-based microgels are more effective retention and drainage aids than conventional colloidal silica. These microgels differ from colloidal silica in their physical structure, which inevitably leads to the difference in their performance as retention and drainage aids. Whereas colloidal silica is composed of discrete spheres of silica, microgels are composed of silica particles linked together to form three dimensional networks and chains. Typically the silica particles used to form the microgel have a diameter of ~1nm.

Microgels can be prepared in many different ways, for example by the acidification of sodium silicate solution using inorganic or organic acids such as sulphuric and acetic acids or by the addition of alkali metal salts of amphoteric metal acids such as sodium aluminate, sodium stannate, sodium zinicate, potassium chromate and potassium vanadate. Both of these methods will initiate polymerization of the silica resulting in the formation of silica particles 1 to 2 nm in diameter. In the first method, pH of the solution will already be less than 7 and there is nothing to be done except wait until the silica particles start to link together to form three dimensional networks and chains. In the second method, pH of the solution will be between 7 and 10. In this case, addition of some salt into the solution is necessary for the microgel networks and chains to form [27]. It is important that sufficient time be allowed for the formation of the microgel networks and chains. This time will vary with the particular mode of operation, but it should be about 10 to 90% of the time required to form a rigid water-insoluble mass form otherwise known as the gel solidification time [26]. The formation of microgel networks and chains is stopped by diluting the solution.

Microgels produced by these methods typically have specific surface areas of about 1200 m²/g, which is 2 to 2.5 times higher than the specific surface area of colloidal silica [25]. Similar to colloidal silica, microgel surface is also covered with hydroxyl groups that can ionize in aqueous solutions above pH 2 such that the silica particles become anionic.
Because of the larger specific surface area of the microgels, their anionic charge density is also higher than colloidal silica per unit mass.

The extent of microgel formation can be expressed as the S-value [28], which is defined as the percentage of silica in the dispersed phase. Thus, a high S-value means a well-dispersed, non-aggregated colloids while a low S-value means that the silica particles are to a large extent linked to form three dimensional networks and chains. It is noted that S-value is dependent on the silica particle size as well because the particles adsorb water on their surface and the proportion of the water to silica increases as the particle size decreases and specific surface area increases. Therefore, meaningful comparisons of S-value between different products can only be done for products having approximately the same particle size. S-value is determined by measuring viscosity of the microgel solution.

Charge density has been identified as one of the two most important properties of colloidal silica [29]. With conventional colloidal silica, the hydroxyl groups on its surface must be ionized in order for the silica to become anionic. However, sometimes it is not sufficient to rely on the ionization process to make the silica anionic, hence the invention of various modified colloidal silica sols.

One example of surface-modified colloidal silica sol is the aluminum-modified silica sols. These aluminum-modified silica sols have been found to offer significant advantages with respect to retention and dewatering in acidic papermaking conditions [30]. Aluminum-modified silica is very similar to conventional colloidal silica except that the surface layer of the silica particles contain both silica and aluminum atoms.

Aluminum-modified silica is produced by modifying the silica surface of a colloidal silica sol with aluminate ions under the appropriate conditions. This is possible because the aluminate ion \( \text{Al(OH)}_4^{-1} \) and \( \text{Si(OH)}_4^{0} \) are geometrically identical. Thus, the aluminate ion can be substituted into the \( \text{SiO}_2 \) surface, generating an aluminum silicate ‘seat’ with a fixed negative charge on the particle surface [27]. At low pH (4 to 6) the aluminate ion is
strongly anionic in character. This strong anionic character at low pH is not obtained with unmodified silica sols because silicic acid is a weak acid with pKₐ about 7.

Apart from aluminum, there are at least three other compounds that have been used to modify silica sol. These compounds are anionic polyelectrolytes [31], boron [32] and nitrogen [33]. The motivation behind these modifications is the same: to increase the anionic charge density of the colloidal silica.

1.3.1.2 Bentonite
Bentonite is a rock that typically contains two or more minerals, at least one of which is from the smectite clay mineral group. It is this smectite that gives bentonite the characteristic interactions with water so critical in the performance efficiency in virtually every application where bentonite is used, especially in papermaking.

Smectites are unique because of the combination of their particle shape, size and charge. Smectite minerals form two dimensional crystals which have a uniform thickness of about 0.9 nm but highly variable lateral dimensions, ranging from a few micrometers to a few nanometers in the largest dimension [19,34]. In the dry state, smectite crystals form stacks of aggregates. When hydrated, they will swell because osmotic pressure causes water to penetrate the spaces in between the smectite crystals that form the aggregates. As a result, the specific surface area increases from about 100 m²/g in the aggregated state up to about 800 m²/g in the dispersed state [34].

There are three layers in the basic chemical structure of a smectite crystal. The centre of the crystal consists of a layer of oxygen octahedral containing magnesium and/or aluminum ions. Layers of oxygen tetrahedra form on either side of the octahedral layer. The corners of the octahedral, where oxygen atoms are not shared with the tetrahedra, consists of hydroxyl ions. Typically each tetrahedra contains a silicon ion.

This “2:1” type of mineral structure is not exclusive to smectites. Pyrophyllite, mica and vermiculite also have the same structure, but they do not belong to the smectite mineral
The number and type of metal ions in the octahedral and tetrahedral layers are the key difference between these minerals and the smectite mineral group. In pyrophyllite, for instance, the net positive charge of all the metal ions is equal to the net negative charge of the anions. In mica and vermiculite there is a lack of structural cations within the crystal, so the crystal carries a large negative charge. Smectites fall in between these two extremes. Overall, they carry a slight negative charge.

It is also important to note that while the negative ions within the crystal structure are stationary, the cationic metal ions are mobile and are readily exchanged for other cations that come near the crystal. When a smectite crystal is hydrated, these exchangeable cations tend to diffuse away from the crystal surface to form an electrical double layer of positive charges around the negative crystal surface [36]. The electrical double layer is very important because it keeps the smectite crystals dispersed in water – without it the smectite crystals would form aggregates. Aggregation results in greatly reduced surface area and smectites in this form have little commercial value, especially in wet end applications in papermaking.

The size of the double layer is dependent on two opposing forces, which are the electrostatic attraction between the negatively charged crystal and the cations and the diffusion of exchangeable cations towards low cation concentration in the bulk of the solution. Greater attraction makes it more difficult for the exchangeable cation to diffuse away from the crystal, whereas greater difference in concentration results in a greater driving force for the cations to diffuse away from the crystal. Therefore, salt concentration and the valency of the exchangeable cation are important factors in the performance of smectites.

In commercial applications, sodium is often the best choice for the exchangeable cation because it allows for the significant formation of the electrical double layer, which results in an easy-dispersing smectite. Multivalent exchangeable cation is undesirable because its strong electrostatic forces of attraction to the negatively charged crystal surface inhibit the formation of electrical double layer and thus inhibit dispersion. Fortunately, smectites
can be easily converted to the sodium form by ion exchange. For instance, most commercial sodium bentonite is produced by treating calcium bentonite with sodium carbonate. In this reaction, calcium carbonate and sodium bentonite are formed.

In most smectites, the crystal charge resides primarily in the octahedral layer. This results from the type and amount of metal ions present. A dioctahedral structure is an octahedral structure in which 2/3 of the octahedral holes contain a metal ion. A trioctahedral structure is an octahedral structure in which all of the octahedral holes contain a metal ion. Smectites exist in both structural forms [35,36]. Negative charges can also exist in the tetrahedral layer, for example if instead of Si$^{4+}$ the metal ions present are Al$^{3+}$ or Fe$^{3+}$. This is generally undesirable because the electrostatic attraction between the exchangeable cation and negative charges on the crystal is much stronger than with charges in the octahedral layer, reducing the dispersibility of the smectites. The most important smectites commercially are montmorillonite and hectorite. Both have most of their charge in the octahedral layer.

Because bentonite is a rock containing smectites and other minerals, the level of impurity has an effect on its performance as a retention and drainage aid. In fact, most bentonites in their natural form are unsuitable for use in many applications. Advances in processing techniques, however, have allowed for the production of pure, high performance bentonite.

In summary, some of the factors that can maximize the performance of bentonite in the wet end include using exchangeable cations that promote better dispersion of the smectite e.g. sodium vs. calcium, increasing hydration time, shear and water temperature during the smectite dispersion or hydration step and using smectites that have a lower crystal charge.

1.3.1.3 Organic micropolymerms
The idea behind the development of polymeric microparticles, or micropolymers, is to incorporate the performance aspects of both inorganic microparticles (highly ionic
surface, sub-micron dimensions and a three-dimensional structure) and polymeric flocculants and coagulants (flexible polymer chains of controlled ionic charge) [37,38,39,40,41]. The result is an anionic water soluble filamentary micronetwork polymer.

Monomers of the micropolymer are referred to as microbeads and they may be made as microemulsions by a process employing an aqueous solution comprising an anionic monomer and a crosslinking agent, an oil comprising a saturated hydrocarbon and a surfactant [39].

Polymerization of the emulsion may be carried out by adding a polymerization initiator. Alternatively, polymerization can also be initiated by subjecting the emulsion to ultraviolet irradiation. The polymer may be recovered from the emulsion by stripping or by adding the emulsion to a solvent which precipitates the polymer, filtering off the resultant solids, drying and redispersing them in water.

These polymeric microparticles (approximate size: 750 nm) have been shown to have similar effects on retention and drainage compared to inorganic microparticles such as colloidal silica and bentonite [38]. This result stems from the structural difference between the micropolymers and the inorganic microparticles [37]. The micropolymer can be visualized as having a “core” network and polymer chains, tails, loops and strands that extend out from this core. As a consequence of having these polymer chains, tails, loops and strands that extend out from the core, the specific surface area can be very high even though the size of the microparticle is significantly larger than the inorganic microparticles. Thus, the retention and drainage performance is comparable to inorganic microparticles. For the same reason, micropolymers also show superior results to solid, non-cross-linked microspheres (approximate size: 50 to 90 nm) [38].

1.3.1.4 Cationic microparticles

Although microparticles are typically anionic, cationic microparticles such as cationic colloidal silica, polymeric microparticle and bentonite are also known.
Cationic colloidal silica is prepared by adding an aqueous colloidal silica prepared in a similar way as previously described to an aqueous solution of a basic aluminum salt [42]. This causes the silica surface to be coated with positive aluminum species, rendering the colloidal silica cationic. Cationic polymeric microparticle is prepared by inverse emulsion polymerization techniques using cationic rather than anionic monomers [43]. Cationic bentonite is manufactured by incorporating cationic organic molecules into bentonite via an ion exchange mechanism similar to one used to incorporate cationic metal ions [44].

1.3.2 Polymers used in conjunction with the microparticles
1.3.2.1 Cationic starches

In the original microparticle retention aid system, cationic starch is used in conjunction with colloidal silica [22]. Thus, starch, particularly its cationic derivatives, has always been in the spotlight as one of the polymers paired up for use with microparticles.

Starch is a plant-based complex carbohydrate that unlike other carbohydrates occurs as discrete particles known as starch granules. These granules have different shapes and sizes depending on the plant they come from. For example, tapioca starch, which is a root starch, has granules 10 – 35 µm in diameter and can be round or oval in shape. On the other hand, waxy maize starch, which is a cereal starch, has granules that are 10 – 25 µm in diameter and can be round or polygonal in shape [45].

Starch granules are insoluble in cold water but they can swell when their aqueous dispersion is heated. Increasing temperature causes the molecules in the starch granule to vibrate and break intermolecular bonds, thus allowing increased interactions with water. Water penetration and the increased separation of starch chains increase randomness and decrease crystallinity in the granule. Continued heating will eventually cause a complete loss of crystallinity and the starch is now in the form of a paste. The temperature range at which this happens is called the gelatinization temperature range and it varies between different starches. During gelatinization, the starch granules swell extensively: water
enters the granules and the swelled granules are pressed tightly against each other, resulting in an increase in viscosity of the starch suspension. Highly swollen granules are fragile and disintegrate easily with mild stirring, causing a decrease in viscosity. Typical uses in the paper machine wet end require the starch to be cooked prior to addition to the furnish. Upon cooling, paste consistency increases due to the formation of side by side molecular associations that increase paste resistance to deformation or flow. Therefore, when cooled, the paste may remain fluid or form gels.

Chemically, starch is composed of two types of molecules, namely amylose and amylopectin. Amylose is a linear polymer of glucose linked with mainly $\alpha (1,4)$ bonds. Amylopectin is a highly branched polymer of glucose linked linearly with $\alpha (1,4)$ bonds and branched with $\alpha (1,6)$ bonds. Amylose molecules have degrees of polymerization of about 350 to 1000, compared to amylopectin which has a degree of polymerization of several thousand [46]. Amylopectin is a much larger molecule than amylose, as shown by their molecular weights (one to several million Daltons vs. 50,000 to 200,000 Daltons). Typically, starches consist of about 75 to 80% amylopectin molecules, but the exact amylose to amylopectin ratio is unique to each plant. For example, tapioca starch is made up of 18% amylose and 82% amylopectin, whereas waxy maize starch is made up of <1% amylose and 99% amylopectin. As a result, starches derived from different plant species have different physio-chemical properties.

While it is difficult to pinpoint the structure – function relationship for starches in wet end chemistry, there is evidence suggesting that both amylose and amylopectin are important for optimum performance as a retention aid. In order for starch to be effective in a microparticle retention aid system, it has to be able to do two things: adsorb to fibers and fillers while also having extended loops and tails in solution to interact with the anionic microparticles. Amylose is found to preferentially adsorb on fibers [47] and microcrystalline cellulose [48], leaving the amylopectin in solution since amylopectin is more hydrophilic than amylose. In [29], it is found that there is a critical colloidal silica size range for optimum retention, which is about 3 to 5 nm. This critical size range corresponds well with the distance between tufts of branches in the amylopectin molecule,
which is approximately 5 to 7 nm. Thus, the reduced retention effect caused by very small colloidal silica particles can be explained by the fact that they are likely to penetrate into the bulk of the amylopectin molecule and lose their flocculation abilities. In [49], it is confirmed that the amylopectin fraction is most responsible for strong microparticle interactions. These findings are consistent with findings from another work [50] where several features of cationic starch that are important for good performance in microparticle retention aid systems are identified. These features include starch molecular weight and hydrodynamic volume, which are directly related to the interactions between amylose and amylopectin in solution.

Thus far the discussion has focused on native starches, however, starches may be modified in various ways, both physically and chemically. With respect to the application in wet end chemistry, starches modified chemically are of the most interest. For instance, the starches may be converted to cationic derivatives. These modifications, which are normally present in very small concentrations in starch preparations, produce dramatic differences in the physio-chemical properties of starch.

Cationic starch is generally prepared by reacting the starch with reagents containing tertiary and quaternary amine groups such as aminoalkyl ethers and ammonium ethers. The reaction is typically carried out under alkaline conditions followed by acidification to produce the desired cationic derivative. Excess reagent is removed by vacuum distillation or solvent extraction. Zeta potential measurements show that these cationic starch derivatives have a net positive charge at a pH of between 4 and 9. Consequently, cationic starch is used exclusively with anionic microparticles.

Modified starches are usually characterized by their degree of substitution (DS), which is defined as the average number of modified hydroxyl groups in a glucose unit. The typical level of derivatization is one or two modified hydroxyl groups per hundred glucose unit. Another way of expressing this is by the percentage of substitution, which is the ratio of molecular weight of the added product (e.g. quaternary amine) on the molecular weight of the starch. Degree of substitution can be calculated using the following formula:
Degree of substitution \[
\frac{\text{grams of nitrogen}}{\text{molecular weight of nitrogen}} \times \frac{\text{grams of glucose}}{\text{molecular weight of glucose}}
\] (Eq. 1.3)

Products with different DS are made by reacting the starch with different concentrations of the chosen reagent. DS can be determined by NMR microscopy. While DS has a large effect on the performance of the starch in the wet end, it is not the only factor as shown in [51], where tapioca and potato starches of comparable DS have different behaviors.

### 1.3.2.2 Polyacrylamides

Among papermakers, the term ‘polyacrylamide’ is commonly used to refer to the most popular varieties of cationic and anionic polymeric retention aids. These ‘polyacrylamides’, however, is usually not the homopolymer poly(acrylamide) but rather copolymers of it, which is composed of mostly acrylamide monomers with a small amount of anionic or cationic co-monomers. These polyacrylamides will be referred to as flocculant in later sections of this thesis.

The utility of these hydrophilic polymers as retention aids is directly related to their physical and chemical structures, charge density and molecular mass. The amide group (-CONH₂) in polyacrylamides provides for its solubility in water and a number of other polar solvents. Polyacrylamides generally have a linear structure, but they can be made to cross-link with the use of cross-linking agents. Acrylamide polymers used as retention aids typically have molecular masses in the range between 2 to 20 million Daltons [52].

The charge density varies from low, medium to high, which corresponds to the mole percent of charged monomers on the polymer backbone. In one study, the range of charge densities run from 0.25 to 3 meq/g [29], which leads to the interpretation of low charge density as <1 meq/g, medium as between 1 and 2 meq/g and high as >2 meq/g. The corresponding percentage of charged monomers is between 2 and 25 mol%.
Some of the monomers used in the production of polyacrylamides and their copolymers are acrylamide, acrylic acid, N,N-dimethylacrylamide, N-isopropylacrylamide, methacrylic acid [52]. For the production of anionic copolymer, the co-monomer is often acrylic acid. Cationic co-monomers typically contain quaternary ammonium groups.

Cationic copolymers dominate the acrylamide polymer market. These copolymers are manufactured by various commercial processes that will be discussed shortly. The most widely used cationic co-monomers are cationic quaternary amino derivatives of (meth)acrylic acid esters or (meth)acrylamides and diallyldimethylammonium chloride [53]. The cationic monomer content can range from 5 to 80 mol% depending on the application. Because the cationic monomers are expensive, the actual composition used is determined by cost – performance relationship in the intended applications.

Diallyldimethylammonium chloride (DADMAC) is probably the least expensive commercially available cationic monomer. It is typically produced by reacting allyl chloride, dimethylamine and sodium hydroxide in an aqueous solutions [54,55]. DADMAC has been found to homopolymerize to form polyDADMAC, without cross-linking [54]. High monomer concentrations (> 1.5 mol/L) used in commercial processes result in greater rates of polymerization and thus higher molecular weight polymer. p-DADMAC with low residual unreacted monomer can be manufactured in water using either persulfate addition or ammonium persulfate with sodium metabisulfite [56]. Polymerization of DADMAC has also been done in a water-in-oil emulsion, in which case the oil-soluble initiator 2,2’-azobis(2,4-dimethylvaleronitrile) and the surfactants sodium di-2-ethylhexylsulfosuccinate and sorbitan monoleate are used [57]. The usefulness of p-DADMAC rests on its very high cationic charge.

There are many requirements for commercial polymers: low insolubles content, low residual monomer content, fast dissolution rate, ease of handling, product uniformity, long term storage stability, high solids content and consistent performance characteristics [53]. Several commercial processes have been developed to meet these requirements.
Solution polymerization basically involves having an aqueous solution of monomers and adding an initiator to it to start the polymerization reaction. The heat evolved in the reaction can be removed by a cooling system. The product polymer is then precipitated out of the solution, dried and milled to the desired particle size. Alternatively, the polymer may be sold in solution.

Inverse emulsion polymerization is another polymerization technique involving the emulsification of the aqueous monomer solution in an oil-containing surfactant, homogenizing the mixture to form a water-in-oil (inverse) emulsion and subsequently polymerizing the monomers in the emulsion [58]. Work on the inverse emulsion polymerization have resulted in processes that can yield fine particles small enough to remain suspended in solution [59,60].

Most retention aids are currently produced and delivered to the mill site in the form of a water-in-oil emulsion. Prior to use, the emulsion needs to be inverted with good agitation and diluted.

1.3.2.3 Guar gum
Guar gum is sometimes used as an alternative cationic polymer in anionic microparticle-based retention aid systems [30,61]. Guar gum is one example of a galactomannan. Similar to starch, galactomannans are plant reserve carbohydrates that occur in the endosperm within the seeds of many plants. During sprouting, galactomannans are degraded to provide nutrition for the growing plant. Guar gum is one such galactomannan that is derived from the seeds of guar plant (*Cyamopsis tetragonoloba*).

Galactomannans are polysaccharides consisting of a mannose backbone with galactose side groups. Specifically, the backbone consists of a β-(1,4)-D-mannopyranose with branch points from their 6 positions linked to an α-D-galactopyranose. The ratio of mannose to galactose varies between plant species, with guar gum having a mannose:galactose ratio of about 1.5:1 [62].
Gum content and viscosity of the aqueous guar gum solution are important quality factors in commercial guar gum products. As with starches, galactomannans also have hydroxyl groups that can be substituted. Cationic derivatives of guar gum are of particular significance in the wet end chemistry application. Similar to cationic starches, cationic guar gum is obtained by reacting guar gum with reagents containing tertiary or quaternary amine groups such as 2-hydroxy-3-chloropropyltrimethylammonium chloride in alkaline conditions.

1.3.3 Factors affecting the performance of microparticle retention aid systems

Some factors that affect the performance of different microparticle retention aid systems will be considered in this section. Most of the following discussion applies to anionic microparticle retention aid systems. Cationic microparticle retention aid systems are covered in a separate section.

1.3.3.1 Electrostatic effects

The role of zeta potential with respect to retention and drainage has been debated long before the introduction of microparticle retention aid systems [63]. For example, when using high charge density cationic additives such as polyethyleneimine or alum, surface charges have a dominant effect [64,65]. These polymers flocculate via patch flocculation, where patches of adsorbed polymer with opposite charge to the surface interact coulombically with uncovered surfaces on other particles. Thus, maximum drainage and retention are often associated with addition rates that achieve an average zeta potential near to zero. This is not necessarily so with high molecular weight, low to medium charge density polymers. These polymers flocculate via bridging flocculation. Bridging between particles do not require a zero zeta potential but only the ability of the polymer to span the combined electrical double layers of the particles to be flocculated [63,66]. Because microparticle retention aid systems typically use this latter type of polymers, it is reasonable to expect that the maximum drainage and retention can occur when the zeta potential of the system is still negative.
Nevertheless, microparticle retention aid systems are significantly affected by charge [29,40,67]. A charge dependant mechanism explains why the effectiveness of microparticle retention aid systems increase with increasing surface area, or decreasing size of the primary particles [5,29]. It has been reported that in order for microparticle retention aid systems to be effective, excess anionic dissolved colloidal and polymeric materials need to be neutralized with alum or a high charge cationic polymer [18,29,41,68]. Otherwise, the charge density of the cationic flocculant or its dosage has to be increased.

While charge issues tend to dominate the interactions involving small colloidal silica particles, interactions involving larger bentonite particles seem to be less affected by charge [69,70]. Studies have found that colloidal silica does not interact with the uncharged monomers in a polymer – it only interacts with the charged groups. If the polymer adsorbs in a flat configuration, the interaction would be weak. On the contrary, bentonite interacts with both the charged (via electrostatic bonds) and non-charged (via hydrogen bonds) segments of the polymer. As a result, it enhances flocculation regardless of the polymer charge density [70].

1.3.3.2 Microparticle bridging and the effect of shear

While macromolecular bridging mechanism has already been established as a mechanism of flocculation by polymers [5], the evidence suggests that microparticles form bridges of a different nature. For example, flocs formed by the combination of microparticle and high molecular weight polymers have different shear resistance and reflocculating ability after redispersion due to hydrodynamic shear forces compared to flocs formed by high molecular weight polymers alone.

The concept of macromolecular bridging mechanism develops from the observation that in the absence of colloidal contaminants, the strongest resistance to hydrodynamic shear forces can be achieved with polyelectrolytes having a low charge density but very high molecular weight - a counterintuitive fact if only charge effects are considered [71,72]. Also, the conditions leading to maximum retention and drainage seldom correspond to
charge neutrality of the surfaces, or zero zeta potential [63,66]. Because the polyelectrolyte have a low charge density and very high molecular weight, once adsorbed on a surface it can form many loops and tails on the surface that are able to bridge two close particles. The formation of polymer bridges between adjacent fibers is considered to be most effective at 50% surface coverage [73]. A higher surface coverage results in less flocculation and eventually in steric or electrosteric stabilization [74].

Flocs formed by bridging flocculation have a high resistance to hydrodynamic shear. This is demonstrated by several experiments in which the resistance to detachment of solid particles from surfaces pretreated with high molecular weight cationic acrylamide copolymers is found to be several orders of magnitudes higher than what can be achieved using charge neutralization [72]. However, once the bridges are broken, the ability of the polyelectrolyte to reflocculate the fibers is greatly reduced. This is because hydrodynamic shear cleaves the polymer chain, resulting in shorter loops and tails. Also, the polymer chain may change its conformation to a flatter form, thus reducing its ability to bridge particles and reflocculate [75].

On the other hand, flocs formed by microparticle retention aid system are at least partially reversible [76,77,78]. This reversible nature of microparticle retention aid system is linked to the fact that the bridging flocculation takes place with the aid of anionic microparticles rather than high molecular weight polyelectrolyte. Upon shearing, polymeric bridges are cleaved and shorter polymer loops and tails result. Some of these shorter polymer loops and tails are still attached to fibers or fillers, whereas others are completely released from fibers or fillers. When microparticles are added, they interact via a charge mechanism with the cleaved polymer segments and cause reflocculation by forming bridges between polymer chains [69]. If the polymer is a highly branched one, such polymer cleavage may be even more advantageous because many more polymer loops and tails will be available for interaction with the microparticles [79]. It has been suggested that the reversibility of microparticle bridging is responsible for the formation of a porous sheet and good fines and filler retention [75].
It has also been shown that bridges formed by microparticles are more shear-resistant than those initially formed by a cationic acrylamide copolymer earlier in the same operation. In one study, fibers treated with cationic polyacrylamide alone forms flocs that decay rapidly with shear [80]. Subsequent addition of colloidal silica yields flocs that have a slower decay rate under continuous agitation. Another study using cationic acrylamide copolymer and montmorillonite shows similar results [81].

1.3.3.3 Dewatering effect of microparticle retention aid systems

A mechanism that explains the dewatering effect of microparticle retention aid system is illustrated in [66]. Because of the very small size of microparticles (e.g. 5 nm for colloidal silica), these particles are able to penetrate into the coiled structure of the adsorbed cationic starch or acrylamide copolymers [29]. Due to the strongly opposite charges, the polymer coils can then be expected to wrap themselves around the particles. This causes the polymer – microparticle complex to contract and expel water [18]. Furthermore, any fine materials connected by polymer bridges will tend to be brought closer to the fiber surface. This explanation is consistent with the observed increased dewatering and higher wet press solids [82,83,84].

1.3.3.4 Microparticle size effects

Microparticle bridging mechanism outlined previously is consistent with the observed increase in flocculation with increasing specific surface area of the particles. There is, however, a limit to how small the microparticles can be before they start being ineffective. For anionic colloidal silica in the presence of cationic starch, this lower limit is about 3 to 5 nm [29,85]. Due to its high width to thickness ratio, montmorillonite is expected to have a high bridging tendency. Consistent with these expectations, in silica-based microparticle systems the polymeric flocculants have a dominant effect on the extent of flocculation [69,86]. For clay-based microparticle systems, the microparticles have a dominant effect [67].
1.3.3.5 Polymer size effects
Polymer bridging effects are expected to be strongly dependent on the molecular weight of the polymer. This is confirmed in [87], but only in the absence of microparticles. With microparticles, there is some dependence on the relative charge densities as well as the molecular weight of the polymer. For instance, low to medium charge density high molecular weight polymer is found to show better retention than high charge density high molecular weight polymer when used in combination with bentonite [88]. This is because with the low to medium charge density polymers, there will be some polymer loops and tails extending out from the surface due to weaker electrostatic interaction with the surface [21].

One reason to expect high molecular weight polymers to be effective as bridging polymers is that they will have many loops and tails extending out from the surfaces of particles on which they are adsorbed. Also, because they have long chains, they will take longer to adapt to a flat conformation. Evidence supporting this comes from the benefits of pretreating the furnish with low molecular weight, high charge cationic polymers [18,89]. Such polymers adsorb on the surface of fibers, fillers and fines via patch flocculation. This prevents the high molecular weight, low to medium charge cationic polymer to adapt to a flat conformation over the surface. This effect is called the site-blocking effect.

1.3.3.6 Necessity of a three-dimensional structure
There seems to be an advantage in the use of either microparticle or polymeric flocculant that have a branched, three-dimensional structure [26,37,79]. It has been proposed that a three-dimensional microparticle is advantageous because they cannot lie flat against a fiber surface and hence they remain effective for bridging between fiber and filler surfaces [90].

It is interesting to note that in many microparticle systems in use today, if the microparticle used is a non-structured type then the polymeric flocculant is chosen to be the branched type. If the polymeric flocculant is a linear type, then the microparticle
chosen is usually the structured, three-dimensional type. For example, the original silica-based microparticle retention aid system consists of non-structured colloidal silica with cationic potato starch, which has a high content of branched amylopectin molecules [22]. In contrast, linear polyacrylamides are paired up with colloidal silica microgels, in which the primary particles are either joined in chains or clusters. This has been confirmed in [29], where it is concluded that in cationic polyacrylamide systems, the size of the anionic colloidal silica must be much larger than in cationic starch systems to achieve an efficient synergistic retention effect.

1.3.3.7 Order of addition effects
The order of addition of microparticles and other polymeric flocculants have a significant impact on the effectiveness of the microparticle system. Fundamental work has shown that the surface on which the polymer first adsorbs is crucial for the effectiveness of the system [91,92]. Montmorillonite is also shown to be very effective at bridging polymer layers that are first adsorbed on a cellulosic surface. On the other hand, polymer adsorbed on montmorillonite gives poorer results compared to polymer adsorbed on fiber or fines. This is explained by different conformations of the adsorbed cationic polyelectrolyte layer on surfaces with different surface charges. A very high negative surface charge, such as those on the montmorillonite, reduces the thickness of the adsorbed layer. This compromises its bridging ability since fewer loops and tails are extending out from the adsorbed layer. In contrast, cellulosic fibers and fines are only slightly anionic. This gives a greater likelihood that the tails and loops of the polymer remain extended from the surface. The conclusion from this work is that the order of addition matters and addition of polyelectrolyte prior to the microparticle is favored. Hence, in most microparticle retention aid systems, the polyelectrolyte is added prior to addition of microparticle.

It is also known to add the polymer and the microparticle to the pulp furnish simultaneously, or even sequentially but in the reverse order [31]. In terms of the adsorption order, these orders of addition are identical to sequential addition described previously because the adsorption of polymers on fibers and fillers are relatively fast.
compared to the adsorption of microparticles, which in this case is bentonite, on these surfaces [93,94].

Split addition of starch, where a portion of the starch is mixed with the filler and the remainder is added directly to the pulp, has been reported to eliminate linting problems in the paper machine [95]. It is known that starch is usually most effective as a retention aid and dry strength agent when it is located on long fibres, therefore the impact of splitting the starch addition on retention and drainage will depend on the split ratio used.

1.3.3.8 Cationic microparticle retention aid systems
Certain aspects of the cationic microparticle retention aid system are identical to those of the anionic microparticle retention aid system. For example, the synergy between cationic microparticles and low to medium charge density polymers is better than that between the cationic microparticles and high charge density polymers. This suggests that polymers of low charge density and high molecular weight interact via a bridging mechanism, where the polymers tails and loops extend far into the solution [96]. This view is supported by the fact that maximum flocculation has been found when the zeta potential is still negative [97]. Also, particle size and charge density of the cationic microparticles are found to be major factors affecting flocculation [98].

The preferred order of addition for cationic microparticle systems is the opposite of that for the anionic microparticle systems [96]. This makes sense considering that furnish components are usually negatively charged. In these systems, typically the cationic microparticle is added first, followed by the anionic polymeric flocculant. Addition of cationic microparticles after the anionic polymer results in large flocs that may be detrimental to the finished sheet formation. However, when the cationic microparticles are added first, small shear resistant flocs are formed. This situation is clearly more favorable for good sheet formation.

A schematic of filler flocculation by cationic microparticle followed by anionic polymer is shown in [99]. The cationic microparticles either bridge between the furnish
components via their negatively charged surfaces or coagulate them by reducing the electrostatic repulsion. Due to their small size, the bridge length is short, resulting in flocs that are small and not easily broken down. When the anionic polymer is added, the floc size grows as a result of polymer bridging between the small flocs through the cationic microparticle patches. Electrostatic repulsion between the anionic polymer and the anionic furnish components expands the floc network, allowing for a more ‘open’ floc.

Cationic microparticles do not only work well with anionic polymers [96,99], they also can have good synergistic effects with cationic polymers [97]. This is in contrast with anionic microparticles, which only work well with cationic polymers. The synergistic effect of the cationic microparticle – cationic polymer system has been attributed not only to the site-blocking effect (minor) but also to the electrostatic repulsion force between cationic microparticles and cationic polymers (major). Such electrostatic repulsion can affect the conformation of the polymer to one where there are many loops and tails extending out from the adsorbed surface as opposed to a flat conformation [97].

### 1.4 Optimization and control of microparticle retention aid systems

To summarize, there are four main steps in a typical microparticle retention aid program:

1. Pretreatment of the furnish with a high charge cationic polymer
2. Addition of high molecular weight, low to medium charge cationic polymer
3. Application of hydrodynamic shear
4. Addition of microparticles

Each of these steps has its own purpose along with some control and optimization strategies.

Pretreatment of the furnish with a high charge, low molecular weight cationic polymer is often, but not always, necessary for the microparticle retention aid system to work well [95,100,101,102]. This is especially true when the furnish contains a high amount of dissolved colloidal materials, such is the case with wood-containing furnishes. This high charge, low molecular weight cationic polymer not only neutralizes some of the anionic dissolved colloidal materials, it also can adsorb on the fibers, fines and fillers for the site-
blocking effect. It is recommended to add just enough of this additive to neutralize the anionic colloidal material while still leaving enough anionic sites on the fiber surface for the cationic flocculant to interact with.

Retention response is most commonly adjusted by changing the dosage of the high molecular weight cationic polymer. The level of hydrodynamic shear is usually adjusted by changing addition point of the high molecular weight polymer. The most common choice is just prior to the pressure screens. Adding the high molecular weight polymer after the screens has the risk of excessive fiber to fiber flocculation in the finished sheet which can lead to poor formation. In fact, the purpose of applying hydrodynamic shear is to break up any fiber to fiber flocs for uniform formation. It has been suggested that best results can be achieved if the dosage of the cationic polymers is somewhat overdosed, resulting in a positive zeta potential [8]. Because of this requirement, the dosage of cationic polymer may be higher in microparticle systems compared to conventional dual retention aid systems [91]. As a result, microparticle retention aid system is more expensive.

Finally, microparticle addition promotes the de-swelling of adsorbed polymers that squeezes water out and thus promote dewatering. It also compensates for the negative effect of shear on fines retention by reflocculating part of the broken flocs. It is common practice to leave the flow of microparticles at a constant level during a production cycle to simplify the control strategy [66].

1.5 Increasing the filler content of mechanical grade papers

Mineral fillers such as PCC are added to the pulp suspension for two main reasons. One is to reduce the amount of fiber required to produce a given amount of paper because mineral fillers are much cheaper than fibers. Second is to achieve certain paper qualities such as brightness, smoothness and opacity. Without fillers, some of these qualities cannot, or are too expensive to achieve [103].
Considering the cost benefits from an increased amount of PCC, it is desirable to increase PCC content beyond the standard currently used in communications grade papers. However, as filler content is increased, paper strength is reduced resulting in poor paper machine runnability. Fillers do not contribute to paper strength, thus its use lower the concentration of load-bearing fibres. In addition, filler particles accumulate on exterior fibre surfaces reducing paper strength by interfering with inter-fibre bonding. Furthermore, as filler content is increased, higher dosages of retention aids would be required to retain them on the sheet to the point that makes it uneconomical.

A novel approach to achieve highly-filled paper is by loading the filler within the fiber lumen, where it does not interfere with fiber to fiber bonding [104]. The basic process of lumen loading involves an impregnation step in which the pulp is agitated in a concentrated suspension of filler to allow the filler particles to enter the lumens via pit apertures. If attractive forces between the filler particles and the fibre surfaces exist, the filler bonds to both exterior and the lumen surfaces of the fibres. In a subsequent step the particles on the exterior surfaces of the fibres are removed by washing the pulp. Handsheets containing up to 40wt% clay has also been reported [105]. Thus, the potential exists for greater filler contents in the paper without sacrificing paper machine runnability.

1.6 Research objectives
The scope of this work is to investigate the retention of precipitated calcium carbonate (PCC) as well as drainage in papers made from mechanical pulps using various microparticle retention aid systems. Both cationic starch and synthetic polyacrylamide flocculant are used in conjunction with aluminum-modified silica microgels. The cationic starch is added primarily as dry strength additive, but it also functions as a retention/drainage aid. Two different starches are used, namely tapioca and waxy maize. Two different synthetic polyacrylamides are used. They have different molecular weight, structure and charge densities. Flocculant 1 has a linear structure and low charge density, whereas flocculant 2 has a branched structure and medium charge density. Flocculant 1 also has a greater molecular weight than flocculant 2.
Dosage of the starch will be fixed at 8 kg/t OD pulp. Dosage of flocculant 1 is varied between 0.4 and 1.0 kg/t OD pulp. Dosage of flocculant 2 is varied between 0.2 and 0.5 kg/t OD pulp based on recommendation from industry partners. Dosage of the silica is varied between 0.25 and 0.75 kg/t OD pulp. For the majority of this work, PCC loading is 250 kg/t OD pulp. In the last part, PCC loading is increased to 300 kg/t and 500 kg/t OD pulp.

All drainage and retention experiments are carried out using a 50 mesh screen (200 µm holes). Elucidation of mechanics will be aided by cationic demand and zeta potential measurements. This is done in all of the experiments except in the first part of the split starch addition experiments.

The specific objectives are:

1. To use factorial experimental design to investigate the effect of flocculants 1 and 2 as well as silica on total and filler retention in the presence of tapioca and waxy maize starches.
2. To compare the performance of tapioca and waxy maize starches in terms of retention and drainage when used in conjunction with flocculants 1 and 2 as well as silica.
3. To compare the retention and drainage performance of flocculants 1 and 2 in the absence of starch but in the presence of silica.
4. To investigate the effects of using split starch addition on retention and drainage. Split starch ratio is first varied with tapioca starch only and with the flocculant 1. The best split starch ratio is then used in split starch additions using all other combinations of starches and flocculants.
5. To investigate the effects of increasing the PCC content of the furnish on retention and drainage. The starch and flocculant identified as the most suitable for this furnish will be used together with the silica.
CHAPTER 2
EXPERIMENTAL DETAILS

2.1 Materials

2.1.1 Pulp
The pulp used in all of the experiments is peroxide-bleached TMP supplied by a pulp and paper mill in coastal British Columbia. It is a mixture of spruce, pine and fir. The pulp is collected from a storage chest following the bleach plant and is received at a consistency of approximately 4%. It is unpreserved and is kept in cold storage at 4°C. Prior to use, the pulp is diluted to 1% consistency using process water. This is done in an effort to emulate mill conditions. 1% consistency is chosen because it is the typical headbox consistency for mechanical paper grades. pH of the pulp is 7.2 ± 0.1.

2.1.2 Process water
Process water is the water obtained by centrifugal separation of the 4% consistency pulp. The pulp is placed in a screen bag and loaded into the centrifugal separator (Bock, Toledo, USA). The pulp is retained in the screen bag and is discarded while water from the outlet is collected and is referred to as process water. It is expected that the process water contains dissolved and colloidal substances.

2.1.3 Precipitated calcium carbonate (PCC)
PCC used in this work is an acid-tolerant PCC obtained at 25wt% solids content from Specialty Minerals Inc (Bethlehem, Pennsylvania, USA). It has an average particle size of 3 µm, brightness of 98% ISO and scalenohedral structure, as shown in Figure 2.1. It has a zeta potential of -15 ± 5 mV in DDW and the pH is 8.7 ± 0.1. Its particle size distribution is shown in Figure 2.2.

2.1.4 Starches
Two different starches – tapioca and waxy maize – are used. These starches are received in dry powder form and are supplied by National Starch Inc. (Surrey, BC, Canada). Prior to use, both starches are made up to 2wt% solids solution and cooked. Further details on
starch cooking are found in procedure section. All starches are used within 24 hours of cooking.

Selected properties of these starches are shown in Table 2.1. Viscosities of these starches are obtained at a solids content of 2% by using the Brookfield viscometer and spindle LV3 at 25°C and 40 rpm. Figure 2.3 shows that both starch solutions are shear-thinning liquids.

2.1.5 Flocculants
Two different flocculants are studied in this work. Flocculant 1 is 6D16, supplied by Nalco (Naperville, IL, USA). It is received in the form of a polymer emulsion. Flocculant 2 is XP1067, supplied by Eka Chemicals (Magog, QC, Canada). It is received in the form of dry powder.

Both flocculants are made up of cationic acrylamide copolymers, but they have different structures, charge densities and molecular weights. Flocculant 1 has a linear structure and low charge density (410 ± 10 µeq/g of active substance) whereas flocculant 2 is branched and has a medium charge density (2100 ± 300 µeq/g of active substance). The polymers’ charge densities are obtained by polyelectrolyte titration. 2ml of 0.1wt% flocculant solution is added to 8 ml of DDW. It is then titrated using 0.001N anionic PVSK and the charge density is subsequently calculated. Viscosities of the two flocculants are obtained at 0.1 wt% solution using the Brookfield viscometer and spindle LV1 at 25°C and 40 rpm. Both flocculant solutions are shear-thinning liquids (Figure 2.4). Table 2.2 shows some properties of these two flocculants. Both flocculants are made down to 0.1wt% solution by mixing with DDW for at least 45 minutes prior to use and are used within 24 hours once they are made down.

2.1.6 Silica
Silica used in this work is aluminum-modified colloidal silica with the trade name NP780. This silica is highly anionic as demonstrated by the zeta potential value of -53 ± 3 mV at a pH of 9.1 ± 0.1. It is also highly structured (Figure 2.5), with a specific surface area of
800 m²/g. This silica is supplied by Eka Chemicals (Magog, QC, Canada). It is received in the form of 8.35wt% solution and is diluted down to 0.1wt% solution prior to use. Both zeta potential and pH measurements are done with the 0.1wt% solution. Once diluted, silica is used within 24 hours.

2.1.7 polydiallyldimethyl ammonium chloride (polyDADMAC)
Analytical grade cationic polyDADMAC is supplied by BTG Americas (Pointe-Claire, QC, Canada). It is received as a 0.001 N solution and stored in a sealed container. It is used as a titrant for polyelectrolyte titrations for negatively charged systems e.g. pulp filtrates.

2.1.8 Potassium polyvinyl sulfate (PVSK)
Analytical grade anionic PVSK is supplied by BTG Americas (Pointe-Claire, QC, Canada). It is received as a 0.001 N solution and stored in a sealed container. It is used as a titrant for polyelectrolyte titrations for positively charged systems, e.g. determination of charge density of the cationic flocculants.

2.1.9 Distilled, deionized water (DDW)
Distilled, deionized water is used primarily for the purpose of preparation of the additives (starch, flocculant and silica). It is also used in the charge and zeta potential measurements, specifically in sample dilutions. Distilled water is deionized using Elgastat UHQ (Ultra High Quality) unit supplied by Fischer Scientific (Nepean, ON, Canada).

2.2 Instrumentation
2.2.1 Malvern Mastersizer 2000 with Hydro MU sample dispersion unit
The Malvern Mastersizer 2000 is a laser diffraction particle size analyzer and is equipped with a Hydro MU sample dispersion unit, which allows for particle size measurements to be done in a wet dispersion.
Laser diffraction particle sizing is based on the principle that particles passing through a laser beam will scatter light at an angle that is directly related to their size. As the particle size decreases, the scattering angle increases logarithmically. Scattering intensity is also dependent on particle size – it decreases as particle size decreases. Therefore, in a laser diffraction particle size analyzer, the primary measurement is the capture of light scattering data from the particles under study.

Particle size distribution is then calculated by comparing a sample’s scattering pattern with an optical model such as the Mie theory. Mie theory provides a rigorous solution for the calculation of particle size distributions from light scattering data and is based on Maxwell’s electromagnetic field equations. It predicts scattering intensities for all particles within the assumptions that the particles being measured are spherical, the suspension is dilute, the refractive indices of the particles and the medium surrounding them is known and the particles are homogeneous. For non-spherical particles, the particles are assumed to be spherical and the particle size is reported as the diameter of the ‘equivalent sphere’ which would give the same response as the particle being measured. All Mastersizer 2000 results are reported as volume-based diameter.

The Malvern Mastersizer 2000 can measure particles ranging from 0.02 µm to 2000 µm. The Hydro MU sample dispersion unit has a capacity of 600 to 1000 ml using standard laboratory beakers and a ‘dip-in’ sample recirculator head with built-in variable speed stirrer (0 to 2500 rpm), ultrasonic probe and a sample recirculation pump.

The Malvern Mastersizer 2000 and Hydro MU sample dispersion unit are supplied by Malvern Instruments (Southborough, Massachusetts, USA). The instrument is shown in Figure 2.6 and it is used to characterize the calcium carbonate filler.

2.2.2 Malvern Zetasizer 2000
Malvern Zetasizer 2000 is used to measure the zeta potential of particles suspended in a liquid by determining the electrophoretic mobility and then applying the Henry equation.
When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. Viscous forces acting on the particles tend to oppose this movement of the particles. When an equilibrium is reached between these opposing forces, the particles move with constant velocity which is dependent on the strength of the electric field, the dielectric constant, the viscosity of the medium and the zeta potential. The velocity of a particle in an electric field is referred to as its electrophoretic mobility. The Henry equation is then used to calculate zeta potential. Therefore, it is the electrophoretic mobility that is directly measured in the Zetasizer 2000, with conversion to zeta potential being inferred from theoretical considerations.

The Zetasizer 2000 consists of a dip cell through which the solution is introduced. A laser beam shines through this dip cell and measures the velocity of the particles. It also contains a pH electrode that measures pH and conductivity. This instrument is shown in Figure 2.7 and is supplied by Malvern Instruments (Southborough, Massachusetts, USA). It is used to characterize the calcium carbonate filler as well as the colloidal silica particles.

2.2.3 Brookfield viscometer
The Brookfield DV-II + Calculating Digital Viscometer is used to measure the viscosity and detect the rheological properties of the starch solutions. The Brookfield viscometer is of the rotational variety – it measures the torque required to rotate the spindle in a fluid sample. The spindle is driven by a motor through a calibrated spring. Deflection of the spring is indicated on the digital display. For a given viscosity, the viscous drag is proportional to the spindle’s speed of rotation and is related to the spindle’s size and geometry. The drag will increase as the spindle size and/or rotational speed increase. Thus, for a given spindle geometry and speed, an increase in viscosity will be indicated by an increase in the deflection of the spring.

For the two starch solutions, viscosity measurements are done at a solids content of 2wt% using the same spindle at different speeds to detect and evaluate their rheological
properties. The spindle used is the disc spindle LV#3 and the beaker size used is 600 ml. For the two flocculants, viscosity measurements are done at a solids content of 0.1 wt% using the cylindrical spindle LV#1 and 600 ml beaker. All viscosity measurements are done at room temperature.

2.2.4 BTG-Mutek PCD-03 Particle Charge Detector
The most common technique used by the paper industry for measuring charge uses a streaming potential measurement in conjunction with polyelectrolyte titration. In this technique, a piston moves a liquid sample back and forth through a narrow gap. The motion produces an AC current across two electrodes contained in the measuring cell wall and the AC current is converted to a streaming potential value. Charge demand is measured by titrating the sample with a known concentration of oppositely-charged polyelectrolyte to its isoelectric point. The quantity of polyelectrolyte consumed at the point of charge reversal is the charge demand of the suspension. It is converted to charge density using the following equation:

\[
\text{Charge density (}\mu\text{eq/g)} = \frac{\text{Volume}_{\text{tirant (ml) } \times \text{Concentration}_{\text{tirant (eq/l)}} \times 1000}}{\text{Volume}_{\text{sample (ml)}}}
\]  

(Eq 2.1)

Polyelectrolyte titration yields a polymer complex arising mostly from ionic interaction between polycations and polyanions. It relies on the fact that complexing by charge neutralization takes place at a stoichiometry of 1:1. Thus, although this technique can be used on whole pulp suspensions containing fibers and fines, the most successful application is for the determination of colloidal dissolved charge only. This is because the charge reaction is not always 1:1 between fiber surface and polyelectrolytes and also because fiber surfaces are porous and the polyelectrolytes can diffuse into the pores.

The BTG-Mutek PCD-03 is a standard instrument that uses the technique described above to measure charge demand. The Mutek PCD-03 cell consists of a plastic vessel with a piston. The piston is connected to an oscillating motor, which makes it moves up and down in the cell orifice. The cell can hold up to 10 mL of sample. An automatic
titrator is connected to the particle charge detector, which titrates to the filtrate to zero charge. The standard polyelectrolytes used for titration are 0.001N cationic poly-DADMAC for anionic samples and 0.001N anionic PVSK for cationic samples. The instrument is shown in Figure 2.8 and is supplied by BTG Americas Inc. (Pointe-Claire, QC, Canada).

2.2.5 BTG-Mutek SZP-06 Zetameter
The BTG-Mutek SZP-06 zetameter uses the streaming potential method to measure the zeta potential of pulp suspensions. By applying a vacuum the sample is sucked into the suction tube and then into the measuring cell, forming a fiber plug on the screen electrode. After a settling time where the fiber plug is stabilized, a set pressure variation of -0.2 bar to -0.4 bar is applied. An oscillating flow of liquid flow through the plug is generated. Diffuse ion layers sheared off the fiber plug induce a streaming potential, which is measured at the electrodes. Zeta potential is calculated based on this streaming potential. The instrument is pictured in Figure 2.9 and is supplied by BTG Americas Inc. (Pointe-Claire, QC, Canada).

2.2.6 pH meter
pH is one of the most important factors affecting zeta potential, thus for every zeta potential measurement, a corresponding pH measurement must also be done. These are performed using the Metrohm 691 pH Meter, which is supplied by Fischer Scientific Ltd. (Edmonton, AB, Canada).

2.2.7 BTG-Mutek DFR-04
The BTG-Mutek DFR-04, shown in Figures 2.10 and 2.11, is used to determine drainage curves and perform retention measurements. This instrument is also supplied by BTG Americas Inc. (Pointe-Claire, QC, Canada).

For the drainage measurements, a pulp suspension is transferred to the stirring chamber where it is exposed to shear forces after chemicals have been added. The suspension is
filtered through a screen and the filtrate weight is determined gravimetrically vs. the drainage time. The drainage weights reported are the weight of filtrate collected over 60s.

Retention is measured according to TAPPI Standard Method T261 cm-94, where the pulp suspension is continuously stirred during filtration. By measuring the solids content of the pulp sample and of the filtrate, the instrument is able to calculate total and fines/filler retention. Prior to making any retention measurements, the instrument is calibrated using the same pulp furnish and the same screen that is going to be used in the experiments.

The main components of the DFR-04 are the dosing unit, stirring chamber, wire screen and the balance. In addition, for retention measurements there is a two-way outlet valve with the RET 20 Lab sensor. For drainage measurements, there is a filtrate outlet.

The dosing unit allows for the automatic addition of various chemicals to the pulp suspension. Sequence of addition as well as the timing of such additions are preprogrammed with the accompanying software. Similarly, stirrer speed is set using the software. The balance is an integral part of the DFR-04 and is used to obtain gravimetric data. The stirring chamber serves as a sample container for the pulp suspension. In retention measurements, the two-way valve serves to separate out the first portion of the filtrate from the remainder.

2.3 Experimental procedures
2.3.1 Starch preparation
As mentioned earlier, both the tapioca and waxy maize starches are received in dry powder form. To be effective as either dry strength aid or retention aid, they must be cooked. During cooking the starch granules are hydrated, which is necessary to fully open up the starch and create the long chains necessary to for it to reach its full potential. When the gelatinization temperature is reached, the granule starts to swell and increase in diameter. At this time, the appearance of the starch solution changes from cloudy to clear. Since there is less room to move, the viscosity also increases rapidly. By continuing to apply more heat, the granules will eventually burst, forming the desired long chains.
In the laboratory, both starches are made as 2wt% solution and cooked in a boiling water bath for approximately 30 minutes after the starch solution has changed color and the rapid increase in viscosity has been observed. After 30 minutes, the solutions are cooled to room temperature and its solids content is checked using a Brix 15HP hand refractometer (Reichert Analytical Instruments, Depew, NY, USA). The procedure consists of placing a drop of starch on the window of the calibrated instrument and reading the concentration through the eyepiece. Solids content are determined by diffraction of light by the glucose groups that make up the starch. The refractometer converts the degree of diffraction into percent solids.

2.3.2 Retention and drainage experiments
Retention and drainage experiments are performed using the DFR-04. A 50 mesh (200µm hole) screen is used for measuring the retention of fibers and filler and also for the drainage measurements.

For retention measurements, the DFR-04 is first calibrated using 1% TMP loaded with 25g PCC per 100g oven dry pulp. The filtrate is dried in a 100°C oven for 2 hours and then its ash content is determined using a 550°C furnace for 12 hours. These values are entered into the DFR-04 and all subsequent retention measurements are based on this calibration.

The same procedure is followed for both retention and drainage experiments. 1000 g of TMP pulp at 1% consistency and a temperature of 50°C is first placed inside the stirring chamber. The additives under investigation are subsequently added to the pulp suspension and allowed to mix at predetermined contact times and shearing rates as shown in Figure 2.12. Each run is repeated three times and the average total retention, filler retention and drainage weight along with the standard deviation is reported. Filtrate from retention experiments are subsequently used to perform cationic demand measurements.
2.3.3 Cationic demand measurements
Cationic demand measurements are performed on the filtrate from the retention experiments. Approximately 2 ml of the filtrate are measured using a graduated cylinder and is diluted with 8 ml of DDW. This dilution is found to be necessary because using either 10 ml of filtrate or a mixture of 5 ml filtrate and 5 ml DDW both result in the samples overflowing out of the cell prior to the point of charge reversal being reached. After the diluted filtrate is placed in the cell, the piston is inserted into the cell and connected to the oscillating motor. The motor is switched on and the piston is allowed to oscillate for one minute. The diluted filtrate is then titrated to the isoelectric point with 0.001N cationic polyDADMAC. The cationic demand is reported as µeq/g of filtrate.

2.3.4 Zeta potential measurements
For zeta potential measurements, 1000 g of TMP pulp at 1% consistency and room temperature is placed in a beaker and is mixed using a variable speed stirrer according to the same sequence of addition, contact times and shearing rates that are used in the retention and drainage experiments (Figure 2.12).

Because an undiluted sample has too a high a conductivity to give reproducible results, the pulp suspension for zeta potential measurements are diluted. The zeta potential measurements are still meaningful for comparison purposes because each sample is diluted by the same amount of DDW. 300 g of the TMP is placed in another beaker and 300 g of DDW is added to it. The diluted pulp is mixed for approximately 10 seconds and its pH is measured. The vacuum pump is then started. A fiber plug is formed and this plug is allowed to stabilize for about one minute, after which the zeta potential measurements are started. Each run is repeated three times and the average along with the standard deviation is reported.

2.3.5 Factorial design of experiments
$3^2$ factorial design of experiments are used to study the effect of the flocculants and silica on total and filler retention as well as drainage in a system containing a fixed amount of either tapioca or waxy maize starches (8 kg/t OD pulp). The PCC loading is fixed at 250
kg/t OD pulp. Each run is repeated three times. The resulting averages along with their standard deviations are reported. Analysis of variance (ANOVA) is also performed. The design matrix is shown in Tables 2.3 and 2.4.

These flocculant and silica dosages are chosen because they are representative of the ranges that are used in industry. PCC dosage is chosen because it is the dosage currently used on a particular paper machine in coastal BC. Tapioca starch dosage is fixed at 8 kg/t OD pulp because previous work has shown that above a dosage of 8 kg/t OD pulp, tapioca starch starts to interact more with the DCS rather than adsorbing to fibers [51].

2.3.6 Effect of starch on retention and drainage
To determine the effect of starch on retention and drainage, a series of experiments are performed with no starch, just the flocculants at varying dosages and silica at 0.75 kg/t OD pulp. The results are then compared to the corresponding experiments with tapioca and waxy maize starches. Cationic demand and zeta potential measurements are also done.

2.3.7 Effect of flocculant on retention and drainage
In this case, a series of experiments are performed where the only additives used are the starch and silica – no flocculants. Starch and silica dosages are fixed at 8 and 0.75 kg/t OD pulp, respectively. These results are combined with previous results to show the effect of flocculant on retention and drainage.

2.3.8 Split starch addition
Through trial and error, it has been discovered that adding a portion of the starch to the PCC and the rest directly to the pulp eliminates linting problems on the paper machine. It is important to ensure that this practice does not have an adverse impact on retention and drainage.

A series of experiments are performed with flocculant 1 and tapioca starch, where varying amount of starch is added to the PCC (0, 2, 4, 6 and 8 kg/t OD pulp) with the
balance being added directly to the pulp (Figure 2.13). Only retention and drainage are recorded.

For other flocculant and starch combinations, only one split addition is considered (2 kg/t OD pulp to PCC, remainder to pulp). Retention, drainage, cationic demand and zeta potential measurements are done for these combinations.

2.3.9 Effect of increasing PCC dosage on retention and drainage
After the most suitable starch and flocculant have been identified, PCC dosage is increased to 300 and 500 kg/t OD pulp. Retention, drainage, cationic demand and zeta potential measurements are performed in exactly the same manner as previously described with the most suitable starch and flocculant discovered from previous experiments.
### Table 2.1 Starch information

<table>
<thead>
<tr>
<th></th>
<th>DS</th>
<th>% Amylopectin</th>
<th>% Amylose</th>
<th>Avg molecular weight</th>
<th>Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waxy maize</td>
<td>0.15</td>
<td>100</td>
<td>0</td>
<td>3.24E8</td>
<td>894 ± 3</td>
</tr>
<tr>
<td>Tapioca</td>
<td>0.13</td>
<td>83</td>
<td>17</td>
<td>2.92E6</td>
<td>310 ± 2</td>
</tr>
</tbody>
</table>

### Table 2.2 Flocculant information

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>Charge density (μeq/g)</th>
<th>Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant 1</td>
<td>410 ± 40</td>
<td>84.8 ± 0.2</td>
</tr>
<tr>
<td>Flocculant 2</td>
<td>2100 ± 300</td>
<td>32.2 ± 0.2</td>
</tr>
</tbody>
</table>

### Table 2.3 Factorial experimental design for flocculant 1

<table>
<thead>
<tr>
<th>Additives</th>
<th>Dosages (kg/t COD pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Flocculant 1</td>
<td>0.4</td>
</tr>
<tr>
<td>Silica</td>
<td>0.25</td>
</tr>
</tbody>
</table>

### Table 2.4 Factorial experimental design for flocculant 2

<table>
<thead>
<tr>
<th>Additives</th>
<th>Dosages (kg/t COD pulp)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Flocculant 2</td>
<td>0.2</td>
</tr>
<tr>
<td>Silica</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 2.1 SEM image of precipitated calcium carbonate
Figure 2.2 Particle size distribution of precipitated calcium carbonate

Figure 2.3 Viscosity vs. spindle speed for tapioca and waxy maize starches done at 2wt% solids content, 25°C, using Brookfield viscometer spindle LV3
Figure 2.4 Viscosity vs. spindle speed for flocculant 1 and flocculant 2 done at 0.1wt% solids content, 25°C, using Brookfield viscometer spindle LV1

Figure 2.5 Non-structured vs. structured silica
Figure 2.6 Malvern Mastersizer 2000

Figure 2.7 Malvern Zetasizer 2000
Figure 2.8 BTG-Mutek PCD-03

Figure 2.9 BTG-Mutek SZP-06
Figure 2.10 BTG-Mutek DFR-04 in the drainage setup

Figure 2.11 BTG-Mutek DFR-04 in the retention setup
Figure 2.12 Sequence of addition

1% TMP @ 50°C in DFR-04

Add cationic starch, 8 kg/t OD pulp

Add PCC (25g per 100g OD pulp)

Add the rest of starch, (8-x) kg/t OD pulp

Add flocculant

Add silica

Drain (50 mesh screen)

Drain

Record:
Retention
Drainage
Cationic demand
Zeta potential

Figure 2.13 Sequence of addition for split starch addition

1% TMP @ 50°C in DFR-04

Add the rest of starch, (8-x) kg/t OD pulp

Add PCC + starch (x) kg/t (25g per 100g OD pulp)

Add flocculant

Add silica

Drain (50 mesh screen)

Drain
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Factorial design of experiments
The purpose of these experiments is to investigate the effect of flocculant and silica dosages on total and filler retention as well as drainage for a given combination of starch, flocculant and silica. It is also of interest to determine whether the effect of one additive is dependent upon the dosage level of another. Four combinations of starch and flocculant, which are tapioca starch and flocculant 1, tapioca starch and flocculant 2, waxy maize starch and flocculant 1 and waxy maize starch and flocculant 2, will be investigated and their performances compared to see which combination gives the best results.

3.1.1 Flocculant 1 and silica with tapioca starch
Retention and drainage experiments are done with tapioca starch fixed at 8 kg/t OD pulp, flocculant 1 varying in dosage from 0.4 to 1.0 kg/t OD pulp and silica varying in dosage from 0.25 to 0.75 kg/t OD pulp.

3.1.1.1 Retention
As seen in Figure 3.1, both total and filler retention increase as flocculant and silica dosages are increased. Without any retention aids (TMP and PCC only, from hereon it is going to be referred as the baseline), total retention is 68 ± 4% and filler retention is 21 ± 4%. At the lowest flocculant and silica dosages (0.4 and 0.25 kg/t OD pulp, respectively), total retention increases to 84 ± 1%, a 24% increase from the baseline, and filler retention tripled to 66 ± 1%. Both total and filler retention continue to increase as flocculant and silica dosages are increased to 1.0 and 0.75 kg/t OD pulp respectively. At these highest dosages, total retention is 92 ± 1%, a 35% increase from the baseline, and filler retention quadrupled to 84 ± 1%. These results show that tapioca starch together with flocculant 1 and silica act effectively as retention aid system, particularly for filler retention.

At a given silica dosage, the largest increase in filler retention is observed as flocculant dosage is increased from 0.4 to 0.7 kg/t OD pulp. Increasing the flocculant dosage to 1.0
kg/t OD pulp does not increase the total and filler retention as much. For example, at silica dosage of 0.75 kg/t OD pulp, filler retention increases from 79 to 84% as flocculant dosage is increased from 0.4 to 0.7 kg/t OD pulp. At a flocculant dosage of 1.0 kg/t OD pulp, the filler retention remains at 84%. Similarly, at a given flocculant dosage, the largest increase in total and filler retention is seen as silica dosage is increased from 0.25 to 0.5 kg/t OD pulp. A smaller increase is observed when silica dosage is further increased to 0.75 kg/t OD pulp. For example, at a flocculant dosage of 1.0 kg/t OD pulp, increasing silica dosage from 0.25 to 0.5 kg/t results in an increase in filler retention from 77 to 82%. Increasing the silica dosage further to 0.75 kg/t OD pulp increases the filler retention slightly to 84%. Based on these results, the optimum dosage levels for filler retention are 0.75 kg/t OD pulp for silica and 1.0 kg/t OD pulp for flocculant 1. Because of the diminishing improvement in total and filler retention as dosage is increased, it becomes uneconomical to use dosages beyond the range investigated in this work.

3.1.1.2 Analysis of variance for total and filler retention

The analysis of variance (ANOVA) is shown in Tables 3.1 and 3.2 for total and filler retention. For total retention, the F₀ value for silica is 13.37, which is greater than the critical F₀.05,2,18 value of 3.55 from the F₀.05 distribution table. This means that silica has a significant role in improving total retention. Similarly, F₀ value for the flocculant is 8.71, which is also greater than the critical F₀.05,2,18 value of 3.55, meaning that the flocculant also has a significant role in improving total retention. For the interaction between the flocculant and silica, the F₀ value is 0.86, which is less than the critical F₀.05,4,18 value of 2.93. An interaction effect exists when differences caused by one factor (e.g. the flocculant) is dependent upon the dosage level of the other factor (e.g. the silica). In this case, interaction effect is insignificant because at a given flocculant dosage, increasing the silica dosage increases filler retention and vice versa.

For filler retention, the F₀ value for the interaction effect between flocculant and silica is 2.31, which is less than the critical F₀.05,4,18 value of 2.93. This indicates that the interaction effect is insignificant because again at a given flocculant dosage, increasing the silica dosage increases filler retention and vice versa. F₀ value for the flocculant is
35.09, which is greater than the critical $F_{0.05,2,18}$ value of 3.55 from the $F_{0.05}$ distribution table. $F_0$ value for the silica is 59.91, which is again greater than the critical $F_{0.05,2,18}$ value. This means both flocculant 1 and silica are significant in improving filler retention.

It makes sense that this combination gives good retention results because tapioca starch has both amylose and amylopectin. Both components are necessary for starch to perform well in microparticle retention aid systems. Amylose adsorbs preferentially onto fibers [47] as well as microcrystalline cellulose [48]. Amylopectin, on the other hand, interacts with the silica [29,49]. The flocculant, which has a low charge density, also adsorbs on the fibers and fillers while having some loops and tails extending out from the surface for interaction with the silica. The silica allows for flocs formed by the starch and flocculant to reflocculate after exposure to shear. Thus, both flocculant and silica are significant in improving total and filler retention. Starch is likely significant in improving retention as well [106], but in this factorial design of experiment its dosage is held constant.

### 3.1.1.3 Drainage

Figure 3.2 shows that as flocculant and silica dosages are increased, drainage weight also increases. Drainage weight for PCC-filled TMP suspension with no retention aids is 204 ± 5 g. At the lowest flocculant and silica dosages, drainage weight increases to 310 ± 6 g, a 52% increase from the baseline. At a given flocculant dosage, as silica dosage is increased drainage weight also increases and similarly, at a given silica dosage, increasing the flocculant dosage increases drainage weight. At the highest flocculant and silica dosages, drainage weight is 109% above the baseline value at 427 ± 6 g. These results show that tapioca starch together with flocculant 1 and silica are effective in improving drainage.

Unlike single or dual polymer retention aid systems, microparticle retention aid systems can achieve good retention and drainage at the same time. The issue with single and dual polymer retention aid systems is that upon shearing, the polymeric bridges are irreversibly broken and retention suffers. In order to maintain a certain level of retention and offset the broken polymeric bridges, the polymer dosage is increased. However, this
may also promote macrofloculation of fibers and the large flocs block the spaces between fibers through which water drains, thus the poor drainage. In this microparticle retention aid system, the silica interacts with the broken polymeric bridges, forming smaller flocs that are more evenly distributed. As a result, both drainage and retention can be improved.

3.1.1.4 Analysis of variance for drainage

ANOVA for drainage is shown in Table 3.3. F₀ values for flocculant 1 and silica are 265.66 and 337.73 respectively. Both of these values are greater than the critical F₀.₀₅,₂,₁₈ value of 3.55 from the F₀.₀₅ distribution table, meaning that the flocculant and silica are significant in improving drainage. Increasing flocculant dosage improves drainage because it floculates the filler particles so they do not become lodged in the fiber mat pores. Increasing silica dosage improves drainage because silica aids in the formation of smaller, more evenly distributed flocs that do not block fiber mat pores.

F₀ for the interaction between flocculant and silica is 7.14, which is greater than the critical F₀.₀₅,₄,₁₈ value of 2.93. As mentioned earlier, an interaction effect exists when differences caused by one factor is dependent upon the dosage level of another factor. In this case, the interaction effect is significant because the same drainage can be achieved at different combinations of flocculant 1 and silica dosages. For example, at flocculant dosage of 0.4 kg/t OD pulp and silica dosage of 0.75 kg/t OD pulp, the drainage is 361 ± 3 g; whereas at flocculant dosage of 1.0 kg/t OD pulp and silica dosage of 0.25 kg/t OD pulp the drainage is 362 ± 6 g.

3.1.2 Flocculant 2 and silica with tapioca starch

Retention and drainage experiments are done with tapioca starch fixed at 8 kg/t OD pulp, flocculant 2 varying in dosage from 0.2 to 0.5 kg/t OD pulp and silica varying in dosage from 0.25 to 0.75 kg/t OD pulp.
3.1.2.1 Retention

Figure 3.3 shows the total and filler retention for flocculant 2 and silica with tapioca starch. At the lowest flocculant and silica dosages (0.2 and 0.25 kg/t OD pulp, respectively), total retention is 75 ± 1% and filler retention is 60 ± 2%. Unlike the previous case (24% increase in total retention and 300% increase in filler retention), the total retention in this case is only a 10% improvement over the baseline. The filler retention is 2.86 times higher than the baseline. An increase in the dosage of either flocculant 2 or silica still results in an increase in total and filler retention. At flocculant dosage of 0.5 kg/t OD pulp and silica dosage of 0.75 kg/t OD pulp, total retention is 90 ± 1% and filler retention is 80 ± 1%.

Note while at the low dosages, the difference between the two combinations is large, as dosages are increased the difference becomes smaller. Also note that while both total and filler retention is slightly worse with flocculant 2 compared to flocculant 1, the dosage of flocculant 2 is half of flocculant 1. This is likely due to two things. One, flocculant 2 has a medium charge density, which allows for good interaction with small, charged fine particles (Figure 3.4). Second, flocculant 2 also has a branched structure, which makes it more difficult for the flocculant to adsorb a flat conformation. It is important to have the polymer loops and tails extending out from the surface where the polymer is adsorbed because it is these loops and tails that consequently interact with silica.

With flocculant 2 and tapioca starch, it is observed that at the medium and high silica dosage, the largest increase in filler retention is obtained as flocculant dosage is increased from 0.2 to 0.35 kg/t OD pulp. Increasing the flocculant dosage further to 0.5 kg/t OD pulp results in a smaller increase in filler retention. For example, at silica dosage of 0.5 kg/t OD pulp, filler retention increases from 65% to 72% as flocculant dosage is increased from 0.2 to 0.35 kg/t OD pulp. At 0.5 kg/t OD pulp, the filler retention only increases to 73%. These results suggest that there is a maximum amount of cationic polymers, be it starch or flocculants, which can be adsorbed on the fibers and fillers. Furthermore, with the dosages of starch (8 kg/t OD pulp) and flocculants (0.2 to 0.5 kg/t OD pulp) used in this work it is a possibility that this maximum is being approached.
Previous work has shown that in a PCC-filled TMP suspension, the maximum amount for tapioca starch alone is 8 kg/t OD pulp [51]. Therefore, increasing the flocculant dosage beyond the dosages investigated here is not a good option to improve retention.

When the flocculant dosage is held constant and silica dosage is varied, however, the largest increase in filler retention is found as silica dosage is increased from 0.5 to 0.75 kg/t OD pulp. For instance, at the flocculant dosage of 0.2 kg/t OD pulp, filler retention goes from 60 to 65 and 74% at silica dosages 0.25, 0.5 and 0.75 kg/t OD pulp. This indicates that for flocculant 2 the use of silica dosages higher than the range used in this work may be an economically viable option for improving filler retention. Addition of more silica may improve retention by helping fillers reflocculate after exposure to shear. Based on these results, within the dosages investigated in this work, the optimum dosage levels for filler retention are 0.75 kg/t OD pulp for the silica and 0.5 kg/t OD pulp for flocculant 2.

3.1.2.2 Analysis of variance for total and filler retention
ANOVA for total and filler retention using flocculant 2 and silica with tapioca starch are shown in Tables 3.4 and 3.5. For both total and filler retention, F0 values for the flocculant and silica are greater than the critical F0.05,2,18 value of 3.55 (for total retention, it is 80.67 for the flocculant and 108.7 for the silica; for filler retention, it is 106.53 for the flocculant and 285.78 for the silica). This shows that both the flocculant and silica have a significant impact on total and filler retention. This makes sense because flocculant 2, with the medium charge density, is able to have both stronger interaction with filler particles and more loops and tails to interact with the silica. As before, the silica is important for improving filler retention because it facilitates the reformation of flocs after the large flocs formed initially are broken due to exposure to shear forces.

The F0 values for the interaction between flocculant and silica for total retention (2.55) and filler retention (1.09) are less than the critical F0.05,4,18 value of 2.93, meaning that the effect of one factor is not dependent upon the level of the other factor. Indeed, increasing either silica or flocculant dosages both result in an increase in retention.
3.1.2.3 Drainage

Figure 3.5 shows the variation in drainage weight as flocculant and silica dosages are increased. Generally, as flocculant and silica dosages increase, so does the drainage weight. Tapioca starch, flocculant 2 and silica gives better drainage weight than tapioca starch, flocculant 1 and silica. For example, at flocculant dosage of 0.2 kg/t OD pulp and silica dosage of 0.25 kg/t OD pulp, drainage weight is 337 ± 6 g, a 65% increase from the baseline. The corresponding drainage weight for flocculant 1 is 310 ± 6 g, a 52% increase from the baseline. At the highest flocculant and silica dosages of 0.5 and 0.75 kg/t OD pulp, respectively, drainage weight is 450 ± 2 g, a 120% increase from the baseline.

These results show that not only tapioca starch together with flocculant 2 and silica effective in improving drainage, but that this combination is more effective compared to the combination involving tapioca starch, flocculant 1 and silica. This can be attributed to the branched structure of flocculant 2 and its medium charge density, which hinder the flocculant from adopting a flat conformation on the fiber surface. As a result, a more porous sheet structure is produced through which water can freely flow out of.

3.1.2.4 Analysis of variance for drainage

ANOVA for drainage is shown in Table 3.6. F₀ for flocculant 2 and silica are 303.43 and 816.62, respectively. Both these values are greater than the critical F₀.₀₅,₂,₁₈ value of 3.55 from the F₀.₀₅ distribution table, meaning that both flocculant and silica are significant in improving drainage. The flocculant’s contribution is in forming the first, relatively large flocs whereas silica’s role is to reflocculate the broken flocs after shearing to form smaller, more evenly distributed flocs that keep the fiber mat pores unblocked. F₀ for the interaction between flocculant and silica is 11.47, which is greater than the critical F₀.₀₅,₄,₁₈ value of 2.93. Similar to the case with flocculant 1, the interaction effect is significant because the same drainage can be achieved at two different combinations of flocculant 2 and silica dosages. At flocculant dosage of 0.2 kg/t OD pulp and silica dosage of 0.75 kg/t OD pulp, the drainage is 415 ± 6 g; whereas at flocculant dosage of 0.35 kg/t OD pulp and silica dosage of 0.5 kg/t OD pulp the drainage is 411 ± 3 g.
3.1.3 Flocculant 1 and silica with waxy maize starch
Retention and drainage experiments are done with waxy maize starch fixed at 8 kg/t OD pulp, flocculant 1 varying in dosage from 0.4 to 1.0 kg/t OD pulp and silica varying in dosage from 0.25 to 0.75 kg/t OD pulp.

3.1.3.1 Retention
Figure 3.6 shows the total and filler retention for flocculant 1 and silica with waxy maize starch. Looking at both the total and filler retention (72 ± 1% and 42 ± 1% at the lowest flocculant and silica dosages), it is clear that this combination is the worst combination seen thus far. The trend is still the same though – as either flocculant or silica dosage is increased, total and filler retention increase. At the highest flocculant and silica dosages (1.0 and 0.75 kg/t OD pulp), total retention is 80 ± 1% and filler retention is 60 ± 2%.

With flocculant 1 and waxy maize starch, at low and medium silica dosages the largest increase in filler retention is found as flocculant dosage is increased from 0.7 to 1.0 kg/t OD pulp. However, at the high silica dosage the highest increase in filler retention is found as flocculant dosage is increased from 0.4 to 0.7 kg/t OD pulp. Increasing the dosage further to 1.0 kg/t OD pulp results in a smaller increase in retention. As before, this indicates the existence of a maximum amount of cationic polymers that can be adsorbed on fibers and fillers. Furthermore, at the dosages used here this maximum is almost reached. Therefore, there is no reason to use flocculant dosages greater than 1.0 kg/t OD pulp.

However, increasing the silica dosage beyond the range investigated here may be helpful in improving retention further. At every flocculant dosage, the largest increase in filler retention is obtained when silica dosage is increased from 0.5 to 0.75 kg/t OD pulp. Addition of more silica improves retention probably by allowing more of the broken polymeric bridges to reflocculate after exposure to shear. Within the dosages investigated in this work, the optimum dosage levels for filler retention are 0.75 kg/t OD pulp for the silica and 1.0 kg/t OD pulp for flocculant 1.
3.1.3.2 Analysis of variance for total and filler retention

ANOVA for total and filler retention using flocculant 1 and silica with waxy maize starch are shown in Tables 3.7 and 3.8. For both total and filler retention, $F_0$ values for the flocculant and silica are greater than the critical $F_{0.05,2,18}$ value of 3.55 (for total retention, it is 26.89 for the flocculant and 5.00 for the silica; for filler retention, it is 118.15 for the flocculant and 63.02 for the silica). This shows that the flocculant and silica have a significant impact on total and filler retention. Again these results are consistent with known mechanisms of how microparticle retention aid systems work. The $F_0$ values for the interaction between flocculant and silica for total retention (0.91) and filler retention (1.02) are less than the critical $F_{0.05,4,18}$ value of 2.93, meaning that the effect of one factor is not dependent upon the level of the other factor. Indeed, increasing either silica or flocculant dosages both result in an increase in retention.

3.1.3.3 Drainage

Figure 3.7 shows the variation in drainage weight as flocculant and silica dosages are increased. Drainage increases as either silica or flocculant 1 increases. It is clearly shown that the combination of waxy maize starch, flocculant 1 and silica gives poorer drainage results than either of the two other combinations seen thus far. At the lowest flocculant and silica dosages of 0.4 and 0.25 kg/t OD pulp, drainage weight is $281 \pm 5 \text{ g}$, only 38% above the baseline compared to the 52% improvement obtained with tapioca starch, flocculant 1 and silica. At the highest flocculant and silica dosages of 1.0 and 0.75 kg/t OD pulp, drainage weight is $350 \pm 2 \text{ g}$, a 72% improvement over the baseline.

The combination of waxy maize starch and flocculant 1 performs poorly in both retention and drainage due to a few reasons. Firstly, waxy maize starch does not have any amylose in it, making it more difficult for it to adsorb onto fibers or fillers. Secondly, flocculant 1 is a linear cationic flocculant with low charge density, which only has minimum interaction with the fillers and fibers and easily unattached from them (Figure 3.4).
3.1.3.4 Analysis of variance for drainage
ANOVA for drainage is shown in Table 3.9. F₀ values for flocculant 1 and silica are 156.09 and 444.5, respectively. As these values are greater than the critical F₀.05,2,18 value of 3.55 from the F₀.05 distribution table, meaning that despite their poor performance, the flocculant and silica are still significant in improving drainage. F₀ for the interaction between flocculant and silica is 13.03, which is greater than the critical F₀.05,4,18 value of 2.93. As with the previous case, the interaction effect is significant because the same drainage can be achieved at more than one combination of flocculant 1 and silica dosages. For example, at the low flocculant dosage of 0.2 kg/t OD pulp, increasing the silica dosage from 0.25 to 0.5 kg/t OD pulp gives very little increase in drainage (281 ± 5g vs. 284 ± 4g). Similarly, at the low silica dosage of 0.25 kg/t OD pulp, increasing the flocculant dosage from 0.2 kg/t OD pulp to 0.35 kg/t OD pulp gives the same increase in drainage (281 ± 5g vs. 284 ± 3g).

3.1.4 Flocculant 2 and silica with waxy maize starch
Retention and drainage experiments are done with waxy maize starch fixed at 8 kg/t OD pulp, flocculant 2 varying in dosage from 0.2 to 0.5 kg/t OD pulp and silica varying in dosage from 0.25 to 0.75 kg/t OD pulp.

3.1.4.1 Retention
Figure 3.8 shows the total and filler retention for flocculant 2 and silica with waxy maize starch. At the lowest flocculant and silica dosages (0.2 and 0.25 kg/t OD pulp, respectively), total retention is 77 ± 2% (13% improvement over the baseline) and filler retention is 48 ± 4% (2.29 times higher than the baseline). Similar to all the previous cases, an increase in the dosage of either flocculant 2 or silica results in an increase in total and filler retention. At the highest flocculant and silica dosages (0.5 and 0.75 kg/t OD pulp, respectively), total retention is 86 ± 1% and filler retention is 74 ± 1%. This combination of flocculant 2 and waxy maize starch gives better total and filler retention than the combination of flocculant 1 and waxy maize starch. Flocculant 2 has a branched structure which makes it more difficult for this flocculant to lie flat on the fiber surface. Flocculant 1 on the other hand has a linear structure, thus it can adopt a flat conformation.
Flat conformation is not advantageous for retention because it is the polymer loops and tails extending out from the surface on which the polymer is adsorbed that interacts with silica.

With flocculant 2 and waxy maize starch, a trend similar to the one seen with flocculant 2 and tapioca starch is observed. At a given silica dosage, the largest increase is seen in filler retention as flocculant dosage is increased from 0.2 to 0.35 kg/t OD pulp; increasing the dosage further to 0.5 kg/t OD pulp, the increase in filler retention is smaller. For example, at silica dosage of 0.75 kg/t OD pulp, the filler retention increases from 50% at flocculant dosage of 0.2 kg/t OD pulp to 70% at 0.35 kg/t OD pulp and 72% at 0.5 kg/t OD pulp. These results again indicate that while increasing flocculant dosage may increase filler retention, the magnitude of the increase becomes smaller with each increase in dosage. Therefore, it is not economical using flocculant dosages beyond 0.5 kg/t OD pulp because it is likely that together with a starch dosage of 8 kg/t OD pulp the system is very close to the maximum amount of cationic polymer that can be adsorbed on fibers and fillers.

At any given flocculant dosage, on the other hand, the largest increase in filler retention is found as silica dosage is increased from 0.5 to 0.75 kg/t OD pulp. For example, at flocculant dosage of 0.5 kg/t OD pulp, filler retention increases from 59% to 62% and 72% as silica dosage is increased from 0.25 to 0.75 kg/t OD pulp. As is the case with flocculant 2 and tapioca starch, these results indicate that for flocculant 2 and waxy maize starch, it may be economical to use higher dosages of silica to improve filler retention. As previously mentioned, this is possibly because an increased amount of silica will aid in reflocculating more of the broken flocs, thus improving retention. Within the dosages investigated in this work, the optimum dosage levels for filler retention are 0.75 kg/t OD pulp for the silica and 0.5 kg/t OD pulp for flocculant 2.

3.1.4.2 Analysis of variance for total and filler retention
ANOVA for total and filler retention using flocculant 2 and silica with waxy maize starch are shown in Tables 3.10 and 3.11. For both total and filler retention, F₀ values for the
Flocculant and silica are greater than the critical $F_{0.05,2,18}$ value of 3.55 (for total retention, it is 11.19 for the flocculant and 17.99 for the silica; for filler retention, it is 64.32 for the flocculant and 29.64 for the silica). This shows that the flocculant and silica have a significant impact on total and filler retention. As with all of the previous cases, this is because the flocculant helps form large flocs with the fillers while the silica helps reform smaller flocs after the large flocs are broken down by shear forces.

$F_0$ value for the interaction between flocculant and silica for total retention is less than the critical $F_{0.05,4,18}$ value of 2.93, meaning that the interaction effect is insignificant. In contrast, the interaction’s $F_0$ for filler retention (4.74) is greater than the critical value, meaning that the interaction effect is significant. In terms of ANOVA, significant interaction effect means that the effect of one factor (e.g. silica) is dependent upon the dosage level of the other factor (e.g. flocculant). In this case, at the low flocculant dosage of 0.2 kg/t OD pulp, increasing the silica dosage has little effect (filler retention values are $48 \pm 4\%$, $49 \pm 4\%$ and $50 \pm 3\%$ as silica dosage goes from 0.25, 0.5 and 0.75 kg/t OD pulp). At medium and high flocculant dosages, however, increasing the silica dosage improves filler retention. At flocculant dosage of 0.35 kg/t OD pulp, filler retention values are $54 \pm 1\%$, $59 \pm 5\%$, $71 \pm 2\%$ and at a flocculant dosage of 0.5 kg/t OD pulp, the filler retention values are $59 \pm 4\%$, $62 \pm 2\%$ and $72 \pm 1\%$ as the silica dosage goes from 0.25, 0.5 and 0.75 kg/t OD pulp. These results make sense because at the low flocculant dosage, there may not be enough flocs to start with therefore there is not enough broken, smaller flocs for the silica to work on. As the flocculant dosage is increased, more flocs are created and thus more broken flocs are available for the silica to interact with.

### 3.1.4.3 Drainage

Figure 3.9 shows the variation in drainage weight as flocculant and silica dosages are varied. As with all the previous cases, as flocculant and silica dosages increase, the drainage weight also increases. However, the combination of waxy maize starch, flocculant 2 and silica does not improve drainage as well as tapioca starch, flocculant 2 and silica. For example, with waxy maize starch, at flocculant dosage of 0.2 kg/t OD pulp and silica dosage of 0.25 kg/t OD pulp, drainage weight is $312 \pm 3\text{g}$, a 53% increase from...
the baseline. With tapioca starch, the corresponding drainage weight is 337 ± 6 g, which is a 65% increase from the baseline. At the highest flocculant and silica dosages of 0.5 and 0.75 kg/t OD pulp, respectively, drainage weight is 439 ± 6 g, which is a 115% increase from the baseline.

These results show this combination (waxy maize starch and flocculant 2) is more effective in improving drainage compared to any combination involving flocculant 1, however, the tapioca starch and flocculant 2 combination is still the most effective one. This is because waxy maize starch does not have the starch component amylose that preferentially adsorbs onto fibers or fillers. Thus, there are less flocs formed with this starch compared to tapioca starch, which contains amylose.

3.1.4.4 Analysis of variance for drainage
ANOVA for drainage is shown in Table 3.12. F₀ for flocculant 2 and silica are 1234.69 and 698.72, respectively. Both these values are greater than the critical F₀.05,2,18 value of 3.55 from the F₀.05 distribution table, meaning that the flocculant and silica are significant in improving drainage for all of the reasons that have previously been outlined. F₀ for the interaction between flocculant and silica is 28.36, which is greater than the critical F₀.05,4,18 value of 2.93. Similar to all previous cases, the interaction effect is significant because the same drainage can be achieved at different combinations of flocculant 2 and silica dosages. For example, at flocculant dosage of 0.35 kg/t OD pulp and silica dosage of 0.75 kg/t OD pulp, the drainage is 393 ± 5 g; whereas at flocculant dosage of 0.5 kg/t OD pulp and silica dosage of 0.5 kg/t OD pulp the drainage is 391 ± 1 g.

3.1.5 Reduction in cationic demand and zeta potential
Cationic demand and zeta potential measurements are done for all of the combinations described above in an attempt to better understand the phenomenon in the system. A reduction percentage is introduced in order to facilitate comparison between the different cases. Original values of the zeta potential along with the pH at which the measurement is made and cationic demand are also reported on the graphs. The baseline for comparison
is the zeta potential and cationic demand for PCC-filled TMP suspension with no additives. The reduction percentage is defined below:

\[
\text{Reduction} \% = \frac{\text{Value of TMP + PCC} - \text{Value of TMP + PCC + Additives}}{\text{Value of TMP + PCC}} \times 100
\]  

(3.1)

All measurements are done in triplicates and the averages with the standard deviations are reported.

The reductions in cationic demand and zeta potential for the combination of tapioca starch, flocculant 1 and silica are shown in Figures 3.10 to 3.12. Figures 3.13 to 3.15 show those for the combination of tapioca starch, flocculant 2 and silica. Figures 3.16 to 3.18 show those for the combination of waxy maize starch, flocculant 1 and silica. Finally, Figures 3.19 to 3.21 show those for the combination of waxy maize starch, flocculant 2 and silica.

In all of the tapioca starch and flocculant combinations, increasing the dosage of either silica or flocculant increases the reduction in zeta potential. Increasing flocculant dosage increases the reduction in zeta potential because there is more flocculant adsorbing to fibers. Increasing silica dosage also increases the reduction in zeta potential because the silica aids in forming smaller flocs that are consequently retained on fibers. However, the increases are very slight. For example, for tapioca starch and flocculant 1 combination, at the silica dosage of 0.25 kg/t OD pulp, the reductions in zeta potential are 34, 36 and 37% at flocculant dosages of 0.4, 0.7 and 1.0 kg/t OD pulp. At silica dosage of 0.5 kg/t OD pulp, they are 36, 36 and 39% at the respective flocculant dosages. At silica dosage of 0.75 kg/t OD pulp, they are 38, 38 and 41%, respectively.

In fact, for a given tapioca starch and flocculant combination, the zeta potential reduction is roughly constant regardless of flocculant or silica dosage. This confirms that there is a maximum amount of cationic polymers, be it the starch, flocculant or their combination, which can adsorb onto fibers or fillers. As previously mentioned in [51], where tapioca
starch is used in a PCC-filled TMP suspension, this maximum amount is 8 kg/t OD pulp. Because in all of the experiments starch dosage is fixed at 8 kg/t OD pulp, it is not inconceivable that this is the reason why the zeta potential reduction does not vary much between the different dosages.

For the waxy maize starch and flocculant combinations, a similar trend is seen where increasing the dosage of either silica or flocculant slightly increases the reduction in zeta potential. For example, for waxy maize starch and flocculant 1 combination, at the silica dosage of 0.75 kg/t OD pulp, the reductions in zeta potential are 24, 25 and 26% at flocculant dosages of 0.4, 0.7 and 1.0 kg/t OD pulp. For a given waxy maize starch and flocculant combination, the zeta potential reduction is also roughly constant regardless of flocculant or silica dosage. The reduction value, however, is typically lower than those for tapioca starch and flocculant combinations. For instance, tapioca starch and flocculant 1 at silica dosage of 0.75 kg/t OD pulp has zeta potential reduction in the range of 38 to 41%, whereas waxy maize starch and flocculant 1 at the same silica dosage has zeta potential reduction in the range of 24 to 26%. This is probably due to the lack of amylose in waxy maize starch, which has been found to adsorb preferentially on fibers and fillers. As a result, it is more difficult for waxy maize starch to adsorb onto fibers and fillers. In turn, this causes poor retention and drainage.

Also note that for the tapioca starch and flocculants combination, the reduction in cationic demand is always much lower than the reduction in zeta potential. For example, for tapioca starch and flocculant 1 at silica dosage of 0.75 kg/t OD pulp, the reductions in cationic demand are 10, 13 and 20% for flocculant dosages of 0.4, 0.7 and 1.0 kg/t OD pulp. The corresponding reductions in zeta potential are 38, 38 and 41%. This shows that these combinations of cationic polymers have a much stronger interaction with fibers and fillers as opposed to interaction with dissolved and colloidal material (DCS) otherwise known as anionic trash. Results described in a later section will confirm that it is the tapioca starch, rather than the flocculants, that is responsible for this behavior.
For waxy maize starch and flocculants combination, this is not the case. In these cases, the reductions in zeta potential and cationic demand are approximately equal. For example, for waxy maize starch and flocculant 2 at silica dosage of 0.5 kg/t OD pulp, reductions in cationic demand are 29, 28 and 31% for flocculant dosages of 0.2, 0.35 and 0.5 kg/t OD pulp. The corresponding reductions in zeta potential are 26, 29 and 29%. This is likely because waxy maize starch is made up of 100% amylopectin, which does not have a preference to interact with either fibers and fillers or anionic trash.

3.2 Effect of starch

In order to clarify the role of starch in the microparticle retention aid systems described above, experiments using no starch, just the flocculants and silica, are performed. Retention, drainage, cationic demand and zeta potential are determined.

Flocculant 1 dosages are 0.4, 0.7 and 1.0 kg/t OD pulp. Flocculant 2 dosages are 0.2, 0.35 and 0.5 kg/t OD pulp. The silica dosage is fixed at 0.75 kg/t OD pulp. Results from these experiments are compared with the corresponding results where tapioca and waxy maize starches are used.

3.2.1 Retention

Figure 3.22 shows the total retention for flocculant 1 using no starch, tapioca and waxy maize starches. In the absence of starch, there is no increase in total retention from the baseline of 68%. In the presence of waxy starch, total retention increases to 75, 77 and 80% as the flocculant dosage is increased. In the presence of tapioca starch, it increases further to 87, 92 and 92% at flocculant dosage 0.4, 0.7 and 1.0 kg/t OD pulp.

Figure 3.23 shows the total retention for flocculant 2 using no starch, tapioca and waxy maize starches. For this flocculant, in the absence of starch total retention ranges from 68% to 74%, which is slightly higher than flocculant 1. For flocculant 2, the difference in total retention between tapioca and waxy maize starches are not as pronounced as in the case with flocculant 1. For example, at the flocculant dosage of 0.2 kg/t OD pulp, total retention is 81% for tapioca starch and 81% for waxy maize starch. At the other two
flocculant dosages, tapioca starch gives slightly higher total retention than waxy maize starch (87 vs. 83% at flocculant dosage of 0.35 kg/t OD pulp; 90 vs. 86% at flocculant dosage of 0.5 kg/t OD pulp).

Figure 3.24 shows the filler retention for flocculant 1 using no starch, tapioca and waxy maize starches. In the absence of starch, the improvement in filler retention is minimal – filler retention is 21, 23 and 26% for flocculant dosage of 0.4, 0.7 and 1.0 kg/t OD pulp. The baseline value is 21%. Presence of either tapioca or waxy maize starch significantly improves filler retention. In the presence of tapioca starch, filler retention quadrupled to 84% at flocculant dosages of 0.7 and 1.0 kg/t OD pulp. At flocculant dosage of 0.4 kg/t OD pulp, the filler retention is 79%. Waxy maize starch also improves filler retention, although not as much as tapioca starch. At flocculant dosage of 0.4 kg/t OD pulp, filler retention increased to 48%. At 0.7 kg/t OD pulp, it is 56% and at 1.0 kg/t OD pulp it is 60%.

Figure 3.25 shows the filler retention for flocculant 2 using no starch, tapioca and waxy maize starches. With flocculant 2, the absence of starch is not as devastating to filler retention as in the case with flocculant 1. While at flocculant dosage of 0.2 kg/t OD pulp there is marginal improvement in filler retention (22%), at 0.35 and 0.5 kg/t OD pulp the filler retention increases to 44 and 58%, similar to the retention levels reached using waxy maize starch and flocculant 1. In the presence of tapioca starch, filler retention increases to 73, 78 and 80% as flocculant dosage increases from 0.2 to 0.35 and 0.5 kg/t OD pulp. With waxy maize starch, filler retention also increases to 50, 71 and 74% at flocculant dosage of 0.2, 0.35 and 0.5 kg/t OD pulp.

Results from these retention experiments show that starch is indeed an integral part of this particular retention aid system regardless of which flocculant is being used. Furthermore, tapioca starch gives better total and filler retention than waxy maize starch when used with either flocculant. This result is in agreement with the idea that both amylose and amylopectin are important for starch to perform optimally as a retention aid.
because while tapioca starch has both amylose and amylopectin, waxy maize starch contains only amylopectin.

Although the total and filler retention are slightly lower for flocculant 2 than for flocculant 1, the dosages for flocculant 2 are half of that for flocculant 1. Moreover, flocculant 2 can improve filler retention without any starch, whereas flocculant 1 cannot. The different behaviors are likely due to differences in the structure and charge density of the flocculants. Flocculant 1 is linear and has a low charge density. Flocculant 2 is branched and it has a medium charge density. Flocculant 1’s low charge density results in weak interaction between the flocculant and fiber/filler, as shown in Figure 3.4. Flocculant 2 is able to adsorb onto the fiber/filler better because it has a higher charge density and the branched structure helps the polymer loops and tails to extend out from the surface as well.

3.2.2 Drainage
Figure 3.26 shows the drainage weight for flocculant 1 using no starch, tapioca and waxy maize starches. Drainage weight for PCC-filled TMP suspension with no retention aids is 204 ± 5 g. In the absence of starch, drainage weights are low at 239, 246 and 258 g for flocculant dosage of 0.4, 0.7 and 1.0 kg/t OD pulp respectively. With tapioca starch, the drainage weights increase linearly to 360, 395 and 429 g for the same flocculant dosages. With waxy maize starch, the improvement in drainage weight is not as great as tapioca starch (312, 343 and 352 g) and it appears to have reached a plateau. These results again show that it is important to use a starch that has both amylose and amylopectin.

Figure 3.27 shows the drainage weight for flocculant 2 using no starch, tapioca and waxy maize starches. Overall, flocculant 2 gives better drainage than flocculant 1, as shown by the higher drainage weights for all three cases. Without any starch, the drainage weights increase from 246 to 264 and 288 g for flocculant dosage of 0.2, 0.35 and 0.5 kg/t OD pulp respectively. With tapioca starch, they are 415, 430 and 450 g and with waxy maize starch, they are 348, 393 and 439 g. The better drainage performance is attributed to the branched structure of flocculant 2, which allows it to form flocs that have a more open
structure. This in turn allows water to freely flow out of the fiber mat, resulting in good drainage.

### 3.2.3 Zeta potential and cationic demand

Figures 3.28 and 3.29 show the reduction in cationic demand and zeta potential for cases where no starch is used, just flocculant 1 and flocculant 2 with silica at 0.75 kg/t OD pulp. The values on the graph indicate the cationic demand, zeta potential and pH at the point of measurement.

In contrast to cases where either tapioca or waxy maize starches are used, in these cases, the reduction in cationic demand is greater than the reduction in zeta potential. Because cationic demand measures the amount of dissolved charge in the system, whereas zeta potential measures surface charges, this result indicates that in the absence of starch, the flocculants are consumed by the dissolved and colloidal substances (DCS) in the pulp suspension rather than adsorbing onto fibers or fillers. Flocculant 1 is especially susceptible to this presumably because of its low cationic charge density, as shown by the 0% reduction in zeta potential at 0.4 and 0.7 kg/t OD pulp and only 7% at 1.0 kg/t OD pulp. Flocculant 2, which has a higher cationic charge density, performs slightly better, with a 0% reduction in zeta potential at 0.2 kg/t OD pulp, 10% at 0.35 kg/t OD pulp and 12% at 0.5 kg/t OD pulp. For both flocculants, the reduction in cationic demand ranges from 15 to 25%. Because the flocculants are consumed by DCS rather than being adsorbed onto fibers or fillers, they become ineffective as retention aid. Therefore, with no starch, total and filler retention as well as drainage are low.

### 3.3 Effect of flocculant

It is clear that starch is a very important component in the microparticle retention aid system and that flocculants are ineffective unless starch is present. It is therefore of interest to see how a microparticle retention aid system consisting of just starch and silica compares to one consisting of starch, flocculants and silica. This is done by comparing the retention, drainage, cationic demand and zeta potential of the PCC-filled TMP
suspension where only starch and silica are used vs. where starch, flocculant and silica are used. From these experiments, the role of flocculants will be clarified.

The flocculant levels used for comparison are the lowest dosages (0.4 kg/t OD pulp for flocculant 1; 0.2 kg/t OD pulp for flocculant 2). This is because factorial experimental design performed earlier shows that retention and drainage will simply increase as flocculant dosages are increased. Starch dosage is fixed at 8 kg/t OD pulp and silica dosage is fixed at 0.75 kg/t OD pulp.

3.3.1 Retention
Tapioca starch and silica alone gives a filler retention of 64 ± 3% (Figure 3.30). Adding either flocculant increases retention further to 79 ± 3% using flocculant 1 and 73 ± 2% using flocculant 2. Flocculant 1 does better than flocculant 2, however, flocculant 1’s dosage is double that of flocculant 2. On the other hand, waxy maize and silica at the same dosages result in a filler retention of only 32 ± 4%. Adding either flocculant increases the retention further (50 ± 3% for flocculant 2 vs. 48 ± 1% for flocculant 1).

These results confirm that flocculants do have an important role in improving filler retention, as suggested by all the analysis of variances described earlier. Flocculant 2 can give comparable performance to flocculant 1 at half the dosage probably because its branched structure prevents it from lying flat on the fiber surface, making more polymer loops and tails available for bridging between fiber and filler surfaces. However, flocculants are only effective when starch is also present in the system. Tapioca starch is better for this purpose than waxy maize starch. It has been previously established that tapioca starch is the best choice for usage in high anionic trash environments because it is not deactivated in the presence of anionic trash [51]. Waxy maize starch, on the other hand, seems to be prone to deactivation by anionic trash.

3.3.2 Drainage
Drainage results are displayed in Figure 3.31. With no starch, the difference between the drainage weights of flocculants 1 and 2 is minimal (239 ± 5 g vs. 246 ± 5 g), although it
is still approximately a 20% increase from 204 ± 5 g where no retention aids are used. Again the reason for this is presumably because without starch neutralizing some of the anionic trash in the system, the flocculants are simply consumed by the anionic trash. As a result, they become ineffective. Tapioca starch is able to adsorb to fiber surfaces while neutralizing some anionic trash at the same time, thus tapioca starch and silica alone gives a drainage weight of 350 g. Flocculant 1 increases drainage weight slightly to 361 ± 3 g, whereas with flocculant 2 it increases to 415 ± 6 g. While waxy maize starch does neutralize some anionic trash, because it does not adsorb preferentially to fibers, the combination of waxy maize starch and silica gives a lower drainage weight of 262 ± 5 g. With flocculant 1 it increases to 313 ± 5 g and with flocculant 2 it is 348 ± 4 g.

These results clearly show that in terms of drainage, the branched flocculant 2 performs better than the linear flocculant 1 probably because its branched structure allows the resulting flocs to have a more open structure. The flocculants, however, are prone to being consumed by anionic trash, thus it is important to have some starch present in the system.

3.3.3 Zeta potential and cationic demand
Tables 3.13 and 3.14 display the reduction in zeta potential and cationic demand for all the flocculant and starch combinations, including cases where there are no flocculants and no starches used.

In the case of tapioca starch, there is only a slight increase in the zeta potential reduction when flocculants are introduced (37% for no flocculant, 38% with flocculant 1, 40% with flocculant 2). For waxy maize starch, on the other hand, the reduction in zeta potential increases from 19% with no flocculant to 24% with flocculant 1 and 32% with flocculant 2. These results again suggest that for tapioca starch, the 8 kg/t OD pulp already makes up for most of the maximum amount of cationic polymer that can be adsorbed. Addition of the flocculants therefore does not affect the reduction in zeta potential much. In the case of waxy maize starch, there is room for flocculants to adsorb on to fibers and fillers because the starch itself does not prefer to adsorb on fibers and fillers.
Tapioca starch without any flocculant shows a reduction in cationic demand of 9% whereas for waxy maize starch without any flocculant, it is 21%. This agrees with the previous conclusion that tapioca starch has a preference to interact with fiber and filler rather than with the anionic trash, whereas waxy maize starch is consumed by it.

For a given starch, flocculant 2 always have a greater reduction in cationic demand than flocculant 1, which suggests a stronger interaction with DCS than fibers. However, flocculant 2’s performance is comparable if not better than flocculant 1. This suggests that some interaction with anionic trash is tolerable as long as the flocculant is still able to adsorb to the fibers and fillers. For a given starch, flocculant 2 also has a greater reduction in zeta potential than flocculant 1.

3.4 Effect of split starch addition
The conventional method of adding starch to the mechanical pulp suspension is by adding the entire amount to the pulp suspension itself since it is known that starch is most effective as a dry strength agent and retention aid when it is adsorbed on long fibers. In an effort to eliminate linting problem in a papermachine in a BC coastal mill, however, it is found that splitting the starch addition between the pulp suspension and PCC solves the problem. Naturally, it is of interest to find out whether splitting starch addition has any impact on retention and drainage, and this is exactly the purpose of the following series of experiments.

3.4.1 Varying the split starch ratio with tapioca starch, flocculant 1 and silica
In these experiments, the starch dosage to PCC is varied from 0, 2, 4, 6 and 8 kg/t OD pulp. The total amount of starch added is fixed at 8 kg/t OD pulp, thus increasing starch dosage to PCC decreases the amount added directly to the pulp suspension. The starch used is tapioca starch and the flocculant is flocculant 1, whose dosage is fixed at 1.0 kg/t OD pulp. Silica dosage is fixed at 0.75 kg/t OD pulp. Retention and drainage experiments are performed.
Figure 3.32 displays the total and filler retention vs. starch dosage to PCC. As more starch is added to PCC, both total and filler retention decrease slightly. Total retention decreases from 92% to 89%, whereas filler retention decreases from 84% to 78% as starch dosage to PCC is increased from 0 to 8 kg/t OD pulp. Similarly, drainage weight decreases from 429 to 410 g over the same increase in starch dosage to PCC, as shown in Figure 3.33.

These results can be explained as follows. When starch is added to PCC first, it forms PCC-starch flocs. When the remaining starch is added to the pulp, it adsorbs to the fiber, but now the PCC has less negative charge because it is mixed with starch. As a result, it is more difficult to bind the PCC to the fibers. This effect is counteracted somewhat when silica is added to the system because it interacts with both the starch on the PCC and the starch on the fibers, allowing the PCC to bind to the fibers through the starch and silica. Thus the reduction in total and filler retention is only gradual. Because the starch is premixed with PCC, it can be assumed that the PCC-starch flocs formed will be larger than the PCC-starch flocs formed when the PCC is dispersed in the pulp suspension first. Even when these large flocs are broken down by shear, it may still be larger than if the starch is added to the pulp. As a result, it is possible that these flocs are less evenly distributed and some of them may block the pores in the fiber mat network, thus decreasing drainage.

Based on these results, the best compromise between resolving linting issues and maintaining high retention and drainage is to add 2 kg/t OD pulp of starch to PCC and the remainder to the pulp suspension.

3.4.2 Effect of starch and flocculant on split starch addition

The previous experiments are only performed using tapioca starch and flocculant 1. Now retention, drainage, cationic demand and zeta potential measurements are done using all of the starch and flocculant combinations. 2 kg/t OD pulp of starch is added to PCC while the rest is added to the pulp suspension. Flocculant dosage is fixed at 1.0 kg/t OD pulp for flocculant 1 and 0.5 kg/t OD pulp for flocculant 2. Silica dosage is fixed at 0.75 kg/t
OD pulp. Results from the split addition are then compared with results from the non-split addition.

The results are shown in Tables 3.15 to 3.18. For any given combination of flocculant and starch, the difference between split and non-split is negligible in terms of total and filler retention. For instance, for tapioca starch and flocculant 2, filler retention is 80 and 78% for split and non-split addition, respectively. In terms of drainage, for tapioca starch the difference is also minimal. For example, with flocculant 2 the drainage is 448 g for split addition vs. 450 g for non-split addition. For waxy maize starch the difference is larger: with flocculant 2, the drainage is 439 g for non-split addition vs. 421 g for split addition. Reduction in zeta potential is either slightly lower with the split starch addition compared to the non-split addition or the same. For example, with flocculant 2 and tapioca starch, reduction in zeta potential is 42% for non-split and 37% for split addition. These results clearly show that the split starch addition of 2 kg/t OD pulp to PCC and 6 kg/t OD pulp to pulp suspension is the best choice for all of the starch and flocculant combinations investigated should the papermaker decide to use the split starch addition approach.

3.5 Effect of increasing PCC content

All of the above experiments have so far been done using TMP suspensions filled with PCC at a dosage of 250 kg/t OD pulp, which is standard for communications-grade papers. Considering the cost benefits from increased amounts of PCC, it is desirable to find ways to make even higher PCC dosages feasible. This feasibility is determined by the ability to maintain good retention and drainage.

In the following series of experiments, PCC dosage is increased to 300 and 500 kg/t OD pulp. Previous results show that tapioca starch and flocculant 2 are most effective for filler retention and drainage, thus they are used in these experiments. Tapioca starch dosage is fixed at 8 kg/t OD pulp and silica dosage is fixed at 0.75 kg/t OD pulp. Flocculant 2 dosage is varied from 0.2, 0.35 and 0.5 kg/t OD pulp.
3.5.1 Retention

Figures 3.34 and 3.35 show the total and filler retention for the three different PCC dosages. Both total and filler retention is highest at the lowest PCC dosage of 250 kg/t OD pulp (total retention is in the 80 – 90% range, filler retention is in the 70 – 80% range). At PCC dosage of 300 kg/t OD pulp, total retention drops to the 75 – 80% range while filler retention drops to 60 – 66% range. The decrease is even more dramatic when PCC dosage is increased to 500 kg/t OD pulp. At this PCC dosage, total retention is in the 55 – 65% range while filler retention is approximately 40%.

These results make sense because while the PCC dosage is increased – that is, there is more filler to be retained, the tapioca starch, flocculant 2 and silica dosages remain the same as the dosages used at the low PCC dosage. To maintain the same level of retention, dosages of the additives have to be increased but doing so may quickly become uneconomical.

3.5.2 Drainage

Drainage results are shown in Figure 3.36. Drainage at PCC dosage of 250 kg/t OD pulp and 300 kg/t OD pulp are very similar that within the average experimental errors of ± 5 g they are essentially the same. For example, at flocculant dosage of 0.35 kg/t OD pulp, drainage weight is 432 vs. 433 g for 250 and 300 kg/t OD pulp of PCC, respectively. At 500 kg/t OD pulp, drainage drops to 390 – 410 g range depending on the flocculant dosage. These results again are expected because increasing PCC dosage while keeping the tapioca starch, flocculant and silica dosages constant results in a greater amount of PCC that is not adsorbed onto fibers via the starch, flocculant and silica. This PCC may then block the fiber mat pores, thereby reducing drainage.

3.5.3 Zeta potential and cationic demand

Table 3.19 shows the zeta potential reduction for the three different PCC dosages. Reductions in zeta potential increase along with increases in PCC dosage. At 250 kg/t OD pulp, the reduction is in the 40 – 42% range; at 300 kg/t OD pulp it is in the 43 – 46% range and at 500 kg/t OD pulp it is in the 60 – 66% range. However, it is important
to note that as the PCC dosage is increased, the zeta potential of the PCC-filled suspension with no additives (the baseline) becomes more negative. This makes sense because as PCC dosage is increased, there is more negatively charged particles present in the system. At 250 kg/t OD pulp, the zeta potential is \(-21.9 \pm 0.6 \text{ mV}\), at 300 kg/t OD pulp it is \(-24.0 \pm 0.6 \text{ mV}\) and at 500 kg/t OD pulp it is \(-29.9 \pm 0.6 \text{ mV}\). Therefore, even though the reductions appear higher as PCC dosage is increased, the actual zeta potential is still least negative at the lowest PCC dosage and most negative at the highest PCC dosage. Again this makes sense because the same dosages of starch, flocculant and silica are used at each PCC dosage. The actual zeta potential values are shown in Table 3.19.

Table 3.21 shows the reduction in cationic demand for the three different PCC dosages. Unlike zeta potential, cationic demand of the PCC-filled TMP suspension does not change much as PCC dosage is increased. At 250 kg/t OD pulp, it is \(4.5 \pm 0.2 \mu\text{eq/g of filtrate}\); at 300 kg/t OD pulp it is \(4.2 \pm 0.2 \mu\text{eq/g of filtrate}\) and at 500 kg/t OD pulp it is \(4.0 \pm 0.2 \mu\text{eq/g of filtrate}\). This confirms that the dissolved colloidal charges originate from the process water rather than dissolution of PCC. As a result, all the values for cationic demand reductions are relatively close to each other (between 22 and 33% for all flocculant and PCC dosage combinations).

All of these results show that while the microparticle retention aid system can cope with increasing PCC dosage to 300 kg/t OD pulp, it is inadequate to obtain good retention and drainage when the PCC dosage is as high as 500 kg/t OD pulp. While simply increasing the dosage of additives, be it the starch, flocculant and silica may work, the costs of doing so will quickly make it prohibitive. Thus, a better approach to retaining mineral filler is needed.
Table 3.1. ANOVA for total retention using tapioca starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>57.64</td>
<td>2</td>
<td>28.82</td>
<td>8.71</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>88.51</td>
<td>2</td>
<td>44.25</td>
<td>13.37</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>11.42</td>
<td>4</td>
<td>2.86</td>
<td>0.86</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>59.57</td>
<td>18</td>
<td>3.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>217.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. ANOVA for filler retention using tapioca starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>284.34</td>
<td>2</td>
<td>142.17</td>
<td>35.09</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>485.50</td>
<td>2</td>
<td>242.75</td>
<td>59.91</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>37.50</td>
<td>4</td>
<td>9.37</td>
<td>2.31</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>72.93</td>
<td>18</td>
<td>4.05</td>
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<tr>
<td>Total</td>
<td>880.26</td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.3. ANOVA for drainage using tapioca starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>14168.52</td>
<td>2</td>
<td>7084.26</td>
<td>265.66</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>18012.07</td>
<td>2</td>
<td>9006.04</td>
<td>337.73</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>761.48</td>
<td>4</td>
<td>190.37</td>
<td>7.14</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>480.00</td>
<td>18</td>
<td>26.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33422.07</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. ANOVA for total retention using tapioca starch, flocculant 2 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>210.94</td>
<td>2</td>
<td>105.47</td>
<td>80.67</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>284.24</td>
<td>2</td>
<td>142.12</td>
<td>108.70</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>13.34</td>
<td>4</td>
<td>3.34</td>
<td>2.55</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>23.53</td>
<td>18</td>
<td>1.31</td>
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<td></td>
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<tr>
<td>Total</td>
<td>532.06</td>
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<td></td>
</tr>
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</table>

Table 3.5. ANOVA for filler retention using tapioca starch, flocculant 2 and silica

<table>
<thead>
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<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>278.56</td>
<td>2</td>
<td>139.28</td>
<td>106.53</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>747.28</td>
<td>2</td>
<td>373.64</td>
<td>285.78</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>5.74</td>
<td>4</td>
<td>1.44</td>
<td>1.10</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>95.68</td>
<td>18</td>
<td>5.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1127.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.6. ANOVA for drainage using tapioca starch, flocculant 2 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>( F_0 )</th>
<th>( F_{critical} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>8872.67</td>
<td>2</td>
<td>4436.33</td>
<td>303.24</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>23893.56</td>
<td>2</td>
<td>11946.78</td>
<td>816.62</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>671.11</td>
<td>4</td>
<td>167.78</td>
<td>11.47</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>263.33</td>
<td>18</td>
<td>14.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33700.67</td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.7. ANOVA for total retention using waxy maize starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>( F_0 )</th>
<th>( F_{critical} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>125.21</td>
<td>2</td>
<td>62.61</td>
<td>26.89</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>23.26</td>
<td>2</td>
<td>11.63</td>
<td>5.00</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>8.46</td>
<td>4</td>
<td>2.11</td>
<td>0.91</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
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<td>18</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>198.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

Table 3.8. ANOVA for filler retention using waxy maize starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
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<th>Degree of freedom</th>
<th>Mean square</th>
<th>( F_0 )</th>
<th>( F_{critical} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>550.15</td>
<td>2</td>
<td>275.08</td>
<td>118.15</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>293.45</td>
<td>2</td>
<td>146.73</td>
<td>63.02</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>9.46</td>
<td>4</td>
<td>2.37</td>
<td>1.02</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>73.78</td>
<td>18</td>
<td>4.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>926.84</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 3.9. ANOVA for drainage using waxy maize starch, flocculant 1 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>( F_0 )</th>
<th>( F_{critical} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>3908.07</td>
<td>2</td>
<td>1954.04</td>
<td>156.09</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>11128.96</td>
<td>2</td>
<td>5564.48</td>
<td>444.50</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>652.59</td>
<td>4</td>
<td>163.15</td>
<td>13.03</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>225.33</td>
<td>18</td>
<td>12.52</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>15914.96</td>
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<td></td>
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</tr>
</tbody>
</table>
Table 3.10. ANOVA for total retention using waxy maize starch, flocculant 2 and silica

<table>
<thead>
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<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>71.75</td>
<td>2</td>
<td>35.87</td>
<td>11.19</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>115.33</td>
<td>2</td>
<td>57.67</td>
<td>18.00</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>9.12</td>
<td>4</td>
<td>2.28</td>
<td>0.71</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>57.68</td>
<td>18</td>
<td>3.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>253.88</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.11. ANOVA for filler retention using waxy maize starch, flocculant 2 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>1216.36</td>
<td>2</td>
<td>608.18</td>
<td>64.32</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>560.52</td>
<td>2</td>
<td>280.26</td>
<td>29.64</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>179.19</td>
<td>4</td>
<td>44.80</td>
<td>4.74</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>170.20</td>
<td>18</td>
<td>9.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2126.27</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.12. ANOVA for drainage using waxy maize starch, flocculant 2 and silica

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F₀</th>
<th>F_critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculant</td>
<td>24510.89</td>
<td>2</td>
<td>12255.44</td>
<td>1234.69</td>
<td>3.55</td>
</tr>
<tr>
<td>Silica</td>
<td>13870.89</td>
<td>2</td>
<td>6935.44</td>
<td>698.72</td>
<td>3.55</td>
</tr>
<tr>
<td>Interaction</td>
<td>1126.22</td>
<td>4</td>
<td>281.56</td>
<td>28.37</td>
<td>2.93</td>
</tr>
<tr>
<td>Error</td>
<td>178.67</td>
<td>18</td>
<td>9.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>39686.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.13. Reduction in cationic demand for all combinations of starches at 8 kg/t OD pulp, flocculant 1 at 0.4 kg/t OD pulp and flocculant 2 at 0.2 kg/t OD pulp with silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>None</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>No starch</td>
<td>19%</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>Tapioca</td>
<td>9%</td>
<td>10%</td>
<td>22%</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>21%</td>
<td>25%</td>
<td>33%</td>
</tr>
</tbody>
</table>

Table 3.14. Reduction in zeta potential for all combinations of starches at 8 kg/t OD pulp, flocculant 1 at 0.4 kg/t OD pulp and flocculant 2 at 0.2 kg/t OD pulp with silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>None</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>No starch</td>
<td>0%</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>Tapioca</td>
<td>37%</td>
<td>38%</td>
<td>40%</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>19%</td>
<td>24%</td>
<td>32%</td>
</tr>
</tbody>
</table>
Table 3.15. Retention and drainage with non-split and split additions of starch with flocculant 1 at 1.0 kg/t OD pulp and silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th></th>
<th>Total retention, %</th>
<th>Filler retention, %</th>
<th>Drainage, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tapioca</td>
<td>Waxy corn</td>
<td>Tapioca</td>
</tr>
<tr>
<td>Non-split</td>
<td>92</td>
<td>80</td>
<td>84</td>
</tr>
<tr>
<td>Split</td>
<td>91</td>
<td>81</td>
<td>82</td>
</tr>
</tbody>
</table>

Table 3.16. Reduction in zeta potential and cationic demand with non-split and split additions of starch with flocculant 1 at 1.0 kg/t OD pulp and silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th></th>
<th>Reduction in cationic demand</th>
<th>Reduction in zeta potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tapioca</td>
<td>Waxy corn</td>
</tr>
<tr>
<td>Non-split</td>
<td>20%</td>
<td>38%</td>
</tr>
<tr>
<td>Split</td>
<td>19%</td>
<td>37%</td>
</tr>
</tbody>
</table>

Table 3.17. Retention and drainage with non-split and split additions of starch with flocculant 2 at 0.5 kg/t OD pulp and silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th></th>
<th>Total retention, %</th>
<th>Filler retention, %</th>
<th>Drainage, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tapioca</td>
<td>Waxy corn</td>
<td>Tapioca</td>
</tr>
<tr>
<td>Non-split</td>
<td>90</td>
<td>86</td>
<td>80</td>
</tr>
<tr>
<td>Split</td>
<td>87</td>
<td>86</td>
<td>78</td>
</tr>
</tbody>
</table>

Table 3.18. Reduction in zeta potential and cationic demand with non-split and split additions of starch with flocculant 2 at 0.5 kg/t OD pulp and silica at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th></th>
<th>Reduction in cationic demand</th>
<th>Reduction in zeta potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tapioca</td>
<td>Waxy corn</td>
</tr>
<tr>
<td>Non-split</td>
<td>30%</td>
<td>32%</td>
</tr>
<tr>
<td>Split</td>
<td>29%</td>
<td>33%</td>
</tr>
</tbody>
</table>

Table 3.19. Reduction in zeta potential for three different dosages of PCC with tapioca starch at 8 kg/t OD pulp, flocculant 2 at 0.5 kg/t OD pulp and silica dosage at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th>Flocculant dosage (kg/t OD pulp)</th>
<th>PCC dosage (kg/t OD pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>0.2</td>
<td>40%</td>
</tr>
<tr>
<td>0.35</td>
<td>41%</td>
</tr>
<tr>
<td>0.5</td>
<td>42%</td>
</tr>
</tbody>
</table>

Table 3.20. Zeta potential values for three different dosages of PCC with tapioca starch at 8 kg/t OD pulp, flocculant 2 at 0.5 kg/t OD pulp and silica dosage at 0.75 kg/t OD pulp. Values in brackets are the pH at the point of measurement.

<table>
<thead>
<tr>
<th>Flocculant dosage (kg/t OD pulp)</th>
<th>PCC dosage (kg/t OD pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>0.2</td>
<td>-13.2 (7.5)</td>
</tr>
<tr>
<td>0.35</td>
<td>-12.9 (7.5)</td>
</tr>
<tr>
<td>0.5</td>
<td>-12.8 (7.7)</td>
</tr>
</tbody>
</table>
Table 3.21. Reduction in cationic demand for three different dosages of PCC with tapioca starch at 8 kg/t OD pulp, flocculant 2 at 0.5 kg/t OD pulp and silica dosage at 0.75 kg/t OD pulp.

<table>
<thead>
<tr>
<th>Flocculant dosage (kg/t OD pulp)</th>
<th>PCC dosage (kg/t OD pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td>0.2</td>
<td>22%</td>
</tr>
<tr>
<td>0.35</td>
<td>24%</td>
</tr>
<tr>
<td>0.5</td>
<td>30%</td>
</tr>
</tbody>
</table>

Figure 3.1. Total and filler retention using silica, flocculant 1 and tapioca starch. 3² factorial experimental design is followed.
Figure 3.2. Drainage using silica, flocculant 1 and tapioca starch. $3^2$ factorial experimental design is followed.

Figure 3.3. Total and filler retention using silica, flocculant 2 and tapioca starch. $3^2$ factorial experimental design is followed.
Figure 3.4. Flocculant 1 (left) has lower charge density thus less interaction with the fiber and/or filler surface. Flocculant 2 (right) has higher charge density, thus more interaction with fiber and/or filler surface.

Figure 3.5. Drainage using silica, flocculant 2 and tapioca starch. $3^2$ factorial experimental design is followed.
Figure 3.6. Total and filler retention using silica, flocculant 1 and waxy maize starch. $3^2$ factorial experimental design is followed.

Figure 3.7. Drainage using silica, flocculant 1 and waxy maize starch. $3^2$ factorial experimental design is followed.
Waxy maize starch dosage: 8 kg/t OD pulp

Figure 3.8 Total and filler retention using silica, flocculant 2 and waxy maize starch. $3^2$ factorial experimental design is followed.

Figure 3.9. Drainage using silica, flocculant 2 and waxy maize starch. $3^2$ factorial experimental design is followed.
Figure 3.10. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 1 and silica. Silica dosage is 0.25 kg/t OD pulp.

Figure 3.11. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 1 and silica. Silica dosage is 0.5 kg/t OD pulp.
Figure 3.12. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 1 and silica. Silica dosage is 0.75 kg/t OD pulp.

Figure 3.13. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 2 and silica. Silica dosage is 0.25 kg/t OD pulp.
Figure 3.14. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 2 and silica. Silica dosage is 0.5 kg/t OD pulp.

Figure 3.15. Reduction in cationic demand and zeta potential for tapioca starch, flocculant 2 and silica. Silica dosage is 0.75 kg/t OD pulp.
Figure 3.16. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 1 and silica. Silica dosage is 0.25 kg/t OD pulp.

Figure 3.17. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 1 and silica. Silica dosage is 0.5 kg/t OD pulp.
Figure 3.18. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 1 and silica. Silica dosage is 0.75 kg/t OD pulp.

Figure 3.19. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 2 and silica. Silica dosage is 0.25 kg/t OD pulp.
Figure 3.20. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 2 and silica. Silica dosage is 0.5 kg/t OD pulp.

Figure 3.21. Reduction in cationic demand and zeta potential for waxy maize starch, flocculant 2 and silica. Silica dosage is 0.75 kg/t OD pulp.
Figure 3.22. Total retention using flocculant 1 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.

Figure 3.23. Total retention using flocculant 2 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.
Figure 3.24. Filler retention using flocculant 1 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.

Figure 3.25. Filler retention using flocculant 2 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.
Figure 3.26. Drainage using flocculant 1 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.

Figure 3.27. Drainage using flocculant 2 with no starch, tapioca and waxy maize starches. Silica and starch dosages are 0.75 kg/t OD pulp and 8 kg/t OD pulp.
Figure 3.28. Reduction in cationic demand and zeta potential where flocculant 1 at various dosages and silica at 0.75 kg/t OD pulp are used without any starch.

Figure 3.29. Reduction in cationic demand and zeta potential where flocculant 2 at various dosages and silica at 0.75 kg/t OD pulp are used without any starch.
Figure 3.30. Filler retention with no flocculant, flocculant 1 at 0.4 kg/t OD pulp and flocculant 2 at 0.2 kg/t OD pulp. Silica and starch dosages are fixed at 0.75 and 8 kg/t OD pulp.

Figure 3.31. Drainage with no flocculant, flocculant 1 at 0.4 kg/t OD pulp and flocculant 2 at 0.2 kg/t OD pulp. Silica and starch dosages are fixed at 0.75 and 8 kg/t OD pulp.
Figure 3.32. Total and filler retention for split tapioca starch addition. Total starch dosage is 8 kg/t OD pulp.

Figure 3.33. Drainage for split tapioca starch addition. Total starch dosage is 8 kg/t OD pulp.
Figure 3.34. Total retention using tapioca starch, flocculant 2 and silica at various PCC dosages.

Figure 3.35. Filler retention using tapioca starch, flocculant 2 and silica at various PCC dosages.
Figure 3.36. Drainage using tapioca starch, flocculant 2 and silica at various PCC dosages.
CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions
The effectiveness of various microparticle retention aid systems in PCC-filled thermomechanical pulp suspensions is studied through retention and drainage experiments complemented by cationic demand and zeta potential measurements. The different microparticle retention aid systems comprise of four combinations of starches and flocculants along with silica. These four combinations are:

1. Tapioca starch, linear with low charge density cationic polyacrylamide flocculant (flocculant 1), anionic colloidal silica
2. Tapioca starch, branched with medium charge density cationic polyacrylamide flocculant (flocculant 2), anionic colloidal silica
3. Waxy maize starch, linear with low charge density cationic polyacrylamide flocculant (flocculant 1), anionic colloidal silica
4. Waxy maize starch, branched with medium charge density cationic polyacrylamide flocculant (flocculant 2), anionic colloidal silica

Factorial experimental design involving retention and drainage experiments using all four starch and flocculant combinations show that in all cases, both flocculant and silica are significant in improving total and filler retention as well as drainage. This result is expected based on the known mechanism of action of microparticle retention aid systems.

For each combination, the highest dosages of flocculant and silica give the best retention and drainage. It may be possible to achieve even higher retention and drainage by increasing silica dosage. However, increasing flocculant dosage is unlikely to improve retention and drainage because the system is already near or at the maximum amount of cationic polymers that can be adsorbed onto fibers and fillers.

Starch is found to be a very crucial component of the microparticle retention aid system. In its absence, retention and drainage performance of both flocculants in conjunction with
silica suffer. Cationic demand and zeta potential measurements reveal that without starch, the flocculants are simply consumed by dissolved and colloidal substances (DCS) in the pulp suspension. They are not adsorbed onto fibers and fillers, which renders them ineffective.

Among the two starches studied, tapioca starch is a better choice for use in high anionic trash environments typical of mechanical pulp suspensions. This is because tapioca starch contains both amylose and amylopectin. Amylose preferentially adsorbs onto fibers and fillers, whereas the amylopectin remains in solution and is available to interact with the anionic silica. Waxy maize starch only contains amylopectin, which makes it more difficult for it to adsorb to the fiber and filler surfaces. Cationic demand and zeta potential measurements support this conclusion. For tapioca starch, the zeta potential reduction is much higher than the reduction in cationic demand. For waxy maize starch, the reductions in zeta potential and cationic demand are approximately equal. Consequently, tapioca starch in conjunction with either flocculant 1 or flocculant 2 and silica generally gives higher total and filler retention as well as drainage than waxy maize starch.

In the presence of starch, flocculant 1, which is a linear, low charge density flocculant gives slightly greater total and filler retention than flocculant 2, which is a branched, medium charge density flocculant. However, it is important to keep in mind that the dosage of the latter is only half that of the former. Even at half the dosage, the branched flocculant is superior in terms of drainage, presumably because there are more loops and tails extending out from the surface, resulting in more porous flocs through which water can drain easily.

Therefore, the combination of tapioca starch and the branched with medium charge density cationic polyacrylamide flocculant with anionic colloidal silica is the combination that yields the best retention and drainage for PCC-filled mechanical pulp suspensions.
Splitting starch addition between PCC and the pulp causes a slight decrease in retention and drainage. This pattern is seen in all four starch and flocculant combinations studied. In order to obtain the benefit of this mode of addition without sacrificing retention and drainage, the split ratio of 2 kg/t OD pulp to PCC and 6 kg/t OD pulp to the pulp is recommended.

When PCC dosage is increased from 250 to 300 kg/t OD pulp, retention and drainage decrease slightly. In other words, the tapioca starch and branched flocculant in combination with silica is able to cope with a small increase in PCC dosage. However, when PCC dosage is increased to 500 kg/t OD pulp, both retention and drainage drastically decrease. This indicates that the retention aid system as it is currently being used is not suitable for such high PCC dosage.

4.2 Recommendations for future work

This thesis focuses on the interactions of different starches, flocculants and silica with the purpose of optimizing their usage in terms of retention and drainage in PCC-filled mechanical suspensions. It is important that the impact of these additives on handsheet properties is studied. The broader objective is to enable the use of higher PCC dosages to reduce the fiber content in paper.

The following are suggested for a more complete knowledge on microparticle retention aid systems in mechanical suspensions and also to achieve the broader objective:

1. Compare tapioca and waxy maize starches in terms of formation, strength and optical properties via handsheet studies
2. Determine whether the use of coagulants will help the performance of the microparticle retention aid systems, especially ones involving waxy maize starch
3. Determine the effects of different modes of addition e.g. premixing of PCC, starch and silica on retention and drainage
4. Determine silica and flocculant dosages needed at PCC dosages of 300 and 500 kg/t OD pulp to match the retention and drainage levels achieved at PCC dosage of 250 kg/t OD pulp
5. Devise novel ways of introducing PCC to the pulp to enable high retention and drainage at high PCC dosages


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