Interaction of Fibres and Additives in Mechanical Pulp Suspensions

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by

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Abstract

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Precipitated calcium carbonate (PCC) is used in the production of high value communication papers from thermo-mechanical pulp (TMP) suspensions to improve optical properties like opacity and brightness. Addition of PCC also reduces the cost of papermaking. However, the increasing use of PCC in producing high value communication papers from bleached TMP has resulted in the requirement for using cationic starch as a strength enhancing agent. Starch addition compensates for the strength loss due to addition of PCC. This thesis examines the interactions of TMP fibres, PCC, starch and other additives used in mechanical grade papermaking. The thesis also illustrates the use of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) as a non-destructive technique to obtain the z-direction PCC filler distribution in paper.

In TMP suspension loaded with PCC high degree of substitution (DS) tapioca starch was found to be better strength developing agent and retention aid compared to high DS potato starch. It was also found that Polyaluminum chloride (PAC) should be used as a coagulant when using potato starch and poly diallyldimethyl aluminum chloride (DADMAC) when using tapioca starch to get maximum benefits in terms of facilitating starch adsorption to the fibres. The effect of poly DADMAC and cationic polyacrylamide (CPAM) on total and fines/filler retention in the presence of starch was studied separately. It was found that the interaction of poly DADMAC and CPAM in the presence of starch does not help in total retention but the interaction is positive for fines/filler retention. Finally, drainage experiments showed that poly DADMAC and CPAM in the presence of tapioca starch increase drainage of TMP suspensions loaded with PCC.

The z-direction filler distribution is important as it affects a number of paper properties. A total of seven industrial paper samples manufactured on the same paper machine (Horizontal

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Bel Baie-III) were used to illustrate the SEM/EDX technique to obtain the z-direction distribution of calcium. The calcium content was related to the filler content in the sheet. The technique for z-direction mineral distribution was further established by analyzing hand sheets prepared with a known amount of calcium carbonate. The method is expected to aid the efforts of papermakers to produce a sheet structure for various end uses if one establishes a relationship between z-direction filler distribution with paper machine operating parameters and additives used.

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Nomenclature

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	Abbreviation	Full Form
	AT	Anionic Trash
	ATC	Anionic Trash Collectors
	CD	Cross Direction
	CPAM	Cationic Polyacrylamide
	DCS	Dissolved and Colloidal Substances
	DDW	Distilled and Deionized Water
	DFR	Drainage, Freeness, Retention Tester
<i>.</i>	DS	Degree of Substitution
	EDX	Energy Dispersive X-ray Analysis
	GCC	Ground Calcium Carbonate
	ICP/MS	Inductively Coupled Plasma/ Mass
		Spectroscopy
	MD	Machine Direction
	OBA	Optical Brightening Agents
	OD	Oven Dry
	PAC	Polyaluminum chloride
	PCC	Precipitated Calcium Carbonate
	PCD	Particle Charge Detector
	PEO	Polyethylene Oxide
	PEI	Polyethyleneimmine
	PFR	Phenol Formaldehyde Resin
	Poly (DADMAC)	Poly diallyldimethyl aluminum chloride
	PW	Process Water
	SEM	Scanning Electron Microscopy
	SKL	Sulfonated Kraft Lignin
	TMP	Thermo-Mechanical Pulp
	TS	Top Side
	WDS	Wavelength Dispersive Spectroscopy
	WS	Wire Side
· .	XRD	X ray diffraction
	XRF	X-ray fluorescence

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Chapter-1

Introduction

1.1 Introduction to Papermaking

Papermaking is the process of formation of a paper sheet from a diluted pulp suspension on a paper machine fabric where the solids are retained and the water is drained through the fabric [1]. The small particles of the papermaking stock are attracted through van der Waals' forces or through polymer bridges to the fibre fines and fibres which are then easily retained by the paper machine fabric. The holes in the paper machine fabric are of larger magnitude than the fines and fillers in the pulp suspension. When water is drained from the fiber mat, capillary forces draw the fibres, fines, and other particles to close contact with each other. Hydrogen bonds are formed between fibers where possible when the rest of the water is removed. The formed sheet from the fabric is transferred into the press section to squeeze the water from the sheet and then finally, dried in the dryer section to get the desired sheet of paper. All these stages require careful control and monitoring to ensure the desired final product [1, 2].

The paper manufacturing fundamental technique has not changed for decades, although improvement in each stage of manufacturing has ensured high quality standards. The paper industry continuously aims to achieve higher quality and uniformity of products, at lower costs, low energy utilization, low water consumption and minimal environmental impact.

There are two types of pulps that are mainly used to manufacture paper: Chemical pulps (mostly kraft pulp) and mechanical pulps. These pulps have different physical, optical and chemical properties and react differently to the additives used in

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papermaking. The papers produced from these pulps have different properties. The papers produced from chemical pulps are commonly known as fine papers. Mechanical pulps contain a higher amount of fines and dissolved and colloidal substances (DCS) compared to chemical pulps. Papers produced from mechanical pulps are weaker and less bright than chemical pulps. However, the low cost of mechanical pulps is always an incentive that attracts papermakers. This is especially true for papermaking in British Columbia.

A wide variety of chemicals are incorporated in a papermaking stock furnish to impart or enhance certain sheet properties or to facilitate the papermaking process. The types of additives to be added also depend on the type of fibres (chemical or mechanical pulp) used in papermaking. Two types of additives are generally used in papermaking: performance additives and functional additives. Performance additives are mineral fillers, sizing chemicals, optical brightening agents, starches and dyes which impart specific properties to the paper product. Functional additives are drainage aids, retention aids, defoamers, pitch dispersants, slimicides and corrosion inhibitors which aid the papermaking process. The additives used in papermaking contribute 10% of the cost of papermaking [2].

Thus a papermaking furnish is a suspension of pulp fibres, fibre fines, mineral fillers and various chemical additives. Retention of these materials in the paper sheet is one of the most important aspects that have to be dealt with in papermaking as it has direct influence on the cost and quality of the paper produced. Pulp fibres are typically 3-5 mm in length for softwood fibres and 1-2 mm for hardwood fibres. These are relatively not easy to retain in the sheet by filtration [1]. The diameter of fibres ranges

from 20 μ m-50 μ m. On the other hand, fibre fines and mineral fillers (1 μ m-2 μ m) have dimensions one to two orders of magnitude smaller than the fibres, and are retained by adsorption on fibres and aggregation into large size flocs which can be physically entrapped in the fibre mat. However, these modes of retention do not retain all the fines and fillers. Some amount of fines and fillers are lost with the white water that drains through the paper machine fabric. Loss of these furnish materials as well as other chemical additives that have adsorbed onto them not only lead to an increase in the raw material supply cost but also move in the system as dead load and affect the papermaking process. These fibre fines and mineral fillers give rise to deposits, scaling, microbial activity, and consume more chemicals thereby reducing efficiency [2]. Low retention places an additional load on the pumping costs and effluent treatment plant. The papermaking stock composition is fixed for a given grade of paper according to the sources of raw material available. Shorter pulp fibres, higher fines and filler content in papermaking stock are very difficult to retain mechanically on the paper machine fabric [3]. The use of mechanical pulps to produce paper therefore comes with additional challenge compared to that with chemical pulps.

The basis weight of paper being manufactured also affects retention. The type of forming unit, drainage elements, paper machine fabric, and the white water system closure also affect retention. With increasing speeds of paper machine the forming time is decreased leading to reduced retention in the wire section. Two basic retention mechanisms occur: filtration or mechanical retention and agglomeration or flocculation. Mechanical retention refers to the retention of the particles in the papermaking stock which are larger than the pores in the forming fabric of the paper machine or the pores in the already formed fibre mat. Coagulants and flocculants are typically polymers that are added to the papermaking stock to aggregate the fibre fines and fillers in order to improve retention. Polymers that are added to increase retention of fibres, fibre fines, and fillers are known as retention aids. Coagulants are low molecular weight polymers with high charge density which adsorb on the fibre fines and fillers to form aggregates of fibre fines and fillers. Flocculants are high molecular substances that form flocs by bridging the aggregates and incorporating them into the fibre mat. It is noted that the action of all these chemicals is based on three fundamental mechanisms: (i) charge neutralization, (ii) bridging and (iii) patch flocculation [4].

Charge neutralization occurs when the electrostatic repulsion between fibres, fines and fillers is reduced by the adsorption of electrolytes or polyelectrolytes of opposite charge on the surface. This brings the particles closer to each other reducing the repulsive energy barrier, after which the attractive forces between the particles lead to coagulation [4]. However, due to the increase in paper machine speeds the importance of charge neutralization as retention aid mechanism has decreased [3]. Bridging takes place when the adsorbed polymers are able to extend into the solution and adsorb onto the other particles in the solution. This leads to the formation of bridges between differently charged regions of the particles [4]. The bridge formation depends on the type of polymer, the contact time, the solution properties and the surface properties of the particles. Polymers with high molecular weight are suited for bridging mechanism. Long chain polymers with a low or non-ionic charge like polyethylene oxide and polyacrylamide (PAM) are used for bridging. Flocs formed by bridging are unstable to shear and reflocculation is slow as the polymer chain breaks due to shear [3]. In patch

model the polymer is adsorbed in cationic patches on the negatively charged particle surface so that partial charge neutralization occurs. Flocculation in this case will take place when the oppositely charged surface of the particles comes together [3]. The driving force in such type of flocculation is the attraction between the adsorbed patches and the unabsorbed sites on other particles [4].

A variety of retention aids are available in the market. High and low molecular weight polymers of both organic and inorganic nature are used for improving retention. The selection of retention aid depends on the grade of paper being manufactured, the quality of the finished product, the type of pulp, the white water system, and finally the cost of the retention aid. Polyacrylamides are inexpensive polymers that are widely used for boards and fine papers. However, they are not cost effective in newsprint and groundwood specialty stocks because of the high concentration of "anionic trash". The term "anionic trash" refers to dissolved and colloidal anionic materials such as lignosulphonates, humic acids, hemicellulose and fine colloidal suspended solids. These interfering substances originate from fresh water, pulping residuals, bleaching residuals and broke [5]. An excessive amount of expensive cationic polymer is often consumed to neutralize these anionic interfering substances before it becomes effective as a retention aid. Polyaluminum chloride (PAC) is used as a neutralizing agent in furnishes with high anionic trash to achieve lower conductivity and charge at a low cost. Therefore, wet-end management is one of the most important tasks in the paper machine. It is necessary to select a retention aid program that suits the requirements of a particular mill and furnish [4]. Although flocculation of fines and fillers improves their retention, it also

deteriorates sheet formation. Overdose of retention aids can cause poor formation due to excessive flocculation.

High molecular weight cationic polymers like polyethylene imines are used for multiply board, newsprint and fluting. Anionic PAM and bentonite are used in newsprint, cationic PAM and bentonite in printing and writing papers. Cationic starch and anionic silica are used in wood-free printing and writing papers, and linerboard [4]. However, the use of starch in mechanical grade papers is increasing due to its ability to provide greater strength and reduction in linting tendency. High molecular weight, non-ionic polyethylene oxide (PEO) has been found to be effective in mechanical paper grades. PEO is capable of retaining wood resins into the paper and prevents pitch deposition [6]. However, PEO only flocculates effectively in the presence of some synergistic compounds known as "cofactors" which are found in groundwood pulp furnishes [6]. Cofactors enhance the flocculating ability of PEO. Some commercial cofactors commonly used in papermaking are kraft lignin and phenolformaldehyde resin (PFR). Various mechanisms have been proposed in an attempt to describe this dual-components system [6-12].

1.2 Calcium Carbonate Filler

Calcium carbonate (CaCO₃) is extensively used as a filler in the alkaline papermaking process [13]. CaCO₃ filler improves brightness, opacity, smoothness, and printability of paper. Due to its buffering ability, paper filled with CaCO₃ has better aging resistance. Precipitated CaCO₃ can be produced cheaply on-site at the paper mill. However, the dissolution of CaCO₃ at acidic pH limits its use in acid papermaking.

Figure 1.1 shows the solubility of calcium carbonate at different pH. At acidic pH calcium carbonate solubility is very high. However, as the pH increases the solubility decreases and at a pH of 9 it is negligible [14].

Both natural ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) are used in filling paper. Calcite is the most stable form of GCC and is available in three types based on the particle size: ultrafine (< 1 μ m), fine (1-3 μ m) and coarse (> 3 μ m). However, GCC contains impurities such as iron and silica which may affect the papermaking process [15]. On the other hand, PCC is relatively free of impurities and its properties, such as particle size, distribution and surface chemistry can be designed for specific mill. A brightness level of 90-95% is one of the most desired properties of calcium carbonate and the main reason for its use in papermaking [16]. PCC can have different crystalline structures depending on how it is produced. The most common forms are scalenohedral calcite, rhombohedral calcite and acicular aragonite. The surface charge of PCC depends on its concentration, varying from negative at low concentrations to positive at higher concentrations [17].

PCC filler is commonly used in chemical pulps to obtain optical properties (brightness, opacity, gloss) and physical properties (smoothness). As papermakers look to reduce cost of papermaking, it has become necessary to incorporate fillers in mechanical grade papermaking not only for reducing cost but also to improve paper properties especially brightness. One challenge that is faced when using PCC is its solubility at acidic conditions.



Figure 1.1: Solubility of calcium carbonate at different pH [14]

As seen in Figure 1.1, the change of pH from alkaline to acidic conditions causes a dramatic increase in the solubility by several orders of magnitude. On the other hand, at alkaline conditions where the solubility of CaCO₃ is small, darkening of pulp may occur [18]. Therefore, pH conditions impose limitations on the use of CaCO₃ in papermaking. The application of CaCO₃ in acidic condition such as newsprint production may become feasible if the dissolution of CaCO₃ can be controlled. The inhibition of the dissolution of papermaking grade PCC filler by various chemicals has found that the presence of trace amount of phosphate lowered the solubility of PCC by 80% at pH 7.5 [14, 19, 20, 21]. Acid tolerant (AT) PCC are available to operate in acid and neutral papermaking. This type of AT PCC is treated with a sequestering agent to make it available for the use in acid and neutral papermaking conditions [22].

1.3 Use of Starch in Papermaking

Papers produced from mechanical pulp suspensions are weak compared to that made from chemical pulp suspensions. This is due to the interference of lignin and hemicellulose in fibre-fibre bond formation. Also mechanical pulp fibres do not swell to the extent of chemical pulp fibres. In the "new world of papermaking" where highest product quality and lower costs are required, it has become essential to add mineral fillers to mechanical pulp suspensions to reduce cost, increase brightness, and improve printing properties. However, the addition of mineral fillers to the pulp suspensions reduces strength of paper. To compensate for the strength losses, dry strength agents are added. Cationic starch is the most widely used strength agent [23].

Starch is found in most plants, particularly in the seed or various roots and tubers. Next to cellulose, starch is the most common polysaccharide in the plant kingdom. Starch is used in the paper industry to improve strength, retention, for surface applications in the size press, as an adhesive in corrugated boards and as a binder in pigment coating. Cationic starches of high molecular mass are used as retention aids whereas oxidized starches are used for surface sizing and coating. The addition point of cationic starch depends on the role it has to play in the papermaking process. If dry strength is required starch is added to the thick stock (3-3.5% consistency). Thick stock refers to the stock consistency in the blending chest. However, if it is to be used as a retention aid it is added to the thin stock (0.5-1% consistency). Thin stock refers to the stock consistency in the approach flow system. Starch solutions used as retention aids must not be exposed to high shear forces to prevent starch molecules from shearing off [3]. The use of starch differs in mechanical and chemical pulp suspensions.

Figure 1.2 shows the similarities in the structure of cellulose and starch. Cellulose is made up of glucose units which are linked together by β -1, 4 linkages. In cellulose the bond connecting carbon-1 and bridging oxygen is oriented in the same plane as the glucose ring (β -link) and the resulting polymer molecule takes an extended ribbon like shape as shown in figure 1.2. Starch is also made up of glucose units but are linked by α -1, 4 linkages. In starch the bond connecting carbon-1 and bridging oxygen is oriented perpendicular to the plane of glucose ring (α -link) and the resulting polymer tends to take on a more coiled helix-like structure. Starch consists of a linear part known as amylose and a branched part known as amylopectin. The amylose chain length varies from 200-2000 glucose units whereas the branched amylopectin consists of large tree-like molecules with 100-200 short linear parts each with a length of 20-30 glucose units. The branching takes place through 1, 6- α -glucosidic bonds [3]. Amylopectin is more important for papermaking than amylose.

Starch for papermaking is obtained mainly from maize, potato, tapioca and wheat. Maize starch granules are polygonal in shape and have a size of 5-25 microns. Potato starch granules are oval in shape and have a size of 15-100 microns and wheat starch granules are spherical and have a size of 5-35 microns. The ratio of amylose and amylopectin varies in starches obtained from different sources. For starch to act as dry strength agent, it is necessary to adsorb starch on the pulp fibres. The adsorption of starch on kraft pulp and mechanical pulps are different. Extensive work is carried on the adsorption of starch on to kraft pulp but very few reports are available on the adsorption of starch on to mechanical pulps.



Figure 1.2.: Structure of cellulose and starch [3].

Wagberg and Kolar (1996) studied the adsorption of differently charged cationic potato starch on the fibre fraction of peroxide bleached TMP. Studies done with the adsorption of cationic starch on bleached chemical pulp suspension show that the adsorption of cationic starch on fibres can be viewed as an ion-exchange process in which the anionic charges of the fibres are compensated by cationic charge of starch [23, 24, 25, 26]. This ion-exchange process is explained by the theories of polyelectrolyte adsorption [27]. However, when the DCS from TMP is introduced, the same do not hold true due to the complex interactions involved between starch and anionic trash. Anionic DCS interact electrostatically with cationic starch making it ineffective to adsorb on the fibre and develop strength. Some studies confirm that the amount of starch to be added to a pulp suspension increases with the increasing anionic trash and fines content. This is due to the fact that fines and DCS have a higher charge density and higher specific surface area than the fibres [28, 29]. If the DCS and fines can be retained with the fibres by a bridging mechanism in the sheet an increase in retention and paper strength is obtained [23]. Therefore, the use of starch in mechanical papermaking requires more investigation to determine the best addition point, sequence and the amount that will help in developing strength of paper and also improve retention.

Retention, formation, dewatering and final sheet properties are interdependent. The objective is to achieve the best possible and not the highest possible. Since retention involves flocculation, the strategy should be to achieve regular structure and size distribution which is easy to dewater in a sheet with balanced properties. The need for the papermaker is to select a starch which gives higher cost/efficiency ratio. There is a wide range of starches available depending on the source of production. The most commonly used starches in the wet end of papermaking are potato starch, tapioca starch, and waxy corn starch. These are all cationic. Cationic starch has smaller charge density than cationic synthetic polymers [30]. Cationic potato starches give a better total retention, sizing and strength when compared to other starches. However, the higher cost of potato starch has led the papermakers to investigate on other types of starches [31]. Most of the work involving starches in mechanical pulp suspensions is done with potato starch and corn starch. The use of other starches like tapioca has not been investigated extensively. There is also a knowledge gap in comparing potato and tapioca starch performance in mechanical pulp suspensions loaded with PCC.

1.4 Dissolved and Colloidal Substances (DCS) in Mechanical Pulp Suspensions

During the production of mechanical pulp almost all the wood components are retained in the pulp suspension. About <10% (by weight) of these materials are dissolved and dispersed in the water phase [36]. The dissolved and/or dispersed fraction contains mainly dissolved carbohydrates from the wood both uncharged and a negatively charged colloidal phase mostly containing lipophillic extractives. These components present in the mechanical pulp suspensions affect the performance of cationic polymers like cationic starch in the papermaking process reducing the efficiency and product quality [36, 37, 38, 39]. These DCS are collectively known as anionic trash.

Mechanical pulp suspensions have 35% fine material that is material smaller than 75 μ m, in addition to DCS, compared to 10% for chemical pulps [24]. Mechanical pulp fibres have anionically charged hemicelluloses bound to the fibres that gives the fibre a charge of 85-110 μ eq/g compared to chemical pulps which have 10-25 μ eq/g [25]. This means that mechanical pulps require higher amount of cationic polyelectrolytes for retention.

1.5 Anionic Trash Collectors (ATC) in Mechanical Pulp Suspensions

When starch is used in systems with high level of anionic trash the presence of anionic trash deactivates the cationic starch thereby making it unsuitable as dry strength additive in a mechanical pulp suspension. The use of synthetic anionic trash catchers before introducing cationic starch helps the starch to perform as a strength additive in mechanical pulp suspensions reducing surface dust, linting and increasing the runnability. Poly-DADMAC, Polyethyleneimmine (PEI) and Polyaluminum chloride (PAC) have been used as anionic trash collectors (ATC) along with starch in mechanical pulp suspensions. For starch to be effective as a dry strength agent in a highly polluted systems with AT, the starch self retention should be high. It is seen that the starch retention increases in the presence of ATC. Therefore, in a system containing high amount of anionic trash, the retention strategy should be to neutralize the anionic trash with an ATC and then introduce starch. This will increase the effect of starch to improve paper strength and total retention [31].

It is necessary to know the mechanism of interactions between anionic trash substances and the different cationic polyelectrolytes to create an electrochemical environment to ensure the highest effectivity of cationic starch. Shielding effects induced by electrolytes or conformational effects as well as the absolute charge level is decisive for the formation and behavior of the polyelectrolytes. Reaction between synthetic cationic polyelectrolytes and AT components finishes in milli seconds and several minutes [32]. However, the reaction between AT and starch is at the slow end of this range [33]. The main goal of starch addition is strength and the retention, drainage and anionic trash reduction are all side effects.

Poly DADMAC is a linear homo-polymer formed from a monomer that has a quaternary ammonium and two unsaturated -CH=CH₂ functionalities. The monomer itself is formed by reacting two equivalents of allyl chloride with dimethylamine. Free-radical polymerization of the "DADMAC" monomers yields a structure in which the quaternary ammonium groups are on rings that are included in the backbone of the polymer chain.



Figure 1.3: Structure of poly DADMAC

Poly DADMAC reduces the cationic demand as against the zeta potential. This shows that poly-DADMAC has a greater affinity towards anionic solubles than fibre fines. There is also a direct correlation between anionic trash catching efficiency and charge density of poly DADMAC. With same charge density, synthetic ATC are more efficient than cationic starches for reduction of cationic demand. The dosage of ATC is less to that of starch for the same cationic demand [31].

Poly-aluminum chloride" or "PAC" refers to a class of soluble aluminum products in which aluminum chloride has been partly reacted with base. The relative amount of hydroxyl ions (OH-), compared to the amount of aluminum ions (Al⁺³), determines the basicity of a particular PAC product. PAC is often expressed in the form $Al_n(OH)_mCl_{(3n-m)}$. Basicity can be defined by the term (m/3n)*100 [34]. PAC products of low basicity (0 to 17%) and medium basicity (17 to 50%) are commonly used in papermaking applications, whereas PAC products of higher basicity are useful for water and wastewater treatment. PAC is a coagulant known to neutralize first the colloidal material and then the fines, whereas poly-DADMAC acts oppositely. Hence, PAC is used when the objective is to reduce cationic demand of DCS and poly-DADMAC when objective is to reduce cationic demand on the fibre surface (blocking polymer). Finally, PAC is compatible with optical brightening agents (OBA) while organic anionic trash collectors have a strong negative effect [35]

PAC is extensively used in neutralizing the anionic trash in mechanical pulp suspensions, paper boards, coated paper, sack kraft and other brown papers. It is also used in fine papers to increase drainage rates in neutral/alkaline papermaking. PAC has become one of the most widely used chemicals for retention aid programs. PAC is also used for neutral sizing with certain rosin-based emulsion products. PAC is replacing papermaker's alum in linerboard production where it can reduce the problem of scaling by decreasing the amount of pH drop and avoiding the addition of sulfate ions. However, the dosage of PAC should be carefully controlled since an overdose will convert the net colloidal charge of the system to a positive sign. One drawback of using PAC is the high degree of corrosion due to the presence of chloride [31].

1.6 Z-Direction Distribution of Mineral Content in Paper

Z-direction refers to the thickness direction of the paper and is an important factor that influences the final product quality. For example the impact of z-direction filler distribution on properties like strength and porosity has been reported [40]. Paper is manufactured according to the needs of the end users. To cater to the needs of the end users there are a variety of changes made to the operating parameters of a paper machine to influence the structure of the sheet. For example base paper for coating purposes requires more filler on the surface to prevent the penetration of the coating color into the base sheet [41, 42]. For copy paper grades, the filler distribution needs to be lower at the surface to prevent dusting [43, 44]. Sheet splitting and adhesive tape methods are the two physical methods used to obtain information about filler distribution [45, 46]. The difficulty in using these methods for lower basis weight sheets has motivated the search for non-destructive image analysis techniques for determining z-direction filler distribution. These are described in the introduction of chapter six of the thesis. A relationship between the z-direction filler distribution to the paper machine operating parameters would enable the papermakers to develop a sheet according to the end uses. However, such knowledge is inadequate at present time. Some information is available. For example, the impact of dewatering conditions on the distribution of fines, and fillers in the z-direction has been reported [43, 44]. It has also been reported that pressing does not affect the z-direction filler distribution [47]. It is also believed that the type of former (twin wire, gap former, fourdrinier etc.) is the major factor in influencing z-direction distribution [48]. However, the impact of chemical additives is not well understood.

1.7 Research Objectives

It is evident that the use of low cost thermo-mechanical pulp (TMP) instead of the more expensive kraft pulp for the manufacture of high value communications papers necessitates the optimization of the use of additives instead of using them in an empirical fashion. Optimization refers to finding the optimal addition amounts (dosage), addition points in the papermaking system and addition sequences. Optimization of the use of additives in mechanical pulp suspensions has not received the attention it has received with chemical pulp suspensions. The scope of this work is to optimize the use of precipitated calcium carbonate (PCC) filler and starch in mechanical papermaking suspensions typical of those used in Coastal mills in British Columbia. In order to accomplish this goal we need to investigate the interactions of peroxide bleached TMP suspensions with PCC, starch, coagulant and flocculant additives. Interactions include aggregation of PCC by starch, adsorption of starch on PCC and fibres, electrostatic interactions. Moreover, assessment of the interactions necessitates determination of the retention of fibres and fines/PCC filler and drainage (speed of dewatering from the fibre web). PCC filler is used in this work because it is the most preferred filler in North America. Two types of starch (potato and tapioca) are used. One inorganic coagulant, poly aluminum chloride, (PAC) and one organic coagulant, poly diallyl dimethyl ammonium chloride, (DADMAC) were used. These coagulants are also termed anionic trash collectors (ATC). Finally, cationic poly acrylamide (CPAM) was used as flocculant.

A hierarchical approach for studying the various interactions is followed. This consists of elucidating first the binary interactions followed by the ternary and so on. Laboratory trials were conducted with mill pulp samples and additives used by the mill. Moreover, experiments were conducted with distilled and deionized water (DDW) and process water (PW). Mill conditions are simulated in the laboratory by using the PW that is squeezed from the obtained pulp suspension (3-4% consistency) using a centrifugal separator. The outcome of the study of the interactions is the knowledge about the optimal use of additives and translation of this knowledge to engineering practice.

The following main objectives were set:

1. to elucidate

- a. the colloidal behaviour of PCC in DDW and PW
- b. the interaction of PCC with starch in DDW at 25°C & 50°C and PW at 50°C
- 2. to determine the optimal conditions under which starch can be used as strength enhancing additive in TMP suspensions loaded with PCC
- 3. to determine the ability of starch to also act as a PCC filler and fines retention aid
- 4. to determine the optimal conditions for the use of coagulant and flocculant in a TMP suspension loaded with PCC in the presence of starch
- 5. to illustrate the use of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) in order to obtain the z-direction mineral content distribution in paper without disturbing the structure of paper.

1.8 Thesis Organization

Chapter 1 discusses basic information about papermaking and the additives used in papermaking process and also includes the research objectives and the organization of the thesis. It also shows why it is important to add different additives to the paper. Also, described are various retention aids used in papermaking and their mechanisms and how they affect the paper properties. It is also shown the importance of various measurements in evaluating the performance of an additive in the papermaking process.

Chapter 2 illustrates the colloidal behaviour of PCC in DDW and PW. The interaction of PCC with starches is determined and how various starches aggregate PCC and adsorb onto PCC in DDW and PW is shown. The material of this chapter has been published.
Modgi, S. B., Michael E. McQuaid, and Englezos, P., "Interaction of Precipitated Calcium Carbonate (PCC) with Starch in Distilled and Deionized Water (DDW) and Process Water (PW)", Nordic Pulp and Paper Research Journal, vol. 21(5), 2006:716-723.

Chapter 3 shows the interaction of starches on TMP suspensions loaded with PCC. In this chapter various parameters like cationic demand, zeta potential, conductivity and pH are determined with two types of starch. Finally, the effect on total and fines/filler retention with the starches is shown. The material of this chapter is under review by the Journal of Pulp and Paper Science (JPPS).

 Modgi, S. B., Michael E. McQuaid, and Englezos, P., "Effect of Starches on TMP suspensions Loaded with PCC", submitted to JPPS.

Chapter 4 studies the effect of coagulants and flocculant on TMP suspensions loaded with PCC in the presence of starch. The effect of two coagulants: PAC and poly DADMAC on cationic demand and zeta potential of the TMP suspension is studied. After selecting the best starch and coagulant for the TMP suspension, the effect of the coagulant, starch and flocculant on the total, fines/filler retention and drainage is determined.

Chapter 5 gives a complete description of the SEM/EDX work conducted on industrial paper samples. It describes the method, the calibration, the effect of starches on z-direction filler distribution and finally the effect of sampling technique on the z-direction mineral distribution in paper. A version of this chapter has been published.

 Modgi, S. B., Michael E. McQuaid, and Englezos, P., "SEM/EDX Analysis of Z-Direction Distribution of Mineral Content in Paper along the Cross-Direction", *Pulp and Paper Canada*, 48-51, May 2006. Modgi, S. B., Michael E. McQuaid, and Englezos, P., "SEM/EDX Analysis: A Technique for Z-Direction Mineral Topography in Paper", Nordic Pulp and Paper Research Journal, vol. 21(5), 2006:659-664.

Finally, the conclusions and contribution to knowledge are discussed in chapter 6. A general summary of the judicious use of additives in papermaking from this work is described followed by the recommendations for future work that will help complete knowledge of additives in mechanical papermaking.

1.9 References

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Chapter-2

INTERACTION OF PRECIPITATED CALCIUM CARBONATE (PCC) WITH STARCH IN DISTILLED AND DEIONIZED WATER (DDW) AND PROCESS WATER (PW)¹

2.1 Introduction

Alkaline papermaking using PCC filler is today the most widely used method for the manufacture of mechanical grade papers. The technical incentives such as improved brightness, ageing stability, strength benefits etc. along with the availability of PCC in USA have helped papermakers to enjoy the benefits of alkaline papermaking [1, 2, and 3]. However, paper grades using wood containing pulp suffer significantly in brightness if manufactured in alkaline media. This phenomenon is referred as "alkaline darkening" and is assumed to be caused by quinine chromophores originating from the lignin components in mechanical pulps [4]. To overcome this effect of alkaline darkening acid tolerant PCC is widely used in mechanical pulp systems. However, there is not much literature on the behavior of acid tolerant PCC in process waters. The study of interaction of PCC with the dissolved and colloidal substances in process water will help in reducing the unnecessary usage of cationic polymers.

It is well known that by increasing PCC loading the strength of the paper deteriorates. In order to compensate for the decrease in paper strength it is important to use cationic starches. These are well known wet-end additives employed to enhance the dry-strength of paper and paper board, and also to promote fines and filler retention [5, 6]. Retention of fillers and fines can result from deposition on fibres in a

¹ "A version of this chapter has been published. Modgi, S. B., Michael E. McQuaid, and Englezos, P., "Interaction of Precipitated Calcium Carbonate (PCC) with Starch in Distilled and Deionized Water (DDW) and Process Water (PW)", Nordic Pulp and Paper Research Journal, vol. 21(5), 716-723, 2006.

papermaking suspension, or by capturing the fines and filler aggregates in the sheet by mechanical entrapment. The mechanism of capturing fines and filler depends on the grade of paper to be manufactured. However, most of the mechanical grade papers incorporate fillers by forming aggregates and then capturing it into the sheet [7]. The use of starch along with PCC provides the opportunity to aggregate PCC and then fix them to the fibres by flocculation. Some mills have also tried pretreating the PCC particles with starch before they add it to the paper making stock. This has also helped them to reduce linting and dusting.

Vanerek et al. (2000a) have studied the aggregation of positively charged PCC with polyelectrolytes like polyacrylamide (PAM). They have shown that the behavior of PCC depends on the type of adsorbed polymer. They have also shown that low dosages of PAM cause flocculation of PCC even in the presence of a large excess of dissolved anionics such as sulphonated kraft lignin (SKL) [8].

While the adsorption of cationic starches on to cellulosic fibres has been studied extensively very few investigations have been reported on the adsorption of starch on to PCC [9, 10, 11, 12, and 13]. Noik (1982) [14] studied the adsorption of cationic amylopectin from corn starch on pure calcite. It was found that the higher the charge density and the lower the molecular weight of the amylopectin the lower is the amount of amylopectin adsorbed on to calcite [14]. Hedborg and Lindstrom (1993) [11] studied the adsorption of cationic starch on commercial calcium carbonate filler (chalk). This filler had a zeta potential of -24 mV. They showed that the lower the CaCO₃ concentration the higher was the starch adsorption [11]. However, this study was carried out with deionized water at 25°C which does not represent the actual mill environment. They were able to

demonstrate that higher molecular weight starch adsorbs more on to CaCO₃ compared to lower molecular weight starch. It is also well known that lower molecular weight starch adsorbs more on to porous cellulose fibres [11]. Hedborg and Lindstrom (1993) [11] also showed that the adsorption behavior of different starches having similar DS on CaCO₃ was same and that the negative charge of the phosphate group present in potato starches is not of major significance for the adsorption behavior [11].

Wagberg and Kolar (1996) have studied the adsorption of differently charged cationic starches onto the fibre fraction of a peroxide bleached TMP. The results show that the adsorption can be viewed as an ion-exchange process in which anionic charges on the fibres are replaced by cationic charges on the starch. However, in the presence of dissolved and colloidal substance (DCS) the starch forms a complex with DCS and prevents its adsorption onto fibres. Due to the higher charge density and higher specific surface area of DCS and fines starch adsorbs preferentially on these materials [12].

The objective of this chapter is to elucidate (a) the colloidal behavior of PCC in different waters containing DCS; (b) the aggregation of PCC particles with two types of potato starch and one type of tapioca starch in DDW at 25°C and 50°C and in process water at 50°C; and (c) the adsorption of starch onto PCC particles in DDW and PW at 50°C. The temperature of 50°C represents the papermaking temperature. The outcome of this work is expected to provide information that will enable papermakers to select the proper type of starch for their papermaking process.

2.2 EXPERIMENTAL

2.2.1 Experimental Materials

2.2.1.1 Precipitated Calcium Carbonate (PCC)

The PCC used for this work is an acid tolerant PCC obtained at a solids content of 33% from Specialty Minerals Inc. It has an average particle size of 1.5 µm and brightness of 98%. This PCC has a scalenohedral structure which is similar to the untreated PCC. This PCC has a negative zeta potential -21.4 mV in DDW. The acid tolerant PCC is specially designed for mechanical paper making systems to prevent alkaline darkening of pulp.

2.2.1.2 Starches

Two types of potato starch (1 & 2) with different degrees of substitution and a tapioca starch were used. Potato starch-1 has a degree of substitution (DS) of 0.1 and potato starch-2 has a degree of substitution of 0.034. Tapioca starch has a degree of substitution of 0.1. Tapioca starch has a higher molecular weight than potato starch-1 and 2. Also, potato starch-1 has a higher molecular weight than potato starch-2. The cationicity of tapioca starch is greater than potato starch-1 and potato starch-1 has a greater cationicity than potato starch-2. The viscosity of starches was obtained at a solids concentration of 2% by using Brookfield viscometer and spindle LV2 at 50°C. The viscosity of potato starch-1 is 550±5 cP, that of potato starch-2 is 350±5 cP and that of tapioca starch is 570±5 cP at 40 rpm. Figure A1 in the appendix shows the viscosity of potato starch-1, tapioca starch and corn starch at different spindles. These starches behave in a similar fashion at different spindle speeds. They are all shear thinning liquids. Corn

starch with a DS of 0.032 was also used for PCC aggregation in experiments with DDW at 25°C. The amylose and amylopectin content of corn starch is 28% and 72% respectively. For potato starches the amylose content is 20% and amylopectin is 80%. Tapioca starch has 17 % amylose and 83 % amylopectin.

2.2.1.3 Water

Two types of water were used: DDW at temperatures of 25°C and 50°C and Process water (PW) was obtained by centrifugal separation of a pulp suspension. This water is known as process water and was obtained from a bleached Thermo Mechanical Pulp (TMP) suspension. The TMP suspension at 4% consistency was put in a special screen bag and loaded in centrifugal separator (Bock, Toldeo, USA). Pulp is retained in the screen bag and the water obtained from the outlet is termed as process water.

This process water obtained from a TMP furnish of Spruce, Pine and Fir contains dissolved and colloidal substances (DCS) and some fibre fines. The particle size distribution of process water was determined using the Malvern Mastersizer described below and is shown in figure 2.1. Other information for this process water is also noted in the figure 2.1. However, PW was not analyzed chemically for its constituents as it was obtained from the same pulp for each experiment.

The colloidal behavior of PCC with respect to change in zeta potential and cationic demand of PCC suspended in DDW and PW pressure filtered with $1.2 \,\mu m$ membrane and $0.1 \,\mu m$ membrane was studied. The water filtered with $1.2 \,\mu m$ membrane contains dissolved and colloidal substances whereas the process water filtered with

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 $0.1 \ \mu m$ membrane is expected to contain dissolved charge. However, all PCC aggregation experiments with starch were performed in both DDW and PW at 25°C and 50°C.



Figure 2.1: Particle size distribution of PW obtained from 4% TMP pulp suspension.

2.2.2 Experimental Methods

2.2.2.1 Colloidal Behavior of PCC

PCC at different concentrations (500, 1000, 1200 and 1300 ppm) was suspended in 140 mL of DDW, 1.2 μ m TMP water, and 0.1 μ m TMP water at room temperature and stirred continuously on a lab rotator (Lab Line Instruments, USA) for 32 hours. Approximately 20 mL of the suspension was taken after 2-3 minutes (referred to as *zero time*), 4, 10, 24 and 32 hours and filtered with 5 μ m membrane in a pressure filter. The supernatant was subjected to zeta potential measurements using Malvern Zetasizer (Malvern Instruments, UK) and cationic demand analysis using particle charge detector (PCD-03 from BTG-Mutek, Germany).

2.2.2.2 Aggregation of PCC

The kinetics of aggregation of PCC particles with starch was studied using the set up shown in figure 2.2. A Malvern Mastersizer which measures the particle size is the central component of the apparatus which also consists of a 800 mL water-jacket 4-baffle plexiglass vessel, fitted with a stirrer, a thermometer and a peristaltic pump. The temperature in the plexiglass vessel is maintained at 50 °C by circulating hot water from a water bath through the water-jacket of the vessel. The colloidal suspension was gently agitated with a stirrer at 300 rpm. The stirrer consisted of three circular blades which are 17.5 mm in diameter and had a pitch of 30°. During the experiment, the suspension was circulated through the Mastersizer by 1.25 m long, 15 mm ID transparent silicone tubing using a peristaltic pump (Cole-Palmer Instruments. Co., USA). The flow rate was maintained at 50 mL/min using a flow controller.

The Mastersizer measures particle size based on laser diffraction technique. Particles scatter light to give a characteristic scattering pattern which depends on the particle size. The Mastersizer is equipped with a flow through cell for online measurement. During a measurement, the scattering pattern of the flowing suspension is continuously captured by an array of detectors. The averaged results are then used to back calculate the particle size by determining a sphere of equivalent volume would create this scattering pattern using the Mie theory. Hence, the particle size calculated is an equivalent volume mean diameter.



Figure 2.2: Experimental set-up for aggregation experiments using the Malvern Mastersizer.

Experiments were performed with DDW at 25°C and 50°C and with process water at 50°C. A 500 g of 0.25 wt. % PCC solution in DDW is taken into the plexiglass vessel. The concentration of PCC is fixed by assuming a pulp suspension at 1% consistency and 25% PCC loading on OD pulp. Similarly, a 0.25% PCC solution in process water is used for aggregation experiments with process water.

At first the background is measured with DDW using the Malvern Mastersizer. If the experimental temperature is 50°C the background is also performed at 50°C temperature. Then the PCC is added to the DDW and stirred for one minute. The particle size of PCC is measured. Then a known amount of starch is added to the suspension through the injection port. The change in the particle size is measured with time using the Malvern Mastersizer. The particles aggregate and reach a maximum and then start decreasing. The maximum size and the time taken to reach this maximum size are used to describe the effect of the starches on PCC. For each starch dosage the experiment is repeated three times and the average is reported along with the standard deviation. Two minutes after addition of starch, around 25 mL of the solution is taken out for zeta potential measurements. The aggregates are directly injected into the Malvern Zetasizer through a syringe to determine the zeta potential. The pH and the conductivity of the suspension are also noted during the measurements.

In case of experiments with PW the cationic demand and zeta potential of PW is measured before adding PCC. For particle size analysis with PW the background measurement is performed using the PW at 50°C. Then PCC is added followed by one minute mixing. Then the known amount of starch is added. Two minutes after addition of starch approximately 30 mL of the solution is collected from the plexiglass vessel and filtered through a Millipore pressure filter using a 5 μ m membrane. The filtrate is used for measuring the zeta potential of the suspended particles using Malvern Zetasizer. The stock solution obtained from the plexiglass vessel is directly used to determine the cationic demand of the suspension using the BTG-Mutek particle charge detector PCD-03. The cationic demand is reported in μ eq/g of PW+PCC suspension.

2.2.2.3 Adsorption of Starch on to PCC

Adsorption of starch onto PCC particles was studied in the same set-up as described above. Three minutes after addition of starch about 30 mL of the PCC solution was taken and subjected to centrifuge at 5000 rpm for 15 minutes. After the centrifugation the supernatant was taken for starch detection by iodine method using a spectrophotometer. For PCC aggregation in PW the supernatant after centrifuge was also used to determine the turbidity along with starch detection by iodine method as described by Shirazi et al [13]. It is important to note that in PW the required amount of iodine to obtain a stable color was four times that in DDW. This might be due to some reaction between the DCS and iodine.

2.3 **RESULTS AND DISCUSSION**

2.3.1 Colloidal Behavior of PCC

Figure 2.3a shows the zeta potential of PCC in DDW at different concentrations at *zero time*. The values on the graphs indicate the pH at the point of measurement. As PCC concentration increases the zeta potential becomes slightly more negative. Figure 2.3b shows the change in zeta potential of PCC with time. As seen zeta potential becomes less negative during a 32 hour period as the calcium carbonate dissociates in water producing Ca^{+2} ions.



Figure 2.3: Zeta Potential of PCC in DDW (a) Different concentrations at zero time & (b) Different concentrations with time.

Figure 2.4 shows the zeta potential of PCC suspended in 1.2 μ m TMP water at *zero time*. The values on the graphs indicate the pH at the point of measurement. 1.2 μ m TMP water has a negative zeta potential due to the presence of DCS. As seen the zeta potential at about 500 ppm PCC is slightly more negative than that in DDW. At higher PCC concentrations the zeta potential becomes less negative. Figures 2.5a and 2.5b shows the change in zeta potential and cationic demand of PCC suspended in 1.2 μ m TMP water respectively with time. As seen the zeta potential becomes less negative for 24 hours and then becomes more negative. This shows that if PCC remains in a papermaking system for more than 24 hours it will add more negative charge to the system. This in turn implies that more cationic polymer like starch is required to reduce the zeta potential of the system. However, the cationic demand decreases with time. This illustrates a case where even though the zeta potential becomes more negative there is not enough surface area to result in a substantial increase in cationic demand. Patton and Lee (1993) nicely illustrated the interplay of zeta potential and charge concentration [15].



Figure 2.4: Zeta Potential of PCC in 1.2 µm TMP water at different concentrations at zero time.



(a) Zeta potential

(b) Cationic Demand

Figure 2.5: Comparison of zeta potential and cationic demand of PCC with time in $1.2\ \mu m$ TMP water.

Figure 2.6 shows the zeta potential of PCC suspended in 0.1 μ m TMP water at *zero time*. The values on the graphs indicate the pH at the point of measurement. As seen in the figure, the zeta potential of this water is more negative than that of the 1.2 μ m TMP one. Moreover, the zeta potential of 500 ppm PCC is about -28 mV, whereas that in the 1.2 μ m water is about – 23 mV. At higher concentrations the zeta potential increases as was the case with the 1.2 μ m TMP water. Figure 2.7a and 2.7b shows the change in zeta potential and cationic demand of PCC suspended in 0.1 μ m TMP water, respectively, with time. The cationic demand is higher at higher concentration compared to lower concentration. Comparing the zeta potential and cationic demand also increases with time. This is in contrast to that observed with 1.2 μ m TMP water. This illustrates a case where even though the zeta potential becomes less negative there is enough surface area to result in a substantial increase in cationic demand [15].



Figure 2.6: Zeta Potential of PCC in 0.1 µm TMP water at different concentrations at zero time.



Figure 2.7: Comparison of zeta potential and cationic demand of PCC with time in $0.1 \ \mu m$ TMP water.

2.3.2 Aggregation of PCC

Figure 2.8a and 2.8b compares the maximum PCC aggregate size and maximum aggregation rate obtained by corn, potato starch-1 & 2 and tapioca starch in DDW at 25°C. The points on the graph indicate the maximum size formed and the rate at which this maximum size is reached. A typical experimental result is shown in figure A2 in the appendix. The average size of the particles increases with time and reaches a maximum and then starts decreasing due to steric repulsion. This size is defined as maximum aggregate size and the aggregation rate is defined as the time taken to reach maximum aggregate size. It should be noted that the objective is not to produce bigger aggregates of PCC but to study the interaction of PCC with starch. The bigger the aggregate size the greater is the interaction of starch with PCC. Figure A3 in appendix shows a typical experimental result where the size distribution of PCC changes with time at different dosages of starch. The PCC aggregate size increases with increasing starch dosage. In

case of corn starch and potato starch-1, beyond a starch dosage of 40 mg/g of PCC there is still room for aggregation. However, a starch dosage beyond 40 mg/g of PCC is not economical for paper production. In case of potato starch-2 and tapioca starch the PCC aggregate size reaches a maximum at a starch dosage of 32 mg/g of PCC. Beyond this dosage the aggregation rate and aggregate size starts decreasing. Comparing the potato starches, the starch with lower DS preformed better than the higher DS potato starch in DDW at 25°C. However, dent corn starch did not reach its maximum aggregate size with PCC for the range of dosages investigated here. Beyond this dosage it is not economical for papermaking. This shows that the reactivity of dent corn starch is low at 25°C. Tapioca starch with a higher DS aggregates PCC at a faster rate compared to the two potato starches. This is because tapioca starch has a higher amylopectin content compared to the other starches [14]. Both tapioca and potato starches come from the same source or in other words both are root









starches. Still they have differences in their granule size, shape, moisture content, amylose, amylopectin and ash content. The ash content refers to the inorganic materials (mainly phosphorous) present in the starch. Potato starch has higher ash content than tapioca starch. These differences in the starch properties might be responsible for the way the starches behave in the TMP suspension.



Figure 2.9: Comparison of zeta potential of PCC aggregates in DDW at 25°C for various starches at different dosages.

Figure 2.9 shows the zeta potential of the PCC aggregates at different starch dosages. The values on the graph indicate the pH at the point of zeta potential measurement. As seen all starches except corn were able at a dosage of 10 mg/g of PCC, to reverse the charge to a stable value near 20 mV. It can also be seen that the higher the cationicity of the starch, the greater is the zeta potential of the aggregates. This shows that even if the zeta potential of PCC aggregates with potato starch-1 is higher than that

of potato starch-2 still the maximum aggregation rate and maximum aggregate size were lower for potato starch-1 (as seen in figure 2.8).

Similarly, figures 2.10a and 2.10b compares the maximum PCC aggregate size formed and maximum aggregation rate reached by potato starch-1 & 2 and tapioca starch in DDW at 50°C respectively. The values on the figure 2.10a indicate the pH at which the measurements were made. It can be clearly seen that tapioca starch which has a higher molecular weight and higher cationicity performs better than the two potato starches.



Figure 2.10: Comparison of maximum aggregate size and maximum aggregation rate of

PCC particles in DDW at 50°C for various starches at different dosages.

However, tapioca starch's performance is slightly better than potato starch-1. Also, comparing the two potato starches with different DS and cationicity we can see that potato starch-1 with a higher DS and cationicity performs far better than the potato starch-2 with lower DS and cationicity. In DDW at 25°C potato starch-2 performed better than potato starch-1. However, at an elevated temperature of 50°C potato starch-1 out performs potato starch-2. This might be explained based on the coverage of starch onto PCC surface. There is an optimum coverage for a particular dosage of starch beyond which the probability of bridge formation decreases as more PCC particles are covered with starch. At full coverage of PCC particles, the particles become dispersed because of steric repulsion [16]. From Figure 2.11 it can be clearly seen that the adsorption of potato starch-2 onto PCC in DDW is greater than the other two starches. Tapioca starch with a higher DS and molecular weight adsorbed slightly higher than potato starch-1 with similar DS at a dosage of 40 mg/g of PCC. However, there is very little difference in the maximum aggregation size and maximum aggregation rate formed with tapioca and potato starch-1.



Figure 2.11: Adsorption of different starches on to PCC (0.25% concentration) at 50°C in DDW.



Figure 2.12: Comparison of maximum aggregate size and maximum aggregation rate of PCC particles in PW at 50°C for various starches at different dosages.

Figure 2.12a and 2.12b compares the maximum PCC aggregate size formed and maximum aggregation rate reached by potato starch-1 & 2 and tapioca starch in PW at 50°C respectively. It is important to remember that the Malvern Mastersizer does a background measurement of the process water and then subtracts the background information from the sample measurement. The values on the figure 2.12a indicate the pH at which the measurements were made. It can be clearly seen that tapioca starch aggregates PCC faster and forms larger aggregate size compared to the two potato starches. This shows that even in the presence of anionic trash the interaction of tapioca starch with PCC is stronger, forming bigger PCC aggregates. Also the aggregation rate is higher. Comparing the two potato starches we can see that potato starch-1 performs far better than the potato starch-2. In the presence of anionic trash we can see that the gap between the tapioca starch performance and potato starch performance increases which was not the case in DDW at 50°C. However, from figure 2.13 it can be seen that the adsorption of tapioca starch and potato starch-1 in PW is identical. This is because the

presence of DCS increases the total amount of starch adsorbed onto PCC. It was shown in literature that the presence of DCS increases the total amount of starch adsorbed onto fibres, provided that the DCS can be retained on the fibres [12].

However, tapioca starch forms faster aggregates and larger PCC aggregate size than potato starch-1 with similar DS and cationicity. This shows that potato starch-1 is consumed in neutralizing some of the anionic trash and does not selectively adsorb onto the PCC particles. The aggregation rate is also lower compared to tapioca starch because some of the potato starch-1 is consumed by the DCS. Potato starch-2 does not perform well in PW as it is consumed by the DCS to form smaller aggregates. The maximum



Figure 2.13: Adsorption of different starches on to PCC (0.25% concentration) at 50°C in PW.

size is already reached at 24 mg/g of PCC and further increase in the starch dosage decreases the aggregate size and aggregation rate. This shows that at higher dosage of

potato starch-2 it prefers to neutralize the anionic trash present in PW compared to adsorption onto PCC. So, potato starch-2 just acts like an anionic trash collector. However, if we compare the performance in PW and DDW it shows that the aggregation rates are lower for all the starches in PW because of the presence of DCS and other particles as shown in figure 2.1. Hence, some of the starch is consumed by these entities present in PW.





(b) Zeta Potential

Figure 2.14: Comparison of cationic demand and zeta potential of PCC aggregates in PW at 50°C for various starches at different dosages.

Figure 2.14a shows the cationic demand of the PCC aggregates in process water at 50 °C. The pH at the point of measurement is same as that shown in figure 2.12a. The first point shows the cationic demand of PW. The second point shows the cationic demand when we suspend PCC in PW. The cationic demand increases. It can be seen that tapioca starch has a very little effect on cationic demand of the PCC aggregates. This shows that its interaction with the anionic trash is low and it is not deactivated in the presence of anionic trash. However, the potato starches reduce the cationic demand considerably showing that they are consumed by the anionic trash present in the PW. Potato starch-2 reduces cationic demand more compared to the other two starches.

Figure 2.14b shows the effect of the starches on the zeta potential of the aggregates. Potato starch-2 has a smaller effect on zeta potential compared to the other two starches. In fact at a dosage of 40 mg/g of PCC it shows an increase in the zeta potential as it prefers the anionic trash compared to PCC. So potato starch-2 acts just like an anionic trash collector. Potato starch-1 which has a higher DS and cationicity compared to potato starch-2 affects zeta potential to a certain extent. This shows that it is neutralized by the anionic trash present in the PW thereby allowing very little starch to interact with PCC. However, in case of tapioca starch we can see that the zeta potential is driven close to the iso-electric point as we increase its dosage. This is due to the selective interaction of tapioca starch and PCC. It might also be possible that the DCS and PCC are aggregated together. We have also seen that tapioca starch does not reduce cationic demand. This shows that tapioca starch is not deactivated in the presence of anionic trash and interacts more with PCC thereby driving the zeta potential towards the iso-electric point.

We have also measured turbidity for the supernatants obtained after centrifuge. Figure 2.15 shows the turbidity of the supernatants of PCC aggregates in PW for different starches. It can be seen that potato starch-1 decreases the turbidity higher than tapioca starch. This shows that it interacts with DCS and forms more complex aggregates with DCS compared to tapioca starch. In case of potato starch-2 the decrease in turbidity shows that it is not capable of forming aggregates even with DCS to decrease the turbidity. It is just neutralized by DCS.



Figure 2.15: Change in turbidity (%) of centrifuge supernatant of PCC in PW for different starches.



particles at different dosages of PAC in DDW at 25°C.

It is well known that polyaluminum chloride (PAC) is used as an anionic trash collector. For comparison purposes PAC received from Raisio Chemicals with a basicity of 30% was used in aggregation experiment with PCC in DDW at 25°C.

Figure 2.16a and 2.16b compares the maximum PCC aggregate size formed and maximum aggregation rate reached in the presence of PAC. The values on the figure 2.16a indicate the pH at which the experiments were carried out. PAC aggregates PCC in DDW at 25°C. However, when we add PAC to PW at 50°C which is suspended with PCC it does not form any aggregates. This shows that PAC has a higher affinity for anionic trash compared to PCC. This justifies the use of PAC as an anionic trash collector. It is interesting to note that PAC had no significant influence on fines and PCC retention when the dual poly ethylene oxide (PEO)/Phenol formaldehyde Resin (PFR) system was used with a TMP suspension [17].

2.4 CONCLUSIONS

The study of colloidal behavior of PCC in the presence of dissolved and colloidal materials showed that the zeta potential of PCC becomes more negative and the cationic demand increases with time over a 32 h period. The implication of this is that the unretained PCC in process waters may add to the negative charge of the papermaking stock and a higher amount of cationic retention polymers will be required.

The study of aggregation of PCC particles in DDW at 25°C and 50°C and in PW at 50°C with different types of starches shows that tapioca starch is not deactivated or neutralized in the presence of anionic trash. This is supported by the observations that the cationic demand is not affected whereas the zeta potential of the PCC aggregates tends towards the iso-electric point. Consequently, tapioca starch is suitable for paper strength development for mechanical paper grades. However, potato starches are neutralized in the presence of anionic trash. The lower DS potato starch just acts like an anionic trash collector. Finally, polyaluminum chloride was found to be able to aggregate PCC

particles in distilled deionized water (DDW) at 25°C. However, in process water (PW) at 50°C PAC was consumed in neutralizing the anionic trash. This confirms the use of PAC as an anionic trash collector.

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CHAPTER-3

EFFECT OF STARCHES ON TMP FIBRES LOADED WITH PCC¹

3.1 INTRODUCTION

In an attempt to reduce the cost of papermaking it is now become compulsory for papermakers to use only mechanical pulps and eliminate kraft pulp for producing high value added communication papers. Mechanical pulps are produced in a process where mechanical energy and heat energy are used to liberate the fibres from the wood. In this type of pulping process all the wood components end up in the pulp suspension. Of this, less than 10% by weight is dissolved and colloidal substances (DCS) which are detrimental to papermaking process. DCS mainly includes wide range of chemical species including hemicellouses, lipophilic extractives and lignin like compounds [1-4]. The dissolved substances comprise mainly hemicelluloses, pectins, lignans and lignin, whereas the colloidal substances are mainly lipophilic extractives [5]. The colloidal fraction has a size distribution ranging from 0.1-1.2 μ m [6]. Advancement in bleaching technology of mechanical pulps has resulted in producing higher brightness mechanical pulps. However, alkaline peroxide bleaching produces more DCS of which polygalacturonic acids are the major part [7].

During papermaking these DCS accumulate in process waters of the paper machine which cause runnability problems and deposits on paper machine parts reducing both efficiency and paper quality [8, 9]. Despite the relatively small fraction of the furnish they constitute a major obstacle when trying to apply cationic polymeric

¹ "A version of this paper is under review in the Journal of Pulp and Paper Science (2007). Modgi, S. B., Michael E. McQuaid, and Englezos, P., "Effect of Starches on TMP fibres Loaded with PCC."
performance chemicals during paper production [10]. To achieve lower costs and to impart specific properties to paper product, the use of inexpensive mineral fillers has become inevitable. The addition of fillers results in lower paper strength which is compensated by adding strength developing agent. Cationic starches are the most commonly used dry strength additive in papermaking. In addition to strength development starches also influence dewatering, retention and formation [11]. The higher demands for retention and dewatering for high speed paper machine makes the selection process of starch more difficult. A substantial amount of cationic starch is neutralized by the DCS in mechanical pulp suspensions [12, 13].

To develop paper strength it is necessary that the starch adsorbs onto the fibres. Therefore, the strategy in mechanical papermaking is to add an anionic trash collector (ATC) to neutralize or fix the DCS before adding starch in order to protect starch [12, 13]. A number of publications are available on the interaction of DCS and polyelectrolytes which are covered in the cited papers [14, 15]. Considerable work has been done on the adsorption of starch on chemical bleached pulps as cited in reference [13, 16, and 17]. These studies show that the adsorption of starch onto fibres is an ion exchange process. Fibre fines adsorb more starch compared to fibres due to high specific surface area. Also, the adsorption onto fibre fines depends on the species and morphology of fines [17]. For chemical pulps it is known that the higher the DS of starch lower is the adsorption on to fibres. In the absence of DCS the same holds true for TMP fibres. However, in the presence of DCS the higher the DS, of starch the greater the adsorption of cationic starch on to PCC in the presence of DCS [18]. Understanding the chemistry and

translating it to industrial practice is necessary for wet-end optimization. The necessity of zeta potential and cationic demand measurements to determine the function of an additive is well established [19].

In this work, we have compared the effect of two high DS starches namely potato and tapioca starch on TMP suspension loaded with PCC. It is an attempt to understand the electrostatic interactions between different starches in a high anionic trash environment by measuring cationic demand, zeta potential, conductivity, pH and retention and translate it to industrial practice.

3.2 EXPERIMENTAL

3.2.1 Experimental Materials

Thermo-Mechanical Pulp (TMP) was obtained from Catalyst Paper mill at 3.5-4% consistency and stored at 4°C without any preservatives. The water from this pulp was drained by centrifuging the pulp suspension in a laundry type centrifugal separator. The water obtained from this separator was used to dilute the TMP pulp to 1% consistency. The filler used in this work is a commercially available Precipitated Calcium Carbonate (PCC). The tapioca starch used in this work had a degree of substitution (DS) of 0.1 and had a higher cationicity and viscosity than potato starch. Potato starch had a DS of 0.1.

BTG-Mutek (Germany) SZP-06 zeta meter used to measure zeta potential and conductivity of pulp fibres. The cationic demand was measured using BTG-Mutek (Germany) particle charge detector PCD-03. The pH of the pulp suspension was measured using Metrohm pH meter (Fisher Scientific, US).

3.2.2 Experimental Methods

500 g of TMP pulp at 1% consistency and 50°C is taken in a 600 ml glass beaker. Then the additives under investigation are added and allowed to mix at the predetermined contact time at 600 rpm with a three blade stirrer. Immediately after the reaction time the pulp suspension is subjected to zeta potential, conductivity, cationic demand and pH measurement simultaneously. Each trial is repeated three times and the average along with standard deviation is reported.

Figure 3.1 shows the sequence used to study the effect of starches on zeta potential, conductivity, cationic demand and pH of 1%TMP suspension.



Figure 3.1: Sequence of addition of starch to the TMP suspension.

Figure 3.2 shows the sequence used to study the effect of starches on zeta potential, conductivity, cationic demand and pH when PCC and starch are added separately to the 1% TMP suspension. PCC loading used is 25 wt. % on oven dried (OD) pulp.



Figure 3.2: Sequence of addition of PCC and starch separately to the TMP suspension.



Figure 3.3: Sequence of addition of PCC+starch mixture to the TMP suspesion.

Figure 3.3 shows the sequence of addition of starch to 1% TMP and PCC. The total starch dosage to TMP is fixed at 8 kg/t of OD pulp. Starch at varying amounts (0, 2, 4, 6 & 8 kg/t of OD pulp) is first mixed with PCC (25 wt. % loading) in a beaker and then

added to 1 % consistency TMP suspension. So for example, if the amount of starch added to PCC is 2 kg/t of OD pulp then 6 kg/t of OD pulp is added to the pulp suspension directly as shown in figure 3.3. Similarly, at zero addition of starch to PCC means that all the starch is added to the TMP suspension directly and no starch is added to PCC. Also when all the starch (8 kg/t of OD pulp) is added to PCC there is no starch which is added to the pulp suspension directly.

Retention experiments were performed using BTG DFR-04 (drainage, freeness, retention tester) which is equipped with automatic dosage unit. A 50 mesh (200 μ m hole) screen was used for measuring retention of fibres, fines/filler. At first a calibration was performed on TMP loaded with 25 wt. % PCC without any starch. Then, the fines/filler and total retention was determined for different dosages of starch as illustrated in figure 3.4. It is important to note that at all times the total amount of starch was fixed at 8 kg/t of OD pulp.



Figure 3.4: Sequence of addition of PCC and starch to determine total and fines/filler retention for different dosages of starch.

3.3 **RESULTS AND DISCUSSION**

3.3.1 TMP and Starch Interactions

Figures 3.5a and 3.5b show how cationic demand and zeta potential of 1% TMP suspension change with the addition of tapioca and potato starch respectively. The sequence of addition was illustrated in figure 3.1. It is known that the change in zeta potential reflects that starch adsorbs on the fibres and reduction in cationic demand means the neutralization of DCS by starch [20]. From figure 3.5a, increasing tapioca starch dosage from 8 kg/t of OD pulp to 10 kg/t of OD pulp is accompanied by a slower rate of zeta potential change whereas the rate of cationic demand reduction increases. This shows that above the dosage of 8 kg/t of OD pulp neutralization of tapioca starch begins to be the dominant process compared to adsorption on the fibres. Similarly, from figure 3.5b we can see that above potato starch dosage of 6 kg/t of OD pulp we see no significant reduction in zeta potential of the pulp suspension, instead there is a decrease in the cationic demand. This means that when using potato starch as a strength developing agent adding more than 6 kg/t of OD pulp is not beneficial.



Figure 3.5: Effect of starch dosages on cationic demand and zeta potential of TMP.

Since in laboratory we use stored pulps, the starting point (cationic demand and zeta potential) for the pulps is different for different experiments. Even though for both tapioca and potato we use the same batch of pulp and process water the starting points are different because of the different timing of the experiment. To facilitate comparison we would like to define a term known as "reduction (%)". This reduction (%) is defined by equation 3.1.



Figure 3.6: Comparison of the effects of different starch dosages on cationic demand and zeta potential of TMP.

The term value in our case is zeta potential and cationic demand. Figures 3.5a and 3.5b can now be compared using the term reduction % as shown in figures 3.6a and 3.6b. It can be seen that the rate of reduction in zeta potential increases considerably after 6 kg/t of tapioca starch dosage and remains practically unchanged for potato starch. Also, it can be seen that the reduction in cationic demand is higher with tapioca starch at all dosages compared to potato starch at the same dosages. Thus, even though tapioca starch

shows an increased affinity for fibres beyond 6 kg/t, it also shows a significant ability to neutralize DCS.

Figures 3.7a and 3.7b show the change in conductivity of the TMP pulp suspension at different dosages of tapioca and potato starch respectively. The trend for both the starches is identical with potato starch showing a steep decrease at lower dosages. The numerical values on the graph indicate the pH at which the measurements were made. Conductivity mainly comes from the TMP pulp fibres, DCS and PCC. However, the bulk of the conductivity comes from TMP fibres and DCS. As we increase tapioca starch dosage to pulp fibres the conductivity does not change much as the adsorption of tapioca starch on to fibres is low at low dosages of tapioca starch. However, at tapioca starch dosage of 8 kg/t of OD pulp the adsorption is higher and therefore the conductivity decreases substantially. In case of potato starch even at low dosages the adsorption of potato starch to pulp fibres is significant and therefore conductivity decreases.



Figure 3.7: Effect of different starch dosages on conductivity of TMP.

3.3.2 TMP, PCC and Starch Interactions

In the next sequence (shown in fig 3.2) we introduce PCC in the mechanical pulp suspension. PCC loading is fixed at 25 wt. % for all the experiments.

Figures 3.8a and 3.8b show the change in cationic demand and zeta potential with increase in tapioca and potato starch dosages respectively. As seen in figure 3.8a it is evident that beyond tapioca starch dosage of 6-8 kg/t the reduction in zeta potential is not as strong as the reduction in cationic demand values. This suggests that beyond tapioca starch dosage of 6-8 kg/t tapioca starch interacts much stronger with DCS (shown as decrease in cationic demand) rather than fibres (shown as less negative zeta potential). Hence, there is no incentive to add more than 8 kg/t of tapioca starch as dry strength agent. Figure 3.8b suggests that the optimum dosage for potato starch is again 6-8 kg/t. It was also seen that increasing potato starch dosage to 16 kg/t has very less impact on cationic demand and zeta potential. For a better comparison of the two starches it is better to observe the % reduction shown in figures 3.9a and 3.9b.



(a) Tapioca Starch (b) Potato starch

Figure 3.8: Effect of Tapioca and Potato starch dosages on cationic demand and zeta potential of TMP loaded with PCC.

Figures 3.9a and 3.9b compare the reduction in cationic demand and zeta potential as we increase tapioca and potato starch dosages respectively. From figure 3.9a we can see that increasing tapioca starch dosage linearly increases reduction % of zeta potential from 10% at 2 kg/t to 26% at 6 kg/t. But with potato starch (figure 3.9b) the reduction of zeta potential increases from 20% at 2 kg/t to 22% at 8 kg/t.. Also at a potato starch dosage of 16 kg/t of OD pulp the reduction % is similar to that of tapioca starch dosage at 10 kg/t of OD pulp. It is important to note that in the presence of PCC the reduction in zeta potential is greater with tapioca starch at dosages up to 6 kg/t (fig 3.9a) compared to the case without PCC (fig 3.6a). The reduction in cationic demand with potato starch at dosages 2-6 kg/t of OD pulp ranges from 16-22% whereas with tapioca starch it increases from 6-14%. These data suggest that tapioca starch is not only a suitable dry strength agent but it also interacts strongly with PCC and it is expected that the retention will also be enhanced. The affinity of tapioca starch to adsorb on to PCC is shown and discussed in chapter 3. Tapioca starch has a higher margin for adsorption on to the TMP fibres compared to potato starch. It is noted that increasing starch dosage beyond 8 kg/t is not economical for papermaking. In this given range (up to 8 kg/t) tapioca starch reduces zeta potential and cationic demand more than potato starch. The conductivity measurements from this sequence were inconclusive.



Figure 3.9: Comparison of different starch dosages on cationic demand and zeta potential of TMP loaded with PCC.

In the next investigation sequence (shown in fig 3.3) we fix the total starch dosage to 8 kg/t of OD pulp as determined from our previous results (figures 3.6 and 3.9). In this investigation we mix PCC with starch at different dosages. Figures 3.10a and 3.10b show the reduction in cationic demand and zeta potential when different dosages of tapioca and potato starch is added to PCC. The X-axis in figure 3.10 shows the amount of starch added to PCC. So for example when a starch dosage of 2 kg/t of OD pulp is added to PCC then the remaining 6 kg/t of OD pulp is added to the TMP suspension.



(a) Tapioca Starch (b) Potato starch

Figure 3.10: Effect of starch dosages on cationic demand and zeta potential of TMP.

In Figure 3.10a, the point TMP shows the cationic demand and zeta potential of the 1% consistency TMP pulp. The point TMP+PCC+starch shows the change in zeta potential and cationic demand when we add 25 wt. % PCC in TMP pulp suspension and then after one minute add tapioca starch at a dosage of 8 kg/t of OD pulp. As we increase the dosage of tapioca starch to PCC which in turn decreases the dosage of starch to TMP we can see that the zeta potential of the pulp suspension becomes more negative. This confirms the findings in figure 3.6a which show that the reduction in zeta potential with tapioca starch is lower at lower dosages of starch. From figures 3.9a and 3.10a we can say that for better performance of tapioca starch as strength development agent we need to add more tapioca starch to the fibres and very less to PCC. Stated another way tapioca starch addition to PCC flocculates PCC to perform the role of retention aid while when added to TMP suspension acts as a dry strength chemical. It is important to note that once starch adsorbs on to the papermaking component remains fixed on that component [21].

From figures 3.10b and figure 3.11b we can see that there is not much change in the reduction of zeta potential and cationic demand as we increase the dosage of potato starch to PCC and reduce starch to TMP. This means that there is a fixed amount of potato starch (6 kg/t of OD pulp) that adsorbs onto fibres and it does not change with increase in potato starch dosage.





(b) Potato starch



As seen from the data above potato starch addition point is not playing any role. Potato starch does not show any preference to act as retention aid or a dry strength chemical.

3.3.3 First Pass Retention with TMP, PCC and Starch

Figure 3.12 shows the first pass retention results obtained with tapioca and potato starch. Figure 3.12a gives the total retention and figure 3.12b gives the fines/filler

retention. The point zero on the X-axis of the graphs shows that PCC and starch are added separately and the starch dosage is 8 kg/t of OD pulp. From figure 3.12a we can see that both the starches perform similarly, with tapioca starch giving slightly higher total retention than potato starch. From figure 3.12b increasing tapioca starch dosage to PCC decreases fines/filler retention. This shows that less tapioca starch is to be added to PCC and more to TMP. Increasing potato starch dosage to PCC increases fines/filler retention compared to potato starch. From figure 3.11a it can be seen that at 2 kg/t of tapioca starch dosage the reduction in zeta potential is higher compared to that with potato starch. However, at a dosage of 6 kg/t to



Figure 3.12: Comparison of total and fines/filler retention with tapioca and potato starch.

PCC, the fines/filler retention is higher for potato starch compared to tapioca starch. This particular dosage of potato starch (6 kg/t) gave the highest reduction in zeta potential (fig 3.11b). This shows that there is an optimum amount of tapioca starch (2 kg/t) that is to be added to PCC first and than (6 kg/t) to TMP suspension to give a higher fines/filler

retention. In case of potato starch the highest fines/filler retention is obtained at 6 kg/t to PCC first followed by 2 kg/t to TMP suspension.

Both tapioca and potato starches come from the same source or in other words both are root starches. Still they have differences in their granule size, shape, moisture content, amylose, amylopectin and ash content. The ash content refers to the inorganic materials present in the starch. Potato starch has higher ash content than tapioca starch.

The main inorganic material in potato starch is phosphorous which is present in the form of phosphate groups and gives an anionic charge to the potato starch. This anionic charge may be one of the reasons why potato starch is not as effective in high anionic trash environment. Comparatively tapioca starch has less inorganic content which means less anionic groups on the molecule which means it gives more positive sites to the starch molecule which helps in high anionic trash environments. This work shows that amphoteric starches may not be the answer for high anionic trash environment if proper starch with a higher DS is selected. However, these are just hypotheses and no definite answer is available at this moment.

3.4 CONCLUSIONS

The effect of adding tapioca starch and potato starch on peroxide bleached TMP suspension loaded with PCC was studied through zeta potential and cationic demand measurements complemented by the determination of first pass retention. The results showed that tapioca starch adsorbs more onto TMP fibres and is not deactivated in the presence of dissolved and colloidal substances (DCS). This means there is no need of an anionic trash collector (ATC) when using tapioca starch. In case of potato starch there is

a necessity to use an ATC because potato starch is deactivated more compared to tapioca in the presence of DCS.

First pass retention experiments showed that tapioca starch gives a higher fines/filler retention compared to potato starch for all dosages except that at 6 kg/t of potato starch to PCC. For high anionic trash environment high degree of substitution (DS) tapioca starch is a better strength developing agent and retention aid compared to high DS potato starch. It is not necessary that only DS is the factor in choosing a particular starch for a particular papermaking system and that the type and source is also important.

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CHAPTER-4

EFFECT OF COAGULANT AND FLOCCULANT ON TMP FIBRES LOADED WITH PCC¹

4.1 INTRODUCTION

Papermaking has evolved with time using high speed paper machines putting greater pressure on additives like retention aids [1]. Faster machines mean greater shear and less time for drainage. There are a number of additives that are commercially available in the market which are added to the papermaking slurry to influence the interactions between the fibres, fibre fines and other components of the papermaking furnish [2]. Mechanical papermaking poses additional challenges for papermakers due to the presence of dissolved and colloidal substances (DCS) which originate during the pulping process. DCS mainly includes wide range of chemical species including hemicellouses, lipophilic extractives and lignin like compounds [3-6]. The presence of DCS interferes with the papermaking process by degrading paper machine runnability and consumes cationic retention aids [7-11]. With increasing closure of the water system the accumulation of DCS in the papermaking system increases. These DCS consume cationic additives that are added to the papermaking furnish like starch. So it is important to fix these DCS with a polyelectrolyte. There a number of research papers that describes various models for the adsorption of polyelectrolyte onto the cellulose fibres are cited in the paper [12].

¹ "A version of this chapter will be submitted for publication:Modgi, S. B., McQuaid, M.E., and Englezos, P., "Effect of Coagulant and Flocculant on TMP Fibres Loaded with PCC."

It has also become necessary to add mineral fillers like precipitated calcium carbonate (PCC) to produce mechanical grade papers not only to reduce the cost of production but also to improve paper properties. However, adding PCC reduces the strength of paper [13]. To compensate for strength loss it is important to add strength additives like starch [14]. However, the DCS in mechanical pulp systems neutralize the cationic starch by forming polyelectrolyte complexes which hinders the adsorption of starch onto the fibres/fibre fines [14]. Therefore, while using cationic starch in mechanical papermaking it is customary to use anionic trash collectors or coagulants to fix the DCS before adding starch to the pulp suspension [15].

A number of retention aid systems and additives are used in mechanical papermaking. The most commonly used retention aids are polyethylene oxide (PEO) [16-18], charged and non-ionic polyacrylamide (PAM) [19], highly charged low molecular weight polymers like poly diallyldimethy ammonium chloride (DADMAC), polyethyleneimine (PEI), cationic starch, poly aluminum chloride (PAC) and polyamines. All these retention aids are mostly used in combination with each other [20]. However, the use of microparticle retention systems using bentonite and silica is increasing in mechanical papermaking due to the need for faster drainage. A number of retention aids used in newsprint manufacture with different levels of system closure is compared. It was found that a PEO-cofactor gives the highest retention with increasing system closure. Also, the increase in DCS concentration was found to decrease the effect of CPAM. [20]. It was also found that as the amount of DCS increases the drainage rate with CPAM decreases [20].

A low molecular weight and high charge density poly DADMAC is widely used as a coagulant to fix the anionic trash mechanical papermaking. This basically helps in neutralizing the DCS that will further help the flocculants like CPAM to aggregate the fibres leading to an increase in retention [21]. However, it was shown that with increasing dosage of poly DADMAC in the presence of CPAM decreases drainage rate considerably [20]. Drainage rate is believed to be affected by the particle size distribution of the papermaking aqueous slurry [22-25]. Papermaking slurries with low fines fraction will have a rapid drainage rate since resistance to fluid flow is low due to the poor packing of large particles yielding an open structure of the sheet [20]. Addition of CPAM improves aggregation of particles by bridging mechanism resulting in more open sheet and a faster drainage rate [21].

In this work we have evaluated the use of poly DADMAC and PAC as an anionic trash collector in the presence of two types of starch: tapioca and potato starch in a thermo-mechanical pulp (TMP) suspension loaded with PCC. After selecting the best starch and ATC for TMP suspension the effect of poly DADMAC and CPAM on retention is determined both individually as well as in combination in the presence of tapioca starch. Further, the impact of tapioca starch, poly DADMAC and CPAM on drainage rate of TMP suspension loaded with PCC is determined.

4.2 EXPERIMENTAL

4.2.1 Experimental Materials

Thermo-Mechanical Pulp (TMP) was obtained from Catalyst Paper mill at 3.5-4% consistency and stored at 4°C without any preservatives. The water from this pulp was

drained by centrifuging the pulp suspension in a laundry type centrifugal separator. The water obtained from this separator was used to dilute the TMP pulp to 1% consistency. The filler used in this work is a commercially available Precipitated Calcium Carbonate (PCC). The tapioca starch used in this work had a degree of substitution (DS) of 0.1 and had a higher cationicity and viscosity than potato starch. Potato starch had a DS of 0.1. A commercially available poly aluminum chloride (PAC) and poly DADMAC were used in this work.

BTG-Mutek (Germany) SZP-06 zeta meter used to measure zeta potential and conductivity of pulp fibres. The cationic demand was measured using BTG-Mutek (Germany) particle charge detector PCD-03. The pH of the pulp suspension was measured using Metrohm pH meter (Fisher Scientific, US). For measuring retention, BTG DFR-04 (Germany) is used.

4.2.2 Experimental Methods

4.2.2.1 Determination of Cationic Demand, Zeta Potential, Conductivity and pH

500 g of TMP pulp at 1% consistency and 50°C is taken in a 600ml glass beaker. Then the additives under investigation are added and allowed to mix at the predetermined contact time at 600 rpm with a three blade stirrer. Immediately after the reaction time the pulp suspension is subjected to zeta potential, conductivity, cationic demand and pH measurement simultaneously. Each trial is repeated three times and the average along with standard deviation is reported.



Figure 4.1: Sequence of addition of PCC + Starch mixture in the presence of PAC.



Figure 4.2: Sequence of addition of PCC + Starch mixture in the presence of

Poly DADMAC.

Figures 4.1 and 4.2 shows the sequence of addition of anionic trash collectors (ATC) PAC and poly DADMAC respectively. PAC was fixed at 1 kg/t of OD pulp and poly DADMAC was fixed at 0.4 kg/t of OD pulp. The dosages were fixed based on common industrial practices. In this sequence the total starch dosage to TMP is fixed at

8 kg/t of OD pulp. At first TMP is treated with ATC and then we add the mixture of PCC+starch at varying starch dosages. Then the remaining starch is added and allowed to mix for one minute before measuring the cationic demand, zeta potential, conductivity, and pH.

4.2.2.2 Determination of Total and Fines/Filler Retention with poly DADMAC and Tapioca Starch

Retention experiments were performed using BTG DFR-04 (drainage, freeness, retention tester) which is equipped with automatic dosage unit. A 50 mesh (200 μ m hole) screen was used for measuring retention of fibres, fines/filler. At first a calibration was performed on TMP loaded with 25 wt. % PCC without any starch. Then the fines/filler and total retention was determined for a fixed tapioca starch dosages of 8 kg/t of OD pulp where 2 kg/t was added to PCC and 6 kg/t was added to TMP suspension.



Figure 4.3: Sequence of addition of poly DADMAC, PCC and Tapioca Starch to

determine total and fines/filler retention.

Figure 4.3 shows the sequence of addition of poly DADMAC, PCC and tapioca starch to determine total and fines/filler retention for different dosages of poly DADMAC. At first poly DADMAC is added to the 1000 g of 1% TMP suspension and allowed to mix for 30 seconds in the DFR-04 at 400 rpm. Then PCC at 25% loading on OD pulp is mixed with tapioca starch (2 kg/t) and added to the DFR-04 container and allowed to mix for one minute. Then tapioca starch at 6 kg/t is added to the TMP suspension and allowed to mix for another minute at 800 rpm stirrer speed. Finally after mixing for another 10 seconds the contents are drained through a 50 mesh screen and total and fines/filler retention are recorded. It is important to note that the experiments are conducted at a temperature of 50 C which is the papermaking temperature at the paper machine.

4.2.2.3 Determination of Total and Fines/Filler Retention with CPAM and Tapioca Starch

The retention sequence with CPAM is shown in figure 4.4. This is similar to the retention procedure with poly DADMAC but the only difference is the addition of CPAM after adding 6 kg/t of tapioca starch and then mixing for 10 seconds before determining retention. It is important to note that there is no poly DADMAC used in this experimental sequence.





4.2.2.4 Determination of Total and Fines/Filler Retention with Poly DADMAC, CPAM and Tapioca Starch

Figure 4.5 shows the sequence used for the 3^2 factorial design of experiment with poly DADMAC and CPAM as the two factors in the presence of tapioca starch. The procedure is similar to that explained above in sections 4.2.2.1 and 4.2.2.2.



Figure 4.5: Sequence of addition of poly DADMAC, PCC, Starch and CPAM to

determine total and fines/filler retention.

Table 4.1: 3² factorial design matrix for retention studies with coagulant and flocculant

Factors	Dosages (kg/t on OD pulp)		
	Low	Medium	High
Poly DADMAC	0.8	1.4	2.0
CPAM	0.4	0.7	1.0

Table 4.1 shows the 3^2 factorial design matrix for retention studies with poly DADMAC and CPAM in the presence of tapioca starch. The sequence of addition of the chemicals is shown in figure 4.5. In this case starch (2kg/t) is added to PCC and the remaining 6kg/t is added to the pulp suspension directly. All the experiments in table 4.1 are repeated three times and the average is reported with the standard deviation in the results.

4.2.2.5 Drainage of TMP Suspension with poly DADMAC and CPAM in the presence of Tapioca Starch

Drainage of 1% TMP suspension loaded with 25% PCC was determined using the BTG DFR-04 tester using a 50 mesh screen for dosages of poly DADMAC and CPAM at which maximum retention was obtained. The screen used is same as that used for retention experiments. At first the drainage of the TMP suspension without any additives was determined. Then the drainage with a mixture of 25% PCC loading and tapioca starch at 2 kg/t followed by addition of tapioca starch at 6 kg/t was determined. The effect of poly DADMAC in the presence of tapioca starch on drainage time was determined. The sequence is same as that used for retention experiments (figure 4.3). The effect of CPAM on drainage of TMP suspension loaded with PCC was determined according to the sequence shown in figure 4.4. Finally, the drainage for the combined effect of poly DADMAC and CPAM in the presence of tapioca starch was determined as shown in figure 4.5.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of ATC, PCC and starch on Cationic Demand and Zeta potential of TMP Suspension

In TMP suspensions it is customary to use an ATC to neutralize the DCS and to protect starch. In this investigation we have evaluated the performance of two commercially used ATC: PAC and poly DADMAC on the effect of tapioca and potato



(a) Tapioca Starch

(b) Potato starch



starch on zeta potential and cationic demand of TMP loaded with 25 wt. % PCC. The sequence of addition is illustrated in figures 4.1 and 4.2. Cationic demand, zeta potential conductivity and pH are measured simultaneously. For this work the combined starch dosage to TMP and PCC was fixed to 8 kg/t, PAC dosage was fixed at 1 kg/t of OD pulp and poly DADMAC dosage of 0.4 kg/t of OD pulp based on industrial practices. Also the X-axis in figures 4.6a and 4.6b indicates the amount of starch added to PCC.

Figure 4.6 compares the change in cationic demand of TMP suspension with only starch (No ATC), and with PAC and poly DADMAC in the presence of starch. Figure 4.6a shows the reduction of cationic demand with tapioca starch and figure 4.6b shows the reduction with potato starch. The point zeros on the X-axis of figures 4.6a and 4.6b show the conditions when ATC is added first followed by PCC to the TMP and then finally starch at a dosage of 8 kg/t. It is important to note that at point zero starch is not mixed with PCC.

From figure 4.6a point zero on the X-axis shows that with tapioca starch alone we can obtain a greater reduction in cationic demand without the requirement of an ATC. Also, as we increase the addition of tapioca starch to PCC which in other words means decreasing tapioca starch to TMP, we can see that poly DADMAC slightly improves the reduction in cationic demand. However, PAC affects negatively on the cationic demand reduction with tapioca starch. So it is advisable not to use PAC when using tapioca starch. From figure 4.6b, in case of potato starch we can see that at point zero on the X-axis the highest reduction in cationic demand is obtained when PAC is used. However, in the presence of poly DADMAC potato starch does not reduce cationic demand. So when using potato starch it is not advisable to use poly DADMAC. PAC helps potato starch in decreasing the cationic demand. Also, comparing figures 4.6a and 4.b we can clearly see that potato starch has a greater effect in reducing cationic demand compared to tapioca starch. So potato starch has a higher affinity for DCS.

Similarly, figure 4.7 compares the change in zeta potential of TMP suspension with only starch (No ATC), and with PAC and poly DADMAC in the presence of starch. Figure 4.7a shows the reduction with tapioca starch and figure 4.7b shows the reduction with potato starch.



(a) Tapioca Starch (b) Potato starch

Figure 4.7: Comparison of the effect of PAC and Poly DADMAC in conjunction with starch dosages on zeta potential of TMP.

In figure 4.7a point zero on the X-axis shows that the reduction in zeta potential is higher when there is no ATC added and PCC and tapioca starch (8 kg/t) are added separately. This shows that tapioca starch does not require an ATC. However, as we increase the addition of tapioca starch to PCC we can see that greater reduction in zeta potential is obtained with poly DADMAC over the entire range. Also, when we add tapioca starch to PCC above a dosage of 2 kg/t of OD pulp we will require an ATC to help in reduction of zeta potential. At a tapioca starch dosage of 2 kg/t to PCC (which means 6 kg/t to TMP) we see a higher reduction in zeta potential than poly DADMAC. In case of potato starch as seen in figure 4.7b we see a greater reduction in zeta potential with PAC compared to that with poly DADMAC. Also, beyond a potato starch dosage of 4 kg/t of OD pulp to TMP and PCC the reduction %in zeta potential decreases with both poly DADMAC and PAC. This shows that there is a limitation for the amount of potato

starch that can be adsorbed on to the TMP with potato starch. It also shows that in the absence of an ATC, potato starch does not reduce zeta potential. So when using potato starch it is necessary to use an ATC to get better adsorption on the fibres as reduction in zeta potential is related to the adsorption on to the fibres.



Figure 4.8: Effect of PAC on conductivity of TMP loaded with PCC in the presence of starch (Numerical values on the graph indicate pH).

Figure 4.8 shows the change in conductivity of the TMP suspension at different starch dosages to PCC in the presence of PAC. The numbers beside the data points in the figures shows the pH at the time of measurement. In figure 4.8 the point zero on the X-axis indicates the conductivity of the TMP suspension without any chemicals. The point 1 on the X-axis shows the conductivity when PAC is added first followed by PCC and then finally starch at 8 kg/t. Comparing figures 4.8a and 4.8b we can see that with tapioca starch the conductivity is higher when all (8 kg/t) tapioca starch is added to TMP. As we increase the addition of tapioca starch to PCC the conductivity increases. However, it slightly decreases when all the tapioca starch (8 kg/t) is added to PCC. In

case of potato starch we get a lower conductivity when all the potato starch is added to TMP suspension. But as we increase the addition of potato starch to PCC (decrease starch to TMP) we see that the conductivity increases. As seen earlier, potato starch in the presence of PAC reduces cationic demand and zeta potential considerably.



Figure 4.9: Effect of Poly DADMAC on conductivity of TMP loaded with PCC in the presence of starch (Numerical values on the graph indicate pH).

Similarly, figure 4.9 shows the change in conductivity of the TMP suspension at different starch dosages to PCC in the presence of poly DADMAC. In case of tapioca starch (figure 4.9a), we see that increasing tapioca starch to PCC increases conductivity. But tapioca starch gives greater reduction in cationic demand and zeta potential with poly DADMAC. In case of potato starch (figure 4.9b) we see that increasing potato starch to PCC increases conductivity, but when all potato starch is added to PCC (8 kg/t) we see that conductivity decreases. As seen earlier, tapioca starch decreases cationic demand and zeta potential and zeta potential with the potential considerably in the presence of poly DADMAC.

4.3.2 Effect of Poly DADMAC and Tapioca Starch on Total and Fines/Filler



Retention in TMP Suspensions

Figure 4.10: Effect of poly DADMAC only on the total and fines/filler retention in the presence of tapioca starch.

Figure 4.10 shows the effect of poly DADMAC on total and fines/filler retention of TMP suspension loaded with PCC in the presence of tapioca starch. The sequence of addition of the chemicals is shown in figure 4.5. The point zero on the X-axis shows the retention with tapioca starch only where 2 kg/t is added to PCC and 6 kg/t is added to TMP suspension. Adding poly DADMAC does not help in increasing retention but in facts decreases total and fines/filler retention. Similar results were observed previously but in the absence of tapioca starch [21]. This shows that even in the presence of tapioca starch poly DADMAC does not help in retention. It is also seen that increasing poly DADMAC dosage does not change both total and fines/filler retention. However, it was found that tapioca starch in the presence of poly DADMAC reduces both cationic demand and zeta potential considerably.



4.3.3 Effect of Tapioca starch and CPAM on Total and Fines/Filler Retention in

TMP Suspensions

Figure 4.11: Effect of CPAM on the total and fines/filler retention in the presence of tapioca starch.

Figure 4.11 shows the effect of CPAM on total and fines/filler retention of TMP suspension loaded with PCC in the presence of tapioca starch. The sequence of addition of the chemicals is shown in figure 4.5. The point zero on the X-axis shows the retention with tapioca starch only where 2 kg/t is added to PCC and 6 kg/t is added to TMP suspension. Adding CPAM at a dosage of 0.4 kg/t increases fines/filler retention by 4%.
Similar results were obtained with CPAM where higher dosages of CPAM decreased retention [21]. However, there is not much change in the total retention. Increasing the dosage of CPAM further to 0.7 kg/t we see a decrease in fines/filler retention and a slight increase in total retention. Even at a dosage of 1 kg/t the fines/filler retention is lower than that obtained at 0.4 kg/t. Therefore, when using tapioca starch in conjunction with CPAM in TMP suspension it is important to add very less (0.4 kg/t) amount of CPAM as a flocculant.

4.3.4 Effect of Poly DADMAC, Tapioca starch and CPAM on Total and Fines/Filler Retention in TMP Suspensions

A 3^2 factorial design of experiments on the first pass total and fines/filler retention was performed using poly DADMAC) and CPAM in the presence of tapioca starch as shown in figure 4.6. Poly DADMAC dosage was fixed at low level 0.8 kg/t, medium level 1.4 kg/t and high level 2.0 kg/t on OD pulp; whereas the CPAM dosage was fixed at low level 0.4 kg/, medium level 0.7 kg/ and high level 1.0 kg/on OD pulp. Tapioca starch dosage was fixed at 8 kg/t where 2 kg/t is mixed with PCC and the remaining 6 kg/t is added to TMP directly. These dosage ranges are typically encountered in the paper industry.

Figure 4.12 shows the total and fines/filler retention results obtained for the dual retention aid system in the presence of tapioca starch. The first number on the X-axis indicates the CPAM dosage and the second number indicates the poly DADMAC dosage. The point (0, 0) shows the retention results without any CPAM and Poly DADMAC but in the presence of starch (8 kg/t). The total retention is 72% and the fines/filler retention

is 52% in the presence of starch only. The highest retention results were obtained at a CPAM dosage of 1 kg/t and poly DADMAC dosage of 1.4 kg/t in the presence starch. However, we can only see an increase of 3% of fines/filler retention and 0.5% of total retention with the addition of the dual retention aids. Therefore, the requirement of a dual retention aid is not necessary in the presence of tapioca starch. As shown previously the presence of poly DADMAC does not help in retention even when used in combination of CPAM and cationic tapioca starch [21].



Figure 4.12: Effect of poly DADMAC and CPAM on the total and fines/filler retention

in the presence of tapioca starch.

The analysis of variance (ANOVA) using a 3^2 factorial design on total retention shows that the effect of poly DADMAC is insignificant. However, for CPAM the effect on total retention is significant. The presence of tapioca starch helps in flocculation of fibres when CPAM is added. However, with only poly DADMAC we will not see any increase in retention which confirms the results in figure 4.10. Also the interaction effects of poly DADMAC and CPAM are not significant on total retention in the presence of tapioca starch. So the presence of poly DADMAC does not influence total retention and it can be eliminated in the presence of tapioca starch and CPAM system.

Performing ANOVA for fines/filler retention we found that the presence of poly DADMAC is not significant on fines/filler retention in the presence of tapioca starch. But, the effect of CPAM is again found to be significant which confirms the results obtained in figure 4.11. The interaction of CPAM and poly DADMAC are significant in increasing fines/filler retention in the presence of tapioca starch. Experiments conducted in our lab with poly DADMAC and CPAM in the absence of starch showed that individually poly DADMAC and CPAM help in retention and so does their interaction [26]. However, in the presence of tapioca starch it is evident that there is no role for poly DADMAC in a CPAM and tapioca starch system.

4.3.5 Drainage Studies of TMP Suspensions with Poly DADMAC, CPAM, Tapioca Starch loaded with PCC

Drainage experiments are performed with 1% TMP suspension loaded with 25% PCC as described in section 4.2.2.5. Figure 4.13 shows the drainage results obtained without any additives, tapioca starch, poly DADMAC, CPAM and finally the combination of poly DADMAC and CPAM.



Figure 4.13: Drainage rate of TMP suspension without any additives, tapioca starch, poly DADMAC and CPAM.

Adding tapioca starch gives a faster drainage to that obtained without any additives. Total tapioca starch dosage was fixed at 8 kg/t of which 2 kg/t is added to PCC and the remaining 6 kg/t is added to the TMP suspension directly as described earlier. To determine the effect of poly DADMAC on drainage in the presence of starch, the best dosage that gave the highest retention with poly DADAMC was chosen. This dosage is 2 kg/t as obtained from figure 4.10. Addition of poly DADMAC at 2 kg/t to the TMP suspension in the presence of tapioca starch only slightly increases the drainage rate and the final volume of filtrate after 60s. However, it was shown previously that the increasing the dosage of poly DADMAC in the presence of CPAM decreased

retention [20]. CPAM dosage of 0.4 kg/t was selected to test the drainage of TMP suspension in the presence of tapioca starch as obtained from figure 4.11. CPAM increases drainage rate of TMP suspension to a greater extent when compared to poly DADMAC in the presence of tapioca starch. Finally, the best dosages for retention with a combination of poly DADMAC and CPAM was selected from figure 4.12. The combination of poly DADMAC and CPAM gives the highest retention at 1.4 kg/t and 1.0 kg/t, respectively. At these dosages the drainage of TMP suspension is faster as shown in figure 4.14.



Figure 4.14: Filtrate weight of TMP suspension after 60s with different additives (Dosages of additives are indicated below each bar).

Note: Drainage with poly DADMAC, CPAM, poly DADMAC+CPAM tapioca starch is always present at 8 kg/t of which 2 kg/t is added to PCC and 6 kg/t is added to TMP.

Comparing the filtrate volumes collected after 60s shows that the combination of poly DADMAC, CPAM and tapioca starch influences drainage. However, it was found that poly DADMAC alone in the presence of tapioca starch does not help in retention, but from figure 4.12 the combination of poly DADMAC and CPAM gives the highest drainage in the presence of starch. Individually the presence of poly DADMAC only slightly increases drainage rate. So the drainage rate with poly DADMAC and CPAM in the presence of starch might be due to the presence of increased dosage of CPAM only. It was previously shown that poly DADMAC and CPAM together does not help in increasing drainage but in fact decreases drainage rate [20]. So we can say that the addition of poly DADMAC is not necessary in a system containing CPAM and tapioca starch.

4.4 CONCLUSIONS

Evaluating the performance of ATC inorganic polymer PAC and organic polymer poly DADMAC it was found that tapioca starch works well with poly DADMAC and PAC works well with potato starch in reducing cationic demand and zeta potential of TMP suspension loaded with PCC. However, it is also found that tapioca starch does not require an ATC for reducing cationic demand and zeta potential whereas potato starch requires an ATC, preferably PAC to enhance its activity.

In presence of tapioca starch poly DADMAC does not help in increasing retention whereas a low amount of CPAM helps in increasing retention slightly. A 3^2 factorial design of retention experiments with a combination of poly DADMAC and CPAM in the presence of starch shows that poly DADMAC is not necessary when tapioca starch and

CPAM are used in conjunction as retention aid. Finally, drainage studies reveal that the combination of tapioca starch and CPAM gives a faster drainage of TMP suspension. It can be concluded from the results in a TMP suspension consisting of PCC, tapioca starch, and CPAM the presence of poly DADMAC does not help in retention as well as drainage. Tapioca starch does not require an ATC when used alone or in combination with CPAM.

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Chapter-5

SEM/EDX ANALYSIS: A TECHNIQUE FOR Z-DIRECTION MINERAL TOPOGRAPHY IN PAPER¹

5.1 INTRODUCTION

Paper is a complex network of fibres, voids and fillers. Due to this anisotropic nature of paper it is very difficult to characterize the structure of paper. The characteristics and the quality of various types of papers are dependent on the quality, quantity and distribution of fibres, fines and fillers in the sheet of paper [1]. For printing papers, the distribution of fillers in the sheet of paper dictates the print quality and runnability on the printing press. The z-direction of paper is defined as the thickness direction of paper. Various methods have been used in the past to characterize the z-direction distribution of fibres, fines and fillers. Beloit sheet splitter and adhesive tape method are the two commonly used physical methods [2, 3]. These methods can be easily used for boards or heavy weight papers which can be easily delaminated. However, due to the increasing use of low basis weight papers it is difficult to characterize the z-direction distribution with these physical methods. Therefore various imaging methods have emerged. Wavelength Dispersive Spectroscopy (WDS), X ray diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDX) and X-ray Synchrotron Radiation Microtomography are the image

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analysis techniques used to study 2D z-direction distribution of fibres, fines and fillers. These methods do not disturb the structure of the sheet.

WDS is used to identify the elements in the paper sample by using one wavelength at a time to obtain a graph of the sample radiation. This graph is then compared with the standards to identify the constituent elements. However, this technique is tedious and difficult to perform for lighter elements. For quantitative determinations, WDS takes more time but the results are quite accurate [4].

X-ray diffraction with some limitations is used in papermaking to identify the raw materials commonly used in the paper industry, namely cellulose fibres and minerals [5]. Samples of paper were subjected to X-ray diffraction and the intensities and areas of diffraction peaks for minerals and cellulose were measured. These data were used to develop linear regression equations to describe the relationship between the ash content and X ray diffraction measurements [6]. However, the difficulty in measuring the cellulose peak area makes it difficult to use this method.

An experimental laboratory set-up using XRF and absorption techniques was studied by Kuusi and Kumpulainen [1] for on line determination of z-direction filler distribution with the aid of mathematical models. Although the preliminary work gave reliable information concerning distribution around a certain nominal distribution, their work was inconclusive [1].

The use of SEM/EDX is more efficient than the XRD method because EDX permits rapid detection of non-crystalline pigments which cannot be determined by the XRD system [6]. The efficiency of using the SEM/EDX technique is also quoted in the study of binder migration in coated papers [7]. Voillot et al. used SEM/EDX along with

an image processing program to acquire X-ray counts from paper samples. Their analysis reported the results as X-ray counts and not the actual calcium concentration [8].

All the image analysis methods described above give a two dimensional (2D) analysis of the filler distribution in paper. To overcome the limitations of 2D analysis, Synchrotron Radiation Microtomography was used to visualize the samples. The structural parameters are extracted from the 3D data which then accounts for the different phases like air, fibre and fillers. With the use of mathematical algorithms it is then possible to evaluate the filler content, porosity and fibre content in the sheet [9]. Although this method looks promising, the cost of analysis may be a limiting factor for its use.

Tanaka et al. [10] studied the effect of retention levels on the z-direction distribution of clay in hand sheets using the adhesive tape method. They showed that with the increasing levels of retention, the z-direction clay distribution changed [10]. Studies carried out on a pilot paper machine to evaluate the relative significance of the main wet end parameters on the filler distribution in the z-direction of paper showed the retention chemical dosage distribution as the major parameter in controlling the z-direction distribution of filler [3]. However, with so many methods available there is no reliable method that is readily available for the papermakers to get an immediate analysis of the z-direction calcium distribution in paper. Physical methods not only destroy the structure of paper but are also tedious and time consuming. They are not reproducible. On the other hand other image analysis techniques are time consuming and expensive.

This chapter exploits the use of the SEM and EDX to provide a non-destructive method for the determination of the mineral content in the z-direction which will fill the

large gap left between the physical destructive methods and expensive image analysis techniques. With the advancement in detector technology (higher resolution and ability to detect lighter elements) combined with robust software it is possible to obtain the concentration of mineral elements in the z direction of the sheet. SEM/EDX technique for determining z-direction mineral distribution is demonstrated with seven industrial paper samples to illustrate how one can study different paper machine operating parameters e.g. the influence of the type of starch on the z-direction mineral distribution in paper and correlate the observed measurements with the actual ash content of the paper. This technique is further demonstrated on hand sheets prepared with bleached Thermo-Mechanical Pulp (TMP) and loaded with different levels of PCC in order to determine the Z direction distribution of calcium. Finally, the impact of sampling on the use of SEM and EDX for z-direction mineral topography is illustrated in two industrial paper samples. This provides an idea of the number of viewing areas required to get a good representation of the paper sample.

5.2 EXPERIMENTAL

5.2.1 The SEM/EDX Technique

Scanning Electron Microscope (SEM) can be used to observe the surfaces of materials at high resolution and magnification. Moreover, a detailed profiling of the elements present on a particular surface is determined by Energy Dispersive X-Ray Analysis (EDX). In this work, SEM and EDX were performed using Hitachi S-3000N microscope. The analysis demonstrates the presence of and location of the elemental

constituents of additives like calcium carbonate. However, EDX cannot provide information on oxidation state or exact molecular composition.

The paper samples are cut using a razor blade and mounted on the SEM sample stub. Backscattering mode is used to obtain SEM images. A 20 kv accelerating voltage is used. Variable pressure (20 kPa) mode is used to obtain the images. The X-ray counts are collected for 100 seconds during each scan. A magnification of 600x is used for analysis in z-direction and 300x for top side and wire side surface analysis.

5.2.2 Materials

5.2.2.1 Paper Samples

Seven paper samples were used to illustrate the technique of using SEM/EDX to determine the z-direction mineral distribution. Table 1 gives the paper machine operating parameters for the seven paper samples used for illustration. Paper A is a 62 g/m^2 basis weight sheet made in the absence of inorganic anionic trash collector (ATC) and starch. Paper B is a 52 g/m^2 basis weight sheet made in the presence of inorganic ATC and potato starch. It is noted that Paper B has a higher unbleached TMP compared to other paper samples. Paper C is a 49 g/m^2 basis weight sheet made in the absence of inorganic ATC and in the presence of potato starch. Paper D, E, F, and G are manufactured without inorganic ATC and with tapioca starch. Paper D is a 52 g/m^2 basis weight sheet whereas paper E, F, and G are 67 g/m^2 .

Paper machine Parameters	Paper A	Paper B	Paper C	Paper D	Paper E	Paper F	Paper G
Basis weight (g/m2)	62	52	49	52.1	66.6	66.6	66.6
H.box (cy%)	1.06	1.02	1.03	0.98	1.07	0.96	0.94
Filler loading (%)	8	8	15	20	18	20	20
ATC (kg/T)	0	1	0	0	0	0	0
Starch (kg/T)	0	8	8	8	8	9.7	9.7
Type of Starch	No Starch	Potato	Potato	Tapioca	Tapioca	Tapioca	Tapioca
Retn. Aid (kg/T)	0.62	0.19	0.63	0.97	0.84	0.77	0.91
Coagulant (kg/T)	0.83	0.00	1.04	2.07	1.70	1.79	1.80
PM speed (m/min)	780	713	814	810	766	745	745
Bleached TMP (%)	86	55	92	80	93	95	95
Broke (%)	0	10	8	20	7	5	5
TMP (%)	14	35	0	0	0	0	0

Table 5.1: Paper Machine Operating Parameters for the Seven Papers

All the papers are manufactured on a Horizontal Bel-Baie-III former. The operating parameters during the manufacture of the papers are tabulated in table 5.1. The vacuum on the paper machine was same for all the papers. Therefore, it can be reasonably assumed that the drainage for all the paper samples is similar. The ash content of paper is determined by using the TAPPI standard method T413 where the paper of known weight is ashed in a furnace at 550°C. The ash content is reported in weight percent. This ash was analyzed for calcium content with Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). The wire side of the paper refers to the conveying wire side and the top side refers to the other side.

5.2.2.2 Hand Sheets

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Hand sheets were prepared using bleached Thermo-Mechanical pulp. Table 5.2 shows the basis weight and thickness of sheets prepared at different precipitated calcium carbonate (PCC) loadings. The ash % is determined by the low temperature ash method at 550 °C as described in TAPPI standard method T413. The ash content is reported in

PCC loading	Basis Weight (g/m²)	Thickness (µm)	Ash (%)	
Blank	51.3	83.5	1.23	
20%	54.4	99.1	6.79	
60%	59.7	108.6	15.32	
100%	66.5	122.9	22.38	

Table 5.2: Properties of Hand Sheets

weight percent. This ash was analyzed for calcium content with Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). For hand sheets the side touching the wire mesh is referred as wire side and the other side is referred as top side. The thickness of the hand sheets is also noted in table 5.2 which is determined after drying in a humidity controlled room using Lorentzen and Wettre micrometer. It is important to note that no polymers or starch were used for filler retention. So all the filler retained in the sheet is due to mechanical retention only.

5.2.3 Illustration of SEM/EDX Sampling Procedure

Paper samples of 8 $\frac{1}{2}$ x 11 inch dimensions obtained for analysis are identified with machine direction (MD) and cross direction (CD) while procuring the sample. This is verified by conducting a bursting strength test to see the line of rupture, which is perpendicular to MD. Top side (TS) and wire side (WS) of the paper sample is also identified while procuring the sample.



(a) Paper Sample showing eight paper specimens



(b) Paper Specimen Dimensions



(c) Dimensions of the viewing area

Figure 5.1: Sampling procedure for SEM and EDX analysis of paper.

Figure 5.1 shows a schematic of the sampling procedure. On each paper sample eight paper specimens with a length of 10 mm (along CD) x 5 mm (along MD) are cut perpendicular to the machine direction at different points on the circumference of the circle using a double edge razor blade as shown in figure 5.1a. This type of sampling procedure covers an orientation of 360° of filler distribution. No chemical treatment is provided to the paper specimen. From each paper specimen two viewing areas having a dimension of approximately (100 µm) x (sheet thickness (µm)) is identified which is representative of the filler distribution in that paper specimen. Care is taken to select an area with the minimum possible voids in the paper specimen.



Figure 5.2: SEM image showing the viewing area for EDX analysis in the z-direction of the paper specimen.

These paper specimens are placed on the SEM/EDX sample stub with its z-direction perpendicular to the plane of the sample stub. First, the whole viewing area of

(100 μ m) x (sheet thickness (μ m)) is subjected to EDX analysis as shown in figure 5.2. EDX analysis provides the elemental concentration (wt. %) in the area selected for analysis. This machine detects all the elements having atomic number greater than 4. Since in these analysis we use PCC filled sheets we are interested in measuring calcium concentrations. The calcium concentration (wt. %) along with other elemental composition is reported by the EDX report as show in figure 5.3. The EDX accounts for the total elemental composition in the selected area as 100 wt % and then detects the % of calcium present in that area in relation to the other elements. Hydrogen is a lighter element and is not accounted for in this analysis.



Element	Line	Method	Intensity	KRatio	ZAF	Concentration	2Sigma	Z	A	F
С	KA	PRZ	699.82	0.102	2.177	22.12 wt%	0.247 wt%	0.893	2.440	0.999
0	KA	PRZ	448.86	0.035	8.906	31.36 wt%	0.271 wt%	0.943	9.449	1.000
Na	KA	PRZ	7.81	0.000	3.192	0.07 wt%	0.014 wt%	1.038	3.080	0.998
Al	KA	PRZ	28.46	0.001	1.658	0.11 wt%	0.009 wt%	1.056	1.581	0.993
Si	KA	PRZ	73.77	0.002	1.346	0.27 wt%	0.010 wt%	1.030	1.323	0.987
S	KA	PRZ	35.02	0.001	1.097	0.13 wt%	0.009 wt%	1.047	1.093	0.958
Ca	KA	PRZ	604.37	0.029	1.324	3.83 wt%	0.032 wt%	1.077	1.229	1.000

Figure 5.3: Elemental composition of the viewing area as determined by EDX.

Subsequently, the (100 μ m) x (sheet thickness μ m)) viewing area is divided into five areas along the thickness direction and each area is analyzed for calcium concentration using EDX as shown in figure 5.4. There is a limitation for the minimum area that can be analyzed with EDX for a particular magnification and thickness of paper sample. In our case, for 600x magnification the number of approximate equal areas that could be analyzed with EDX was five.



Figure 5.4: SEM image showing the five areas for EDX analysis in the entire thickness of paper A.

The entire procedure is repeated again for the second viewing area in the same paper specimen. So in total for one paper sample ($8 \frac{1}{2} \times 11$ inch) the complete z-direction analysis is done for 8 paper specimens and 16 viewing areas. So the results are reported as the average of the 16 readings along with the standard deviation.



Figure 5.5: SEM image showing the EDX analysis of one of the paper surface on Top

Side.



Figure 5.6: SEM image showing the EDX analysis of one of the paper surface on Wire

Side

Finally, a sample of paper is cut on either side of the paper specimen (10 mm) in the MD as indicated by circles in figure 5.1. Both top side (TS) and the conveying wire side (WS) samples are taken and subjected to EDX analysis as shown in figures 5.5 and 5.6. The surface calcium concentration is noted for top side and wire side.

This technique was further demonstrated using hand sheets prepared with known PCC loadings. However, in case of hand sheets four paper specimens and one viewing area per specimen were selected for each hand sheet. Figure 5.7 shows the schematic of the sampling procedure for hand sheets. Therefore, the results shown are an average of four readings along with standard deviation.



Figure 5.7: Schematic of the sampling procedure for hand sheets.

SEM/EDX technique was further illustrated by selecting two industrial paper samples paper sample C and paper sample G on the impact of sampling on the use of SEM and EDX for Z-direction mineral topography. Paper Sample C is a newsprint grade of 49 g/m² basis weight manufactured without anionic trash collector and with potato starch. Paper sample G is an uncoated specialty grade of 67 g/m² basis weight sheet manufactured without anionic trash collector and with tapioca starch. The procedure for SEM/EDX analysis is described above. In this section the effect of the number of viewing areas on the z-direction mineral topography is determined. In particular, instead of two, five viewing areas were selected per paper specimen with industrial paper samples (C and G). So the total number of areas of analysis is equal to 8 * 5 = 40 areas per paper sample instead of 16. So the results are reported as the average of the 40 readings along with the standard deviation.

5.3 **RESULTS AND DISCUSSION**

5.3.1 Calcium Content of Industrial Paper Samples Using EDX

Paper A is a 62 g/m^2 basis weight sheet made in the absence of anionic trash collector (ATC) and starch. Figure 5.8 shows the SEM of the z-direction of one of the areas of the paper specimen. Figure 5.9 shows the top side and wire side surface of paper A.



Figure 5.8: SEM of Z-direction of paper A.



Figure 5.9: SEM of the Top and Wire Side surface of paper A.

Figure 5.10 shows the calcium content in the z-direction of paper A from the wire side to the top side. Each point in the graph is the average of 16 measurements (8 paper specimens x 2). It is noted that the actual ash content of the paper is 5.3 % and is determined by the ash method independently. Thus, in our demonstration of the method five calcium concentrations in the z-direction are presented along with two surface (wire side and top side) concentrations of calcium. The surface analysis for the top and wire side involves an area of approximately 200 μ m x 200 μ m. However, the five areas in the

z-direction have an approximate area of analysis of 100 μ m x sheet thickness (μ m). Since paper A is manufactured without any starch we can use this to compare the effect of starch on z-direction distribution of calcium.



Figure 5.10: Variation of calcium content in the z-direction of paper A.

From figure 5.10 it is seen that paper A has higher filler content below the wire side surface compared to that below the top side surface. The calcium level at the centre of the sheet is higher than towards the surfaces. However, the difference in the calcium levels is only 1%. It should be noted that the ash content of the sheet is 5.3 % only.

Paper B is a 52 g/m² basis weight sheet made in the presence of inorganic ATC and potato starch. No coagulant was added during the manufacture of paper B. However, a very low amount of retention aid was added. Figure 5.11 shows the SEM of the z-direction of one of the areas of the paper specimen.



Figure 5.11: SEM of Z-direction of paper B.

Figure 5.12 shows the top side and wire side surface of paper B. The ash content of paper B is 4.7% as obtained from the ashing method. It can be seen that the calcium content is higher on the top side surface of the sheet compared to the wire side surface.



(a) Wire Side

(b) Top Side

Figure 5.12: SEM of the Top and Wire Side surface of paper B.

Figure 5.13 shows the variation of calcium content in the z-direction of paper B from the wire side to the top side obtained by the EDX method. As seen, the concentration of calcium at the centre of the sheet is equal to that at the top side and lower to that on the wire side. All the other calcium levels are within a range of 0.5%. The ash content of paper B is only 4.7%.



Figure 5.13: Variation of calcium content in the z-direction of paper B.

Paper C is a 49 g/m² basis weight sheet made in the absence of inorganic ATC and in the presence of potato starch. We know from our previous findings (Chapter 5) that potato starch requires ATC for better retention and strength. This might be one of the reasons why Paper B has a different filler distribution compared to paper C. The main difference between paper B and paper C is the presence of inorganic ATC in paper C. However, the filler loading in paper C is 15% compared to 8% in paper B. Figure 5.14 shows the variation of calcium content in the z-direction of paper C from the wire side to the top side obtained by the EDX method. The ash content of paper C is 8.4 %. Paper C has higher calcium content near the top side surface. Comparatively, the calcium content near the wire side surface is low. As we move from the wire side surface towards the top side surface the calcium content in the sheet gradually increases from 7% to 12.5%. This type of distribution is more common in a horizontal Bel-Baie former [11]. One may say that in this case the former effect combined with the effect of ATC is dominant on z-direction calcium distribution.



Figure 5.14: Variation of calcium content in the z-direction of paper C.

Paper D is a 52 g/m² basis weight sheet made without inorganic ATC and with tapioca starch. Figure 5.15 shows the SEM of the z-direction of one of the areas of the paper specimen. Figure 5.16 shows the top side and wire side surface of paper D. Paper D has higher calcium content on the top side surface compared to the wire side surface.



Figure 5.15: SEM of Z-direction of paper D.



(a) Wire Side

(b) Top Side

Figure 5.16: SEM of the TS and WS surface of paper D.

Figure 5.17 shows the variation of calcium content in the z-direction of paper D from the wire side to top side obtained by the EDX method. The ash content of paper D is 12.9%. The five calcium contents in the z-direction are within a range of 2 %. There appears to be 1% to 1.5% more calcium towards the top side (on the average).



Figure 5.17: Variation of calcium content in the z-direction of paper D.

Papers E, F, and G are 67 g/m^2 basis weight sheets made in the absence of inorganic ATC and in the presence of tapioca starch. Figure 5.18 shows the variation of calcium content in the z-direction of paper E, F, and G. Papers F and G have higher dosage of tapioca starch than Paper E. For papers F and G tapioca starch addition was done at two points. The first point is the addition of starch at machine chest pump outlet and the second point is before the fan pump. At the machine chest pump outlet 5.7 kg/t of starch was added and 4 kg/t at the thin stock. However, for paper F, 8 kg/t of starch was added at the machine chest pump outlet.



Figure 5.18: Variation of calcium content in the z-direction of paper E, F, G.

Paper E and Paper F show a similar z-direction distribution, although the levels of calcium are different. Paper G has higher calcium content at the centre of the sheet. However, from table 5.1 we can see that paper F and paper G have similar paper machine operating parameters, filler loading and furnish. The only difference is the slightly higher addition of retention aid for Paper G. Paper samples D, E, F, and G, manufactured with tapioca starch show similar z-direction calcium distribution, although the levels of calcium are different. The fact that papers F and G have more ash% is probably due to higher filler loading 20% compared to 18% in paper E.

Comparing paper A and paper B (figures 5.10 and 5.13) we can say that potato starch influences z-direction calcium distribution. Paper B has lower calcium at the centre of the sheet compared to paper A at the centre of the sheet. The amount at the centre shifts from a value same as the wire side of paper A to a value similar to that in top side of paper B. The filler loading is same for both the papers. However, no coagulant was used in the manufacture of paper B. Comparing paper A and paper C (figures 5.10 and 5.14) we can clearly see that potato starch influences z-direction calcium distribution. The main difference between paper A and paper C is only the presence of potato starch in paper C. The calcium content increases gradually as we move from the wire side surface towards the top side surface in paper C. Paper C has lower basis weight compared to paper A. Also the filler loading in paper C is 15% compared to 8% in paper A.

Papers D, E, F and G have similar type of calcium distribution in the z-direction. Papers D, E, F and G are manufactured with tapioca starch. Comparing papers E, F and G with paper A having similar basis weights, it is seen that papers E, F, G have similar values of calcium levels on both top side and wire side whereas the levels at the centre is slightly higher compared to top side and wire side. For paper A, as discussed above the calcium content is higher on the wire side and centre of the sheet compared to the top side. It is important to note that paper A is manufactured without any starch and papers E, F, G are manufactured with tapioca starch.

Comparing paper D with paper B we can see the difference in the z-direction calcium distribution (figures 5.13, and 5.17). Paper B, manufactured with potato starch has higher calcium near the wire side compared to that at the centre and top side. Also the levels at the centre and top side are similar. For paper D, manufactured with tapioca starch the calcium level at the wire side is lower compared to that at the centre and top side, with top side calcium level being greater than the levels at the centre of the sheet.

Since all the papers used retention aid and coagulant (except paper B) we can say that in this case the z-direction calcium distribution is influenced by starch only. It is noted that potato starch and tapioca starch give different z-direction calcium distribution. It is also important to note that all the papers were manufactured on the same paper machine and the vacuum on the paper machine was same for all the papers investigated here. However, to arrive at definite conclusions there is a need to obtain more data with paper samples with same basis weight, operating parameters but with different type of starch.

5.3.1.1 Relation between EDX Calcium (%) And Ash (%) for Industrial Paper Samples

The amount of calcium indicated in the EDX is higher than the actual calcium present in the sheet. One reason is the fact that EDX does not account for the weight of elements whose atomic number is less than 4. Other reasons might be relevant and as a result a calibration of the SEM/EDX measurements is needed. For that purpose independent measurements were carried out. The calcium in the sheet was determined by doing an ICP/MS analysis on the ash obtained from the paper samples. Assuming that all the ash of the paper is calcium carbonate we may also calculate the calcium content in the sheet based on the molecular formula of CaCO₃. The results for all paper samples are shown in figure 5.19. As seen we obtain a good correlation between ICP/MS calcium and that from the calculated one. The calculated calcium is higher than ICP/MS calcium as expected, because in reality the ash is not 100 % CaCO₃. However, EDX calcium is always higher than that from ICP/MS and the calculated calcium. It should be noted that

the reported EDX calcium is the average of the calcium in the 5 areas in z-direction of the sample.



Figure 5.19: Calcium content in the paper samples with different methods.

Figure 5.20 shows the relation between EDX calcium percent and ICP/MS calcium in paper for the paper samples examined. The correlation can be described by equation 5.1.

$$Y = 0.37 * X - 0.46$$
 (5.1)
Where Y= ICP/MS Calcium (%)
X= EDX Calcium (%)


Figure 5.20: Relation between EDX calcium (%) & ICP/MS Ca (%) in paper samples.



Figure 5.21: Relation between EDX calcium (%) and Ash (%) in paper samples.

As it is more common to refer to ash percent in paper, we plotted the relation between EDX calcium percent and ash percent in paper for the paper samples examined. Figure 5.21 shows this correlation. The correlation is described by equation 5.2.

$$Y = 1.07 * X - 0.98$$
 (5.2)
Where Y= Ash in Paper (%)

X= EDX Calcium (%)

Table 5.3 compares the ash percent of the paper samples and the ash percent obtained from the correlation in equation 1. We can see that for all the paper samples investigated the error is less than $\pm 8\%$.

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 Table 5.3: Comparison of Ash (%) In Paper with That Obtained From the EDX Calcium

 Calibration Curve.

Sample	EDX Ca (%)	Ash Method	Ash (%) from	Error (%)	
Dample		Ash in paper (%)	Calibration		
Α	6.16	5.28	5.60	6.15	
В	4.99	4.68	4.35	-6.96	
C	9.17	8.35	8.82	5.64	
D	12.1	12.9	11.95	-7.35	
E	13.29	12.34	13.22	7.15	
F	13.41	14.09	13.35	-5.24	
G	14.8	14.5	14.84	2.32	

It is reasonable to propose the existence of a correlation between the EDX calcium percent and the ash in the sheet. The quality of the correlation will depend significantly on the number of data points (samples examined). There are still issues to be examined given that that all the paper samples were manufactured on the same paper machine with similar operating parameters. It will be interesting to determine whether

this correlation holds true for other paper samples manufactured on different paper machines.

5.3.2 Calcium Content of Hand Sheets Using EDX

Figure 5.22a shows the SEM micrograph of Z-direction of one of the hand sheet specimens prepared without any PCC and figure 5.22b shows the calcium distribution in the z-direction. Each point in the graph of figure 5.22b is representative of four readings. As seen there is some calcium concentration in this hand sheet which may probably be attributed to the calcium associated with the fibre.



Figure 5.22: Z-direction calcium distribution for hand sheet without any PCC loading.

Similarly, figure 5.23a shows the SEM micrograph of z-direction of one of the hand sheet specimens made with 20 % PCC loading. Figure 5.23b shows the calcium distribution in the thickness of the hand sheet. The ash retention was 22.1% and the sheet ash was 6.8 %. It can be clearly seen in figure 5.23b that the calcium level in the top side

exceeds that in the wire side and that this sheet had the most calcium at the centre. The latter is a characteristic of hand sheets



(a)SEM micrograph

(b) Z-direction Ca distribution

Figure 5.23: Z-direction calcium distribution for hand sheet with 20% PCC loading.



(a)SEM micrograph

(b) Z-direction Ca distribution

Figure 5.24: Z-direction calcium distribution for hand sheet with 60% PCC loading.

Figure 5.24a shows the SEM micrograph of Z-direction of one of the hand sheet specimen made with 60 % PCC loading. Figure 5.24b shows the calcium distribution in

the Z-direction of the thickness of the hand sheet. The ash retention was 20.5 % and the sheet ash was 15.3%. Again there is more calcium is present at the centre of the sheet and towards the top side.

Similarly, figure 5.25a shows the SEM micrograph of Z-direction of one of the hand sheet specimens made with 100 % PCC loading and figure 5.25b shows the calcium distribution. The ash retention was 20.7 % and the sheet ash was 22.4 %. Most of the calcium ends up in the middle and top layers of the sheet. The figures show that as the filler loading is increased in hand sheets more calcium is present at the centre of the sheet and towards the top side. In addition, the ash retention is always in the range of 20 %-22 % for PCC loading of 20 %, 60 % and 100 %.



(a)SEM micrograph

(b) Z-direction Ca distribution

Figure 5.25: Z-direction calcium distribution for hand sheet with 100% PCC loading.

5.3.2.1 Relation between EDX Calcium (%) And Ash (%) in Hand Sheets

It is important to relate the calcium levels obtained by SEM/EDX measurements to the actual calcium present in the sheet is determined through independent measurements. The calcium in the sheet was determined by conducting ICP/MS analysis on the ash obtained from the hand sheets. Assuming that all the ash in the hand sheet is CaCO₃ we may also calculate the calcium content in the sheet based on the molecular formula of CaCO₃. The latter is called calculated calcium. The results for all hand sheets are shown in figure 5.26. As seen there is a very good correlation between ICP/MS calcium, calculated calcium and that obtained by EDX. It should be noted that the reported EDX calcium is the average of the calcium in the five areas in Z-direction of the hand sheet.



Figure 5.26: Calcium content in the hand sheets with different methods.

Figure 5.27 shows the relation between EDX calcium percent and ICP/MS calcium in paper for the hand sheet examined. The correlation can be described by equation 1.



Figure 5.27: Relation between EDX calcium (%) and ICP/MS Ca (%) in hand sheets with different PCC loading.

Y = 0.84 * X + 0.46 (5.3) Where Y= ICP/MS Calcium (%) X= EDX Calcium (%)

Since it is more common to use ash percent in paper making we obtained a correlation between the EDX Ca (%) verses the ash (%), we get a correlation as described by equation 5.3. Figure 5.28 shows this correlation.



Figure 5.28: Relation between EDX calcium (%) and Ash (%) in hand sheets with different PCC loading.

Y = 2.27 * X + 1.53 (5.4) Where Y= Ash in Paper (%) X= EDX Calcium (%)

From the above correlations it is obvious that there is a definite correlation between the EDX calcium percent and the ash in the sheet. The correlation is actually a linear relationship with a correlation coefficient equal to 0.98 as seen in figure 5.28. It is noted that a similar linear relationship was found for seven industrial paper samples manufactured on the same paper machine as seen in figure 5.21.

It is expected that the calibration curve will depend on the manufacturing process. One can then examine a large number of samples that capture the inherent variability of the process so that a meaningful correlation is obtained.

5.3.3 Effect of the Number of Viewing Areas On Z-Direction Mineral Distribution Using SEM/EDX

Figure 5.29 shows the SEM micrograph of five paper specimens of industrial paper sample G manufactured with tapioca starch.



Figure 5.29: SEM micrograph of five paper specimens of industrial paper sample G manufactured with tapioca starch.

From the micrograph it is not possible to observe if the filler is uniform along the thickness direction. Some pockets of very high filler content are seen as well as some areas without any filler. In this context the accuracy of any method of analysis for Z-direction distribution of filler will rely on an adequate representation of the entire paper sample.

Figure 5.30 shows the comparison of Z-direction calcium distribution using SEM/EDX technique. Figure 5.30a shows the distribution with two areas of analysis

which is representative of the entire paper specimen. So each point in the figure is the average of 16 readings from the entire paper sample. Figure 5.30b shows the distribution of calcium based on five areas per paper specimen. Thus, each point in figure 5.30b is the average of 40 readings from the entire paper sample. In both figures the 95 % confidence intervals are also seen. It is clearly seen that the trend of PCC distribution is same but there is a decrease in the levels of calcium when the areas of analysis are five instead of two.





(b) Five Areas per specimen



The results of the analysis from another industrial paper C which is manufactured with potato starch are shown in figure 5.31. The 95 % confidence intervals are also seen. It is also seen here that while the calcium distribution profile is the same the calcium level is lower when five areas per specimen are used in the sampling. In both figures the standard deviations are shown and they have decreased as the number of areas of analysis increased.



(a) Two Areas per specimen (b) Five Areas per specimen

Figure 5.31: Comparison of Z-direction calcium distribution with two and five areas of analysis per paper specimen for paper C.

The above results clearly illustrate that sampling is important in the determination of the filler distribution across the z-direction of the sheet. As seen the calcium levels are greater when two viewing areas are used compared to five viewing areas, while the trend of filler distribution is not affected. In our opinion this is attributed to the irregularity in filler distribution in paper. As discussed above figure 5.29 illustrates the irregularity within a paper specimen (randomly located pockets of high filler content) as well as between the specimens of the same paper sample.

The irregularity in calcium distribution between paper specimens is captured by cutting eight paper specimens per paper sample perpendicular to the machine direction at different points on the circumference of a circle as seen in figure 3.1. The variability within a specimen is the focus of this section. While a specimen is under the SEM examination the experimenter may manually scan the entire specimen and then choose as many areas as required to cover the entire spectrum from the highest to the lowest density of calcium pockets. It should be noted that the SEM/EDX machine that was employed in this study restricts the area of analysis to 100 μ m X (thickness) for a magnification of 600 x. Considering that the length of the specimen is 10,000 μ m then one has a maximum of 100 viewing areas. Obviously, the time required for the analysis and the associated cost are directly related to the number of viewing areas for analysis. By choosing five viewing areas one captures more effectively the filler variability. The question is what the optimum number is? One approach would be to divide the entire width of the paper manufactured on the paper machine into various zones based on the cross direction slices on the head box. Then analyze the filler distribution in each of these zones. One may then be able to determine which zone of the scope of this work. However, the fact that the trend in the filler distribution was not found to be affected by the number of viewing areas demonstrates that SEM/EDX is a reliable technique in determining z-direction mineral distribution in paper.

5.4 CONCLUSIONS

SEM/EDX technique is an excellent non-destructive tool to quantify calcium distribution across the z-direction of the sheet. The z-direction calcium distribution was investigated for seven paper samples with similar operating parameters and different levels of chemical addition. The study showed z-direction calcium distribution varied with the type of starch (potato or tapioca) used for the manufacture of the paper. However, due to the difference in filler loadings the paper samples had different calcium

levels. Thus, z-direction distribution not only depends on the paper machine operating parameters but also on chemical additions.

A correlation was also established between the EDX calcium percent to the ash percent obtained from ash method. This enables the SEM/EDX method to be used to determine the z-direction ash content in the paper based on the EDX calcium percent without disturbing the structure of the sheet. The hand sheet study also showed that a definite correlation exists between the calcium determined by EDX and the actual calcium in the hand sheets or paper sample determined by an independent analytical technique.

The impact of sampling on the use of SEM/EDX for the determination of calcium content in the z-direction of paper samples was illustrated with two industrial paper samples. It was found that while the number of viewing areas for analysis in a particular paper specimen does not have any effect on the filler topography but affects the quantity or level of calcium determined.

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CHAPTER-6

CONCLUSIONS, CONTRIBUTION TO KNOWLEDGE AND RECOMMENDATION FOR FUTURE WORK

This thesis dealt with the issues arising in the use of precipitated calcium carbonate (PCC) as filler in mechanical pulp suspensions. One of the issues is related to the optimal use of starch as an additive to improve strength. Other additives that need to be optimized simultaneously include coagulants and flocculant to facilitate the papermaking process. The methodology was based on a hierarchical study of the various interactions in the pulp suspension. The thesis also illustrated a non-destructive technique to quantify the topography of PCC filler in the z-direction of paper. The major conclusions of the study and the recommendations for further work are discussed below.

6.1 Conclusions

Chapter 2 investigates the colloidal behavior of PCC and the interactions of PCC with starch in distilled de-ionized water (DDW) and process water (PW). Two types of potato starch (1 & 2) with different degrees of substitution (DS) and one type of tapioca starch was used in DDW and PW to study the aggregation of PCC. All three starches were able to aggregate PCC in DDW at 25°C and 50°C and PW at 50°C. However, tapioca starch gave the highest rate of aggregation and aggregate size compared to the potato starches. Similarly, poly aluminum chloride was able to aggregate PCC particles in DDW but not in PW. The study also showed that tapioca starch is not deactivated or neutralized in the presence of anionic trash but has an affinity for PCC whereas the other starches are affected by the presence of the anionic trash.

Chapter 3 shows the comparison of the effect of tapioca starch and potato starch with similar degree of substitution (DS) on TMP fibres loaded with 25 wt. % PCC. Using starch in mechanical pulp suspension as a strength enhancing additive requires caution due to the neutralization of starch by the dissolved and colloidal substances (DCS) originating during the pulping process. It is also important to fix PCC into the paper web to eliminate printing problems. The results showed that for high anionic trash environment high degree of substitution (DS) tapioca starch is a better strength developing agent and retention aid compared to high DS potato starch.

Chapter 4 compares the effect of coagulant and flocculant CPAM on TMP fibres loaded with 25 wt. % PCC in the presence of starch. The effect of two commercially used coagulants poly aluminum chloride (PAC) and poly diallyldimethyl ammonium chloride (DADMAC) in conjunction with tapioca and potato starches was also studied. It was found that tapioca starch reduces zeta potential more compared to potato starch. It was also found that PAC should be used as a coagulant when using potato starch and poly DADMAC when using tapioca starch to get maximum benefits in terms of facilitating starch adsorption to the fibres.

The effect of poly DADMAC and cationic polyacrylamide (CPAM) on retention of fines/filler in the presence of starch was studied separately. A 3² factorial design of experiments showed that the interaction of poly DADMAC and CPAM in the presence of starch does not help in total retention but the interaction is positive for fines/filler retention. Finally, drainage experiments showed that poly DADMAC in the presence of tapioca starch does not help in increasing drainage of TMP suspensions loaded with PCC. CPAM and tapioca starch gives a faster drainage. Thus, in a system containing tapioca starch and CPAM there is no role for poly DADMAC.

Finally, chapter 5 illustartes the use of Scanning Electron Microscopy (SEM) and Energy dispersive X-Ray Analysis (EDX) technique to determine z-direction calcium distribution in paper. With decreasing basis weight of papers the use of traditional physical methods does not help in giving an accurate z-direction mineral distribution and moreover the methods are not repeatable and destroy the structure of the paper. SEM/EDX analysis does not destroy the structure of the sheet which helps in accurate determination of calcium distribution. A calibration was performed by ashing the seven industrial paper samples and analyzing the calcium content using Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). The EDX calcium levels correlates very well with the ICP/MS calcium levels and the ash % obtained. Further this calibration was performed with laboratory hand sheets produced with different amounts of PCC loading. Again a very good correlation was obtained with EDX analysis and that obtained by ICP/MS.

The z-direction distribution of calcium was compared with the paper machine operating parameters like the addition of different types of starch. The analysis with seven industrial paper samples manufactured on the same paper machine shows that the type of starch affects z-direction distribution. Similar results were shown previously with hand sheets using adhesive tape method [1]. Finally, the impact of sampling on the z-direction calcium distribution was illustrated with two industrial paper samples manufactured on a Horizontal Bel Baie-III paper machine. It is found that as we increase the number of areas of analysis covering the irregular filler distribution in a paper sample, the calcium levels decreases compared to fewer areas of analysis while the shape of calcium distribution does not change.

6.2 Contribution to Knowledge

Knowledge from this work provides insight to the interactions of various additives in mechanical pulp suspensions. from an applications point of view it enables papermakers to select the appropriate chemicals to be used, the proper dosage of the various chemicals, the addition points and sequence of addition. It was rewarding to see that some of our conclusions have already been confirmed with industrial practice at a BC coastal mill. The SEM/EDX technique for z-direction filler distribution when used to obtain a substantial database is expected to enable papermakers to correlate sheet properties and structure with paper machine and papermaking chemistry parameters e.g. additives. More specifically, the contributions are as follows:

- Effect of tapioca starch and potato starch on the aggregation of PCC in pure system like distilled and deionized water and in the presence of anionic trash like process waters showed that tapioca starch has a higher affinity in aggregating PCC even in the presence of DCS. In case of potato starch it gets deactivated in the presence of DCS.
- 2. Comparing the effect of tapioca and potato starch on TMP suspension loaded with PCC shows that tapioca starch has greater affinity for fibres.
- 3. The sequence of addition of starch and PCC shows that when tapioca starch and PCC are mixed together it is important to add a low amount of tapioca starch to PCC and a higher amount to the TMP directly. However, in case of potato starch the amount of

potato starch to PCC or to the TMP does not affect the reduction of cationic demand and zeta potential. There is a limitation for the amount of potato starch that can be adsorbed on the TMP fibres. However, in case of tapioca starch there is a higher margin for adsorption as it is not neutralized in the presence of DCS.

- 4. Tapioca starch is a better strength developing agent compared to potato starch in high anionic trash environments.
- 5. Poly DADMAC should be used as a coagulant when using tapioca starch and PAC should be used when using potato starch.
- 6. Poly DADMAC in the presence of tapioca starch decreases retention and drainage rate.
- Low dosage of CPAM in the presence of tapioca starch increases retention. However, at higher dosages of CPAM retention decreases.
- 8. The combination of poly DADMAC and CPAM in the presence of tapioca starch increases retention slightly. However, in a system containing tapioca starch and CPAM there is no role for poly DAMAC for retention as well as drainage purposes.
- 9. A non-destructive SEM/EDX technique for determination of z-direction mineral distribution in paper was illustrated and was actually utilized by a BC coastal mill.
- 10. The calcium obtained by the SEM/EDX method correlates with ash% in the sheet.

6.3 **Recommendations for Future Work**

This thesis dealt with the elucidation of the interactions with the purpose of optimizing the use of PCC filler and starch in mechanical pulp suspensions. The study employed industrially used materials in order to approximate to the best possible degree

papermaking conditions. It is then reasonable that such an applications-oriented study would inadvertently leave some knowledge gaps. Moreover, the impact of the additives on hand sheet properties is another area for study. Thus, the following are suggested for a further and deeper understanding of the issue of interactions in mechanical papermaking suspensions:

- 1. At different amount of tapioca and potato starch determine strength properties, formation and optical properties by making hand sheets.
- 2. Determine the effect of poly DADMAC and PAC on the strength properties, formation and optical properties using tapioca and potato starch in hand sheets.
- 3. Determine the effect of CPAM on the strength properties, formation and optical properties using tapioca and potato starch in hand sheets.
- 4. Determine the structural and other differences between tapioca and potato starch in order to explain their different behavior.
- 5. Investigate the idea that some DCS should be mixed with PCC before adding to the pulp suspension. However, it is also important to see that this does not affect the optical properties of the sheet specifically brightness.
- 6. In order to produce faster, accurate and more reliable results with the SEM/EDX technique the sampling should be done across the entire width of the paper machine. This entire width can be divided into various zones depending on the slices across the width of the machine thus, giving a higher control across the width of the machine. The SEM micrographs across the width of the sheet can also be analyzed by using image analysis programs that will help differentiate the inorganic and the organic

material in a sheet of paper depending on the intensity and volume of grey and dark spots in the micrographs.

6.4 ACKNOWLEDGEMENTS

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6.5 **REFERENCES**

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Figure A1: Viscosities of starches at different spindle speeds at 53 C.





Figure A2: Typical experimental result for aggregation of PCC using starch.



Figure A3: Change in particle size distribution with time during aggregation of PCC with tapioca starch.

Table A1: 32 Factorial design to study the significance of flocculant cationicpolyacrylamide (C-PAM) and coagulant poly diallyl dimethyl ammonium chloride(DADMAC) in the presence of tapioca starch on Total Retention.

Factor B	Factor A								
		Flocculant (kg/t) (C-PAM)							
Coagulant (kg/t)Poly DADMAC	Low (0.4)	Medium (0.7)	High (1.0)	Low (0.4)^2	Medium (0.7)^2	High (1.0)^2			
	71.87	72.99	74.02	5165.30	5327.54	5478.96			
Low (0.8)	70.79	72.4	72.34	5011.22	5241.76	5233.08			
	70.97	73.02	72.38	5036.74	5331.92	5238.86			
	71.27	71.39	73.95	5079.41	5096.53	5468.60			
Medium (1.4)	70.41	71.28	71.13	4957.57	5080.84	5059.48			
	70.24	71.4	72.05	4933.66	5097.96	5191.20			
	71.2	71.82	72.78	5069.44	5158.11	5296.93			
High (2.0)	70.86	71.74	72.79	5021.14	5146.63	5298.38			
	70.96	71.76	72.79	5035.32	5149.50	5298.38			

Table A2: Summation of all the trials for total retention

Factor B					
Coagulant (kg/t)Poly DADMAC	Floco	ulant (kg/t) (C-I	Sum of Rows		
Coagdiant (kg/t): Ciy BABIIIAC	Low (0.4)	Medium (0.7)	High (1.0)		
Low (0.8)	213.63	218.41	218.74	650.78	
Medium (1.4)	211.92	214.07	217.13	643.12	
High (2.0)	213.02	215.32	218.36	646.7	
Sum of Columns	638.57	647.8	654.23	1940.6	Sum of All r

Table A3: Analysis of Variance to study the significance of flocculant cationic polyacrylamide (C-PAM) and coagulant poly diallyl dimethyl ammonium chloride (DADMAC) in the presence of tapioca starch on Total Retention.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F0	F-Critical	ANOVA
Coagulant (Poly DADMAC)	2.90	2	1.45	3.53	3.55	Not Significant
Flocculant (C-PAM)	14.52	2	7.26	17.63	3.55	Significant
Interaction	1.16	4	0.29	0.70	2.93	Not Significant
Error	7.41	18	0.41			
Total	25.99	26				

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Table A4: 3² Factorial design to study the significance of flocculant cationic polyacrylamide (C-PAM) and coagulant poly diallyl dimethyl ammonium chloride (DADMAC) in the presence of tapioca starch on Fines/Filler Retention.

Factor B	Factor A							
	Flocculant (kg/t) (C-PAM)							
Coagulant (kg/t)Poly DADMAC	Low (0.4)	Medium (0.7)	High (1.0)	Low (0.4)^2	Medium (0.7)^2	High (1.0)^2		
	35.48	38.97	42.77	1258.83	1518.66	1829.27		
Low (0.8)	36.32	41.2	53.11	1319.14	1697.44	2820.67		
	37.46	40.83	53.19	1403.25	1667.09	2829.18		
	34.06	38.63	58.52	1160.08	1492.28	3424.59		
Medium (1.4)	38.4	38.8	54.82	1474.56	1505.44	3005.23		
	39.2	39.6	52.79	1536.64	1568.16	2786.78		
	40.45	37.81	44.79	1636.20	1429.60	2006.14		
High (2.0)	33.54	49.84	38.95	1124.93	2484.03	1517.10		
	36	54.69	41.06	1296.00	2991.00	1685.92		

Table A5: Summation of all the trials for Fines/Filler retention

Factor B					
Coagulant (kg/t)Poly DADMAC	Floce	ulant (kg/t) (C-l	Sum of Rows		
Coaguiant (kg/t): Ciy DADinAC	Low (0.4)	Medium (0.7)	High (1.0)		
Low (0.8)	109.26	121	149.07	379.33	
Medium (1.4)	111.66	117.03	166.13	394.82	
High (2.0)	109.99	142.34	124.8	377.13	
Sum of Columns	330.91	380.37	440	1151.28	Sum of All runs

Table A6: Analysis of Variance to study the significance of flocculant cationic polyacrylamide (C-PAM) and coagulant poly diallyl dimethyl ammonium chloride (DADMAC) in the presence of tapioca starch on Fines/Filler Retention.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F0	F-Critical	ANOVA
Coagulant (Poly DADMAC)	19.89	2	9.95	0.59	3.55	Not Significant
Flocculant (C-PAM)	669.71	2	334.85	19.96	3.55	Significant
Interaction	384.41	4	96.10	5.73	2.93	Significant
Error	302.01	18	16.78			
Total	1376.01	26				