Christin Zscherneck

Evaluation of functionalized PCC fillers on the papermaking properties of Eucalyptus Kraft pulps

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UNIVERSIDADE DE COIMBRA

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Abstract

The aim of this work is to develop and evaluate a new filler for the paper industry. This new filler is obtained through the surface modification of PCC with silica via the sol-gel method. Depending on the process conditions, different amounts of silica can be deposited on the surface of PCC. In this study, silica modified PCC (with 28 wt%) was produced and compared with unmodified PCC and previously prepared 16% silica modified PCC.

Thermogravimetric analysis, SEM imaging and particle size determination were performed to determine and confirm the silica deposition on the surface. The silica modification shifted PCC's zeta potential from 7 mV to -40 mV. In order to determine the best additives for paper production, drainage and retention tests were performed in a DDA, which lead to the choice of Percol as the best retention agent. Therefore, handsheets using Percol were produced with different silica modified PCC, as well as unmodified for control. The addition of retention aid in the handsheet former proved to be inefficient since retentions below 60% were obtained, whereas in the DDA the retention was always higher than 90%. Therefore, different polymer addition procedures were experimented, and for higher consistency conditions, retentions of up to 85% filler were achieved.

The use of silicated PCC increased bulk and improved ALL mechanical properties, even at slightly higher filler loading. Other properties were not detrimentally affected, with perhaps the exception of opacity that seems to slightly decrease. Another interesting conclusion is that it seems to exist an optimum amount of silica deposition on the filler surface, as 16% silica content seems to result in the best properties. In fact, for this silicated PCC, tensile index increased up to 50% when compared to unmodified PCC, whereas handsheets with 28% silicated PCC only improved tensile by 8-10%.

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1 Introduction

1.1 Motivation

Inorganic fillers have innumerous applications in paper products. For instance they can be engineered and used as functional agents conferring special characteristics to papers such as flame retardant, deodorant, antimicrobial, magnetic and conductive properties. However, their biggest use is as filler for writing and printing papers. This function is extremely important not only because fillers improve the papermaking process' economics by lowering the production cost, but also because they improve several optical, aesthetic and printing properties (such as formation, opacity, brightness, printability, smoothness, gloss, etc) that otherwise would not be achievable. However, the incorporation of mineral fillers in paper has certain disadvantages, mainly the decrease in the fiber-to-fiber bonding and bulk, both of which will have a negative effect on paper's mechanical properties (tensile, stiffness, tear, burst, etc). Therefore the optimum amount of filler (20-25%) will always be dependent on a compromise between hindered mechanical properties and improved aesthetics, optical and printing properties and cost. In order to overcome the loss of mechanical properties, fillers' surface can be chemically modified in order to improve the fiber-to-filler-to-fiber bonding, thus allowing for a greater amount of filler to be used without detrimentally affecting the mechanical properties. This modification needs to be efficient in terms of production cost and operating conditions (retention) without hindering the optical properties. If such a filler modification is successful, and filler amounts can be increased without loss of mechanical properties, its amount will still be limited due to bulk constrains. Therefore, the motivation for this work is to develop a new filler (by doing the surface modification of existing filler, namely precipitated calcium carbonate (PCC)) that is able to improve the fiber-to-filler-to-fiber bonding, thus minimizing the negative effect that fillers have in the mechanical properties of paper. By doing so, the filler amount can be increased, which would translate in vast savings.

1.2   Objective

The goal of this work is to evaluate both the efficiency of modifying the surface of PCC with silica and the effect of silica-modified PCC particles on filler-to-fiber bonding in paper, retention, paper strength and optical properties such as brightness and gloss. Additionally, the filler loading is eventually to be increased.

Therefore, silica is to be deposited on the surface of scalenohedral (rosette-shaped) PCC particles using an in situ sol-gel method. The modified and unmodified filler particles will be characterized in terms of their morphological and chemical characteristics, flocculation and retention in the final product, when adding internal sizing and retention aids according to those used in the paper industry. Furthermore, laboratory handsheets will be produced and structural, mechanical, optical and printing properties evaluated.

1.3   Outline / Structure of the document

This documented has been divided into the following chapters:

- ♦ 1 Introduction
    - ◊ The chapter serves to explain the purpose of the study and how it was structured.
- ♦ 2 Literature Review
    - ◊ In this chapter, previous studies in the area of the present work regarding PCC filler modification have been reviewed.
- ♦ 3 Materials and Methods
    - ◊ Materials and Methods used in this work were described in this chapter, so that results obtained can be reproduced by others.
- ♦ 4 Results and Discussion
    - ◊ Results regarding the PCC characterization and the influence of filler modification on drainage, retention and paper properties are presented and discussed.
- ♦ 5 Conclusions
    - ◊ This chapter summarizes the conclusions from all results.

- ♦ 6 Future work
  - ◊ Several suggestions of work that was not possible to perform in the present study are given.
- ♦ Appendixes
  - ◊ This chapter includes data and information that could be important for better understanding of this work.

2 Literature review

2.1 Papermaking

In its broader definition, paper is every material made of cellulose fibers derived mainly from wood, rags and certain grasses, deposited on a screen from an aqueous suspension. Paper can be processed in several different ways, from flexible sheets for printing, drawing, wrapping or cover walls, to sturdy resistant sheets used for packaging of goods, in the production of money, personal cleaning products (tissue paper), food industry and specialty products (cigarette paper, sandpaper, magnetic and conductive paper, antibacterial paper etc). Its applications are very vast, but printing papers are still the most relevant paper product and wood is the main source of cellulosic fibers [1].

Papermaking is a complex process in which paper is produced from wood (or other cellulosic fiber source), water and chemicals. The process starts with the production of pulp using a chemical and/or mechanical process. High quality printing papers are usually produced using high quality chemical pulps. This pulp is mixed with recycled production (broke), chemicals, fillers and water and fed to a paper machine, where the paper web is formed by the removal of water. The removed water is recycled back into the production process [1,2].

Initially the suspension's consistency is of about 0.1-0.2% and as the paper web travels through the paper machine where water is removed, forming a paper sheet. In the forming section, water is removed by gravity, pulsation and vacuum, to consistency values of approximately 15-25%, depending on paper grade, paper machine design and furnish composition (fiber and additives used). Afterwards water is removed by mechanical compression in the press section, achieving consistency values of 35-56%, also depending on paper grade and machine design. The remaining water (roughly 3-4% of the all water used in the process) is removed by evaporation in the dryer section, reaching final consistency values of 93-97% [1]. Although only a small fraction of water is removed in the dryer section, this is the most expensive step in the paper production process as it is highly energy demanding. Therefore any gain in

consistency prior to the dryer section translates into serious energy, and consequently money, savings. As a rule of thumb a 1% gain in consistency prior to the dryer section translates into a 4% energy reduction required for drying the paper [1].

Paper does not only contain fibers, but also non-fibrous components such as wet and dry strength resins, dyes, pigments and fillers (depending on paper grade) [1]. Dry strength additives such as starch and polymers promote hydrogen bonding between fibers and wet strength resins such as alkyl ketene dimer (AKD) and alkyl succinic anhydride (ASA) help increasing the strength properties of paper by forming covalent bonds between cellulose fibers. Dyes are added to stock in order to impart a color to the final product [3]. Fillers and pigments give opacity, brightness and better printability to the Paper. Fillers are added into the furnish and pigments are applied in surface coating.

2.2   Characteristics and function of filler

Inorganic minerals are an important additive in the production of paper, comprising up to 20-25 wt% of fine writing and printing papers, being the second most important component in paper. These inorganic minerals have a high influence on paper properties, and can be introduced into paper as a coating (pigments) or added to the furnish suspension before the paper machine (fillers).

Fillers reduce cost, by replacing fibers with a much cheaper material; promote energy savings (which also translates into cost reduction), by improving drainage and allowing for higher consistencies prior to the drier section; and improve some end-product properties such as opacity, brightness, gloss, smoothness, bulk, printability, dimensional stability and aging [1,4,5]. Furthermore, the use of specialty or functionalized filler(s) can be optimized to create smart papers, such as antibacterial paper [6], deodorant paper [7], antimicrobial paper [8], fire retardant paper [9], magnetic paper [10] and conductive paper [11], among others.

Fillers can also be of organic nature. However, organic fillers are only suitable for special applications due to their high price. Therefore, inorganic fillers are the dominant type used in papermaking [4].

The most important fillers are silicates (such as kaolin clay, talc and bentonite), carbonates, sulfates (such as calcium aluminum sulfate – alum) and oxides (such as titanium dioxide) [13].

Kaolin clay is a layered silicate mineral that is mostly used for paper coatings and has a brightness of 75-85 %. Kaolin is especially useful to confer high gloss and smoothness to the paper, at the cost of bulk, especially when subjected to (super) calendaring. Kaolin can be used over a wide range of pH. Talc is a layered magnesium silicate with a high specific surface area and can be used either as filler, coating or as pitch control. It has a brightness of 70-90 % and it also contributes for improving smoothness and opacity when used as filler. The optimum pH range for its use is 7-7.5. Bentonite is chemically similar to clay but with a very high negative surface charge and a large active surface. Therefore, although it is sometimes used as coating of very fine papers, it is mostly used as pitch control and as a retention aid (in dual systems in conjunctions with cationic retention aids) or in wastewater treatment as it bonds with impurities. Titanium dioxide is an artificial pigment of very high opacity and brightness but very expensive, and therefore not as often due to its high costs. Calcium carbonate, along with clay, is one of the most important pigments in the paper industry. It has a production yield of almost 100 %, it is available in high quantities and therefore is a low-cost filler. It is used for neutral or alkaline papermaking both when added directly to the furnish, and also as a coating pigment. It has a brightness of 85-97 %. Ground calcium carbonate (GCC) is the natural-occurring anionic form of the pigment, and precipitated calcium carbonate (PCC) is the man made version of it. PCC is brighter than GCC and it is typically produced on site from calcinated calcium carbonate, which allows for a great reduction of cost. In the Portuguese paper mills, PCC is the most used filler, and therefore PCC was the filler chosen to undergo surface modification in the scope of this study. The following figure (Figure 1) shows the functional properties of calcium carbonate, kaolin and talc [14].

Figure 1 - Functional properties of paper fillers [14]

	Calcium Carbonate	Kaolin	Talc
ISO-Whiteness [%]	85-97	75-85	70-90
refractive index	1.65	1.55	1.57
aspect ratio	1	5-15	5-100
pH	8.6	3-5	7
abrasivity AT 2000 [mg]	3-20	10-20	10

2.3 Calcium carbonate

Calcium carbonate is a salt produced by the reaction of carbon dioxide with burnt ($CaO + H_2CO_3 \rightarrow CaCO_3 + H_2O$) or slaked lime ($Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2 H_2O$). Calcium carbonate decomposes in acidic environment like all carbonates with the following reaction: $CaCO_3 + 2 HCl \rightarrow CaCl_2 + CO_2 + H_2O$. It is polymorphous and can occur in the three crystal modifications aragonite, calcite and vaterite, calcite being the dominant form in nature and is mostly found in limestone rocks. Calcite is one of the most abundant minerals in earth's crust and can have three different crystal forms (Figure 2): rhombohedron (a), scalenohedron (b) and prism (c); the last two being the most common.

a   b   c
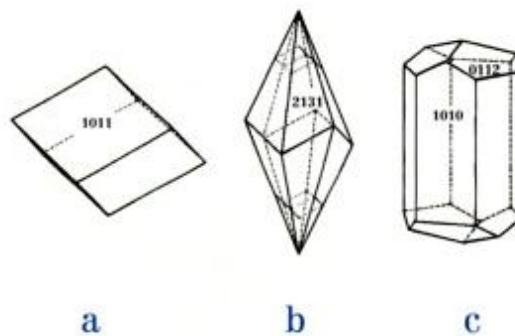
Figure 2 – Crystal structures of calcite [14]

Calcium carbonate is furnished in two forms, ground and precipitated. Commercial GCC is typically treated with a dispersant, giving a negative charge to the particle surfaces. Therefore, they are colloidally stable due to electrostatic repulsion, but do not deposit onto negatively charged fibers and retention aids are necessary to incorporate GCC into paper. PCC is typically not treated and can

have a positive charge in pure form, which promotes its deposition on fiber surfaces. But its charge is not sufficiently strong to provide a stable colloidally stable dispersion, which leads to aggregation of PCC particles in water [12].

Ground calcium carbonate (GCC) is the natural occurring form of calcium carbonate and precipitated calcium carbonate is synthesized using the following reaction [13]:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
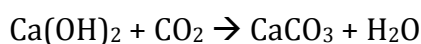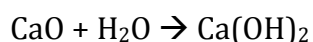
Precipitated calcium carbonate is used in alkaline papermaking, as it decomposes in acidic environments. It has the best quality/price relationship compared to other fillers and offers therefore economic advantages.

Papers containing calcium carbonate as filler show a resistance to acid decomposition, which results from its buffer effect on mineral acids (such as sulphuric acid). The yellowing and ageing of the paper can be slowed down by 90 %, therefore complete decomposition of the paper can be avoided. However, PCC may be contaminated with residues from calcium hydroxide that has not reacted during precipitation, in which case the pH at the surface of the filler can be as high as 12 or above. This can lead to undesired chemical reactions with other components in the paper and result in yellowing [14]. Another advantage is the possibility of cheap PCC production on-site at the paper mill [15].

2.4 Filler modification of PCC

Increasing the filler content has different advantages. On one hand, it allows to protect the environment by decreasing the fiber content in the paper. Therefore, extra pulping energy can be saved and the production capacity increased. The quality of most paper grades can be enhanced by improving opacity, brightness, gloss, porosity and printability. Furthermore, a sheet with higher filler content will drain and dry better and therefore energy in the dryer section can be saved.

However, increasing the content of filler in the paper reduces mechanical properties such as strength not only because of a lower fiber content in the sheet and therefore less fiber to fiber bonding, but also because the contact area between remaining fibers decreases. Higher filler content also favors dusting, abrasion and size demand because of the fillers' high surface area. Furthermore, filler retention is negatively affected leading to higher solid contents in the circulating system [16,4].

Due to the above-described reasons, filler content in the paper is typically limited to 20-25%. Studies have been done to modify the surface of filler surfaces with the purpose of increasing the filler content by improving fiber to filler bonding. Also, for functionalization of fillers their modification is indispensable. Modifications with the purpose of enhancing optical, mechanical, retention, drainage and acid tolerant properties have been done using inorganic substances, natural and synthetic polymers as modifiers.

2.4.1   Inorganic Substances

Calcium-chelating

As calcium carbonate decomposes in acidic environment, a modification of PCC with calcium-chelating agents, which are believed to reduce the solubility of PCC when applied to the surface, was patented by Passaretti [17] to obtain an acid-stabilized PCC filler. The objective of this invention is to produce acidic paper such as groundwood paper using modified PCC without having a negative impact on the final paper properties.

The modification process includes the addition of a calcium-chelating agent and/or a conjugate base (sodium hexametaphosphate) to calcium carbonate, followed by a weak acid (phosphoric acid), in a solid-liquid reaction and coating process. The new filler can be used in acidic or neutral papermaking, improving pigment scattering coefficient, opacity and brightness of the paper. The obtained filler is still less expensive than titanium dioxide and calcined clay.

Another way of producing acid-resistant PCC filler is done by using a weak base and a weak acid as modifiers (Wu [18]), where at least one of the components is derived from an organic polymeric acid and the preferred mixture of base and acid may be sodium hexametaphosphate / polymaleic acid, sodium polyacrylate/ phosphoric acid and sodium hexametaphosphate / polyacrylic acid.

Shen *et al* [15] used phosphoric acid / sodium hexametaphosphate and sodium silicate/ phosphoric acid/ sodium hexametaphosphate modified acid-resistant PCC in papermaking of deinked pulp derived from recycled newspaper and found that brightness could be improved comparatively to unmodified filler. Also, the system pH was lower when adding the filler slurry into the pulp compared to unmodified filler. They found that the best filler retention for the sodium silicate/ phosphoric acid/ sodium hexametaphosphate modified PCC according to the ash content and mechanical properties also showed best results for the same modified filler.

Salts

Chapnerkar [19] mixed the calcium carbonate slurry with a pH of between 11 and 12 first with a sodium silicate, then with gaseous carbon dioxide and then zinc chloride resulting in a surface-modified filler with precipitated silicate and excellent resistance to acid conditions.

In another patent Wu [20] described a second method for producing acid-resistant PCC adding aluminum salts such as aluminum sulfate, aluminum ammonium sulfate, aluminum potassium sulfate, chromium ammonium sulfate and aluminum hydroxychloride among others. It is believed that the acid resistance is a result of the inactivation of the PCC surface.

Drummond [21] patented a method to produce a modified PCC slurry with a pH of between 6 and 7 for the use of acidic paper production. The slurry consists of water, PCC and an acid-stabilizer (water-soluble calcium salt), which can optionally be used together with a weak acid or chelating agent. Preferred

calcium salts include calcium sulfate, calcium acetate, calcium nitrate, calcium citrate, calcium halide (e.g. calcium chloride), and mixtures thereof.

An acid resistant PCC slurry can also be prepared by modifying PCC with sodium aluminate (typically containing the Al^{3+} ion in an ionic hydroxy- or oxo-complex) and a weak acid such as phosphoric acid, metaphosphoric acid, hexametaphosphoric acid, ethylenediaminetetraacetic acid (EDTA), citric acid, sulfurous acid, boric acid, acetic acid, and mixtures thereof (Snowden *et al* [22]). With this method, the optical properties of neutral to weakly acidic paper can be improved using this composition.

Shen *et al* [23] found another way of producing acid-resistant PCC by using sodium silicate / zinc chloride based modifiers and investigated its use in papermaking of deinked pulp derived from recycled newspaper. When using 10 wt%, 3 wt%, 1 wt% and 0.2 wt% of sodium silicate, zinc chloride, sodium hexametaphosphate and phosphoric acid, respectively, the acid-resistant property of the filler could be improved significantly under certain modification conditions (temperature, PCC concentration and aging time), evaluated using alum consumption and pH measurements. Also, brightness and light scattering could be improved while the mechanical properties were very little influenced.

Acid resistant PCC is not the goal of this study, since most of the current processes use alkaline conditions. Therefore, other methods need to be presented.

Silica

Gamelas *et al* [24] used an in situ sol-gel method to precipitate silica on the surface of PCC via hydrolysis of tetraethyl orthosilicate (precursor) in ethanol/water solutions under alkaline conditions. They obtained a modified filler with a silica content of up to 25 wt% without major alterations in the particle size distribution. However, the effect of this new modified filler on the paper properties has not yet been investigated. This modification is the basis for this study, and the same procedure will be used to modify the PCC particles. However, not only the characteristics of the new modified filler will be studied, but also their impact on retention, formation and paper properties. Distinct

amounts of silica as well as different retention aids and varying strategies of laboratory sheet formation will be used, as detailed later.

2.4.2 Natural polymers

Starch and starch derivatives

Zhao *et al* [16] coated the PCC filler with swollen starch giving the filler a shell structure of starch gel. For a filler content of 20 wt% they achieved a tensile strength of 21 Nm/g, while handsheets with an unmodified PCC content of 18 wt% only achieved 14,5 Nm/g. Tensile strength still decreased with increasing PCC content. The opacity and brightness could be increased with higher PCC content without obvious detriment to mechanical properties of paper.

Kurrle *et al* [25] treated the surface of calcium carbonate with an anionic starch-soap complex, which allowed the papermaker to increase filler content and improve sizing efficiency. The complex is precipitated onto the surface of the filler by replacing sodium ions by calcium ions, which provides bonding sites for sizing agents, thus improving water repellency. With this method, coated and uncoated fine papers, bleached board products and other paper grades could be produced with increased filler loading. Besides improved size efficiency the advantages of this modification are improved smoothness and print quality, less fiber consumption and possibly elimination of cationic starch as a wet end additive.

Laleg [26] modified fillers such as PCC with a swollen starch-latex composition prepared in presence or absence of anionic or cationic co-additives. The swelling of the starch must be controlled in terms of temperature, pH, mixing and mixing time in order to avoid rupture of the starch granules. This mixture is added to the filler suspension, and only during drying of the paper the starch granules with PCC particles will rupture. Solid components will be bond in the sheet by liberating amylopectin and amylose macromolecules during rupture. Filler retention and strength properties of paper could be improved with this method comparatively to the use of starch or latex alone, and filler loading could be increased in paper as seen in Figure 3.
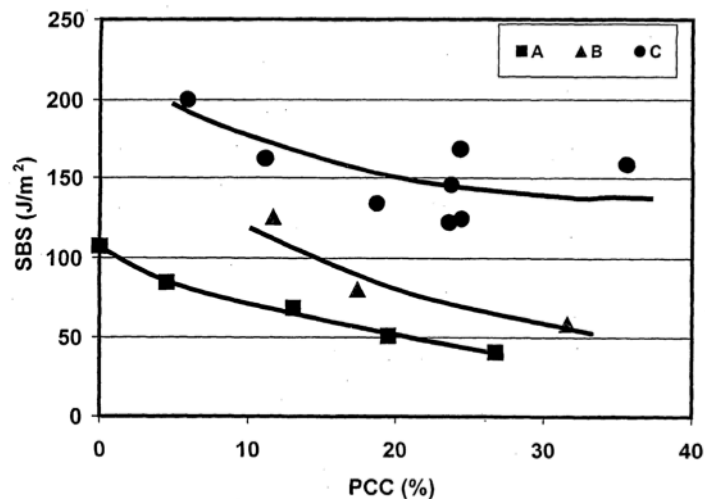
Figure 3 – Scott Bond Internal Strength vs filler content for: A – normal PCC, B – PCC modified with 1.5% starch, C – PCC modified with swollen starch-latex composite. Adapted [26]

Cellulose and cellulose derivatives

Carboxymethyl cellulose in combination with alum can also be used to improve filler retention and optical properties such as opacity and brightness without impairing mechanical properties of paper (Shen *et al* [27]). It was shown that, compared to unmodified filler, the modified filler particles were more effectively adhered to the pulp fibers.

Myllymäki *et al* [28] provided new composite materials such as paper and board derived from water-insoluble polysaccharides and light scattering materials such as fillers. With this method, filler loading could be increased and its retention improved.

Xanthan Gum or anionic guar gum

Fairchild *et al* [29] modified a cationic PCC with an anionic or anionically modified polysaccharide, such as xanthan gum or anionic guar gum, for the use in alkaline papermaking. The breaking length of handsheets improved significantly using treated PCC comparatively to handsheets with the equivalent amount of untreated PCC. The modification was performed at different

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temperatures and increased temperature additionally improved paper strength properties.

2.4.3   Synthetic Polymers

Niinikoski *et al* [30] did a pretreatment of filler using a hydrophobic polymer in order to create a hydrophobic film on the filler surface and to make it more difficult for water to penetrate into the filler layer. The polymer is produced in presence of a polysaccharide, such as starch, that acts as a stabilizing agent, and is made from a monomer mixture comprising 40 to 70 % acrylates and 30 to 60 % styrene. The polymer is then added as a solution or dispersion at a temperature of typically 0 to 70 ℃, thus generating a film on the filler surface. These authors claim that this method not only improves hydrophobicity of paper but also reduces linting, and enhances wet and dry strength of paper.

2.5   Sol-gel method

The sol-gel method allows to produce inorganic or organic-inorganic composites at a fairly low temperature. It consists of hydrolysis of the constituent molecular precursors and polycondensation to glass-like form. The precursors consist of a metal or metalloid element surrounded by various ligands. The most frequently used ligands belong to one of two classes: alkyl (methyl, ethyl, etc.) and alkoxy (methoxy, ethoxy, etc.). A precursor, where the metal or metalloid element is surrounded by an alkoxy ligand, is called metal alkoxide. The most common metal alkoxides are silicates, aluminates, titanates and zirconates, as they have a high reactivity towards water. Since they have a metal- oxygen- carbon linkage, they are also called metalorganic compounds. The most typical example for a metal alkoxide is silicon tetraethoxide (or tetraethyl orthosilicate TEOS) $Si(OC_2H_5)_4$. The hydroxyl ion becomes attached to the metal ion as shown in the following hydrolysis reaction [31]:

$$Si(OC_2H_5)_4 + H_2O \rightarrow HO\text{-}Si(OC_2H_5)_3 + C_2H_5OH$$
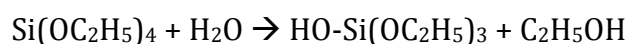
Several works have been done using the sol-gel method with tetraethyl orthosilicate to modify materials surfaces. Sol-gel films can be used for the production of e.g. protective coatings [32], organic silane modified silicas [33]

and silica-aerogels for thermal superinsulators in solar energy systems, refrigerators, thermo flasks, efficient catalysts and catalytic supports, among others [34]. Optimized TEOS based sol-gel matrices are used for development of optical biosensors in the field of medical technology [35], novel organic-inorganic hybrid materials [36] and low-cost membranes for proton exchange membrane fuel cells able to work at higher temperatures than 100 ℃ [37].

3 Materials and Methods

The purpose of this study was to evaluate the effect of silica-modified PCC on drainage, retention and optical and mechanical paper properties. This work is divided into three parts. First, the modification of PCC particles and their characterization in terms of silica content, particle size, zeta potential etc. had to be done. Then, drainage and retention tests were performed on the Dynamic Drainage Analyzer, using different polymers and to choose the most efficient retention aids for improved retention results. Handsheets were produced on the batch handsheet formers in the research center RAIZ with the chosen polymers, and the retention on the handsheets and paper properties were determined. For all studies, the filler content was 20 %.

3.1 Raw materials and additives

Fiber

The fiber furnish was mainly obtained from eucalyptus wood using the Kraft cooking method, followed by ECF bleaching and was supplied by a domestic pulp and paper mill. The pulp used for all trials was collected at the same time to guarantee the same properties resulting from cooking and bleaching conditions. At the time of collection the fiber was unrefined and treated only with additives such as biocides. The refining was done in a PFI mill in order to achieve a refining degree of 33 °SR.

Mineral filler

The mineral filler used was a scalenohedral precipitated calcium carbonate (PCC). It was supplied by a paper mill as an aqueous suspension, which was stirred to homogenize, filtered using Büchner funnel (0.2 µm) and dried in the oven at 105 °C for 24 hours. Then it was ground in a porcelain crucible before direct use or modification reactions. The characteristics of the PCC particles

were determined according to the methods described in section 3.2.2 and evaluated in section 4.1.

PCC modification

For the surface modification of PCC, tetraethyl orthosilicate (TEOS, 98%), absolute ethanol and ammonia (25%) from Sigma-Aldrich were used, as detailed in section 3.2.1.

Internal Sizing agents

In order to assess the strength properties, handsheets were prepared using pulp fibers and PCC as filler, but also internal sizing agents and retention aids. For internal sizing an alkenyl succinic anhydride (ASA) was used, which was provided by a paper mill. Because of the high tendency to hydrolysis with water, ASA needs a protective colloid, usually cationic starch, with which the ASA solution needs to be stabilized [13]. Therefore, ASA is added to the starch solution during preparation.

Strength agents

For the retention, drainage and formation tests, cationic starch in powder form was used. The starch solution was prepared from powder as described in Appendix 1 and used to prepare the ASA solution, in order to improve retention and resistance of the sheet.

Retention aids

Retention aids form bonds with fiber surfaces and fines, fillers and internal sizing agents. They are often polymers that rely either on high charge density (such as polyethylenimine or polyDADMAC) or, in case charge density is low, on high molecular weight (such as cationic or anionic polyacrylamides) [3].

Eight different retention aids were used in this study, because the zeta potential of the PCC changed drastically after modification with silica. Therefore the retention aid needed to be adapted according to that change. Two cationic

polyacrylamides (CPAM), Percol supplied from Rivaz Química, S.A. and E2++++
(intrinsic viscosity 977 ml/g, charge density 40%, degree of branching = 4) from
AQUA+TECH, and three anionic polyacrylamides (APAM) Z0 (M = 24 x 10^6 g/mol;
charge density 50%), T1 (M = 15 x 10^6 g/mol; charge density 20%) and X0 (M =
25 x 10^6 g/mol; charge density 30%, linear), which were also supplied from
AQUA+TECH. Furthermore, an amphoteric polymer (M = 2.85 x 10^6 g/mol,
viscosity 4900 cP) supplied by North Carolina State University was used. Two
metallic salts, aluminum sulfate and iron sulfate, were purchased commercially
and also studied.

3.2 Experimental Methodology

3.2.1 Surface modification of PCC with silica

For the surface modification of PCC, distilled water, ethanol and ammonia were
mixed inside a beaker under continuous agitation (200 rpm). PCC followed by
TEOS were added and the mixture was agitated for 24 hours at room
temperature ($\sim$ 21℃), starting from the moment TEOS is added. The beaker
needed to be closed with Parafilm to minimize ethanol and ammonia
evaporation. The obtained solid was filtered and washed with 300 ml ethanol
and dried in a desiccator under vacuum for 4-5 days, before it was gently ground
in a porcelain crucible. The exact amounts of each component are shown in Table
1.

The final solution had a TEOS concentration of 0.2 mol/dm^3 and an ammonia
concentration of 0.3 mol/dm^3.

Table 1 – Amounts of chemicals used for the modification of 15 g PCC

Added component	Amount
Water	135 ml
Ethanol	1265 ml
Ammonia	33.7 ml
PCC	15 g
TEOS	67.5 ml

3.2.2 Characterization of PCC particles

The modified and unmodified PCC particles were characterized using different techniques, such as laser diffraction for Particle Size, Zeta-Potential, Scanning Electron Microscopy (SEM) for surface imaging, Thermogravimetric Analysis (TGA) for decomposition rates, and spectroscopy for Brightness measurements. Elemental analysis was also carried out to determine the presence of certain elements and their quantities, but not for all samples.

Laser diffraction

The particle size was determined by laser diffraction spectroscopy using Malvern Mastersizer 2000. The Malvern Mastersizer 2000 can measure particle sizes in the range of 0.02 – 2000 μm in form of emulsions, suspensions or powders.

During the laser diffraction, the particles are passed through a focused laser (He-Ne, 640 nm) beam (Figure 4). The light is scattered by the particles at an angle that is inversely proportional to their size. 52 photosensitive detectors measure the angular intensity of the scattered light. The particle size is calculated using the map of scattering intensity versus angle with the Lorenz-Mie theory [38].
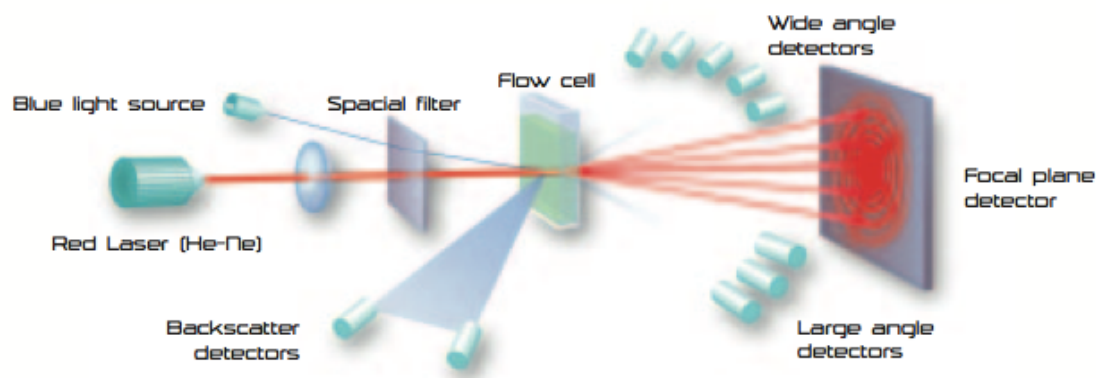
Figure 4 – Principle of the particle size measurement [38]

A suspension of 1% (w/w) of PCC in distilled water was prepared, where one drop of ammonium polycarbonate (Targon) was added to the PCC as a dispersant before adding the water. The suspension was first stirred using a magnetic stirrer for 20 min and then placed in a sonication bath for 15 min (50 kHz). A small volume of the suspension was added to around 700 ml of water in

the equipment vessel until the reached obscuration was around 10-20%. The measurement was carried out under stirring (2000rpm).

Zeta Potential

Zeta potential is based on the measurement of the magnitude of the electrostatic attraction or repulsion between particles evaluated at the double layer. This parameter is known to affect the stability of a suspension, emulsion or dispersion. It gives insight into causes of dispersion and flocculation and retention aids can be chosen accordingly, especially after PCC surface modification [39].

For the zeta-potential measurements the Zetasizer nano ZS from Malvern Instruments was used .

Again, a suspension of 1% (w/w) of PCC in distilled water was prepared, stirred for 20 min and placed in the sonication bath for 15 min (50 kHz). A low volume of the prepared suspension is filled into the loading cuvette and placed into the equipment for measurement.

Scanning Electron Microscopy

The surface of the PCC particles was observed using scanning electron microscopy. The surface of a specimen is bombarded with an electron beam, and the back-scattered electrons are collected and displayed at the same scanning rate on a cathode ray tube. The surface needs to be electrically conductive, and therefore nonconductive materials need to be coated with a thin metallic coating. Magnification from 10 to 50 000 times can be achieved [40].

The images were obtained on a Jeol model JSM-5310 and the samples were sputter coated with gold before the performance of the test.

Thermogravimetric analysis

Thermogravimetric analysis is applied to determine the amount and rate of weight changes of a material in function of temperature (up to 1000 °C) or time

in a controlled atmosphere. The method is fast, accurate and its results are reproducible [41].

In this study, this analysis was used to determine not only the amount of silica at the surface of modified PCC, but also water amounts (due to silica's hygroscopy) and additive amounts coming from the PCC suspension. The analysis was performed on a TGA-50 Shimadzu thermobalance between 25 °C and 900 °C with a heating rate of 10 °C/min under air atmosphere.

Spectroscopy

For brightness measurements, tablets of PCC powder were made and measured using the L&W Elrepho equipment.

Elemental Analysis

Elemental Analysis was done to quantify hydrogen, carbon, nitrogen, sulfur and oxygen in the PCC samples before and after modification using the EA 1108 elemental analyzer from Fisons Instruments. The sample is burned at slightly above 1000 °C in a helium flow with the addition of oxygen right in the beginning to guarantee full combustion. The combustion gas mixture passes through an oxidation catalyst zone and then through a subsequent copper zone, where nitrogen oxides and sulphuric anhydride (eventually formed during combustion) are converted into elemental nitrogen and sulphurous anhydride and the oxygen excess is being retained. The components of the combustion mixture are separated by gas chromatography and quantified by a thermal conductivity detector in the sequence N_2, CO_2, H_2O and SO_2 [42].

3.2.3   Retention and Drainage (DDA)

To study the drainage and retention behavior of a fibrous suspension, a Dynamic Drainage Analyzer (DDA) from Eurocon, available in Raiz, was used. The drainage is defined as the time that is necessary to drain the water of the suspension until a sheet is formed and until air passes through the sheet.

Retention is defined as the ratio between the quantity of material that effectively is retained in the final fibrous matrix and the quantity of material that was added to form it [43]. Drainage refers to the ease with which water is released from the paper furnish.

For the drainage and retention tests, a suspension of about 1 % solids content is introduced into the equipment with the quantities and addition times shown in Table 2 and Table 3. Information about stirrer settings is shown in Table 19 and Table 20 of Appendix 2. The fiber and PCC suspension were prepared to a concentration of 1%, the starch solution to around 3%, the ASA concentration in the starch solution to around 8×10^{-4} % and the polymer solution was prepared to a concentration of 0.025 % (w/w). The preparation of the starch suspension with ASA and of the polymers is described in the Appendix.

Table 2 – Amounts of each component for each DDA trial and addition times

Component	Industry scale kg/ton of paper	Industry mode %	Laboratory Scale %	Laboratory Scale g
Fiber	786.85	78.69	79.11	4
PCC	196.71	19.67	19.77	1
Starch	12.79	1.28	0.99	0.05
AKD	0.98	0.10	-	-
ASA	-	-	0.10	0.005
Polymer	0.20 (Percol)	0.02	0.02	0.001
Bentonite	2.46	0.25	-	-

The addition times of each component to the equipment are shown in Table 3.

Table 3 - Addition times for DDA trials

Component	Addition time (s)
Fiber	0
PCC	0
Starch	120
ASA	120
Polymer	285

3.2.4 Production of Handsheets

Handsheets were made using the equipment (handsheet former) of Raiz, Aveiro. 30 g OD pulp were disintegrated in 2.5 l of water and diluted to approximately 8 l. The consistency of the suspension was determined by weighing a handsheet made of 500 ml of suspension. For handsheets that were prepared with additives such as PCC, starch and ASA, the addition times were the same as for the drainage tests. For the addition of polymer, different procedures were used, as its quantity and contact time needed to be optimized for modified PCC.

Therefore, a suspension of fiber and PCC (necessary for a handsheet with 1,6 g dry weight equivalent to 80 OD g/m² grammage) was prepared and stirred (magnetic stirring) for 120 s. Starch with ASA was added and stirred for another 165 s. Table 4 shows the amounts to be used for each handsheet. 6 different series were prepared for the addition of polymer, as detailed in Table 5. Also, a series of handsheets made only from fiber (Serie F, Table 5) and a series containing fiber, starch and ASA (Serie FA) have been prepared as references.

The filling time of the former was 17s, stirring time was 5 s, decantation was 5 s and drainage 3s.

Table 4 – Amounts of each component per handsheet for series 1

Component	Quantity Former (g)	Quantity DDA (g)
Fiber	1.27	4
PCC	0.32	1
Starch	15.8×10^{-3}	50×10^{-3}
ASA	1.58×10^{-3}	5×10^{-3}

Table 5 – Polymer addition conditions

Serie #	Quantity Polymer (g)	Addition spot	Contact time* (s)
F	0	---	0
FA	0.32×10^{-3}	Former	0+13
1	0.32×10^{-3}	Former	0+13
2	0.40×10^{-3}	Former	0+13
3	0.47×10^{-3}	Former	0+13
4	0.32×10^{-3}	Beaker	5+20
5	0.32×10^{-3}	Beaker	10+20
6	0.32×10^{-3}	Former (10s stirring)	0+18

- * - Contact time in beaker + contact time in former

3.2.5 Characterization of paper properties

The handsheets were characterized in terms of structure (grammage, thickness, bulk, permeability and roughness), optical properties (opacity, brightness, yellowness and light scattering coefficient) and mechanical properties (tensile, burst and tear strength, stiffness and internal resistance), using the common ISO or TAPPI standards (Table 6). The conditions of the laboratory (humidity = 50 ± 2 %, T=23 ± 1°C) are according to NP EN 20187, and the handsheets were cut according to standard ISO 5269/1.

Table 6 – Standards and equipments for measured paper properties

	Property	Unit	Equipment	Standard
Structural	Grammage	g/m^2	Scale Mettler HK160	ISO 5270
	Thickness	μm	Micrometer SE 051 D2	ISO 534
	Bulk	cm^3/g	Calculated	EN 534
	Permeability (Gurley)	s/100ml	Gurley SE 121	ISO 5636-5
	Roughness (Bendtsen)	ml/min	L&W Bendtsen	ISO 8791-2
Optical	Opacity	%	L&W Elrepho	ISO 2471
	Brightness R457	%	L&W Elrepho	ISO 2470
	Light scattering coefficient	m^2/kg	L&W Elrepho	ISO 9416
Mechanical	Internal Resistance	J/m^2	Scott Internal Bond Tester Model - B	TAPPI T 403
	Tensile strength	kN/m	Alwetron TH1 65F	ISO 1924/2
	Stiffness	kN/m	Alwetron TH1 65F	ISO 1924/2
	Stretch	%	Alwetron TH1 65F	ISO 1924/2
	Burst strength	kPa	Burst-O-Matic 04.BOM	ISO 2758
	Tearing Resistance	mN	Elmendorf 125	EN 21974

4 Results and Discussion

In this study, unmodified PCC (PCC 0) and silica modified PCCs were used. Various PCC modifications were done using approximately 20 g of filler, followed by a thermogram to determine the silica content on the filler surface. Therefore, the modified calcium carbonates are referred to as PCCx throughout the document, x being the amount of silica in percent on the surface.

4.1 Characterization of PCC particles

The PCC particles were characterized before and after modification in terms of particle size, zeta potential, thermal decomposition and elemental composition. Also, SEM was used to verify the difference of surface appearance before and after modification with silica.

Thermogravimetry

The test cycle for every sample was 20°C – 900°C at 10°C/min. Figure 5 shows the thermogram of unmodified PCC (PCC0). It shows a weight loss between 250°C and 580°C, which is due to the degradation of additives used in the synthesis process of PCC. Between 580°C and 840°C, weight decreases by another 42% due to degradation of calcium carbonate into carbon dioxide and calcium oxide [24]. The total weight loss is 44.06 at 900°C. The amount of PCC additives was 4.8 %, which was calculated as follows:

Equation 1 – Formula to calculate the amount of additives in the PCC sample

$$100 - [(\text{weight loss from } 580°C \text{ to } 840°C) \times 100.1 / 44.01],$$

where 100.1 g/mol and 44.01 are the molecular weights of $CaCO_3$ and CO_2, respectively.
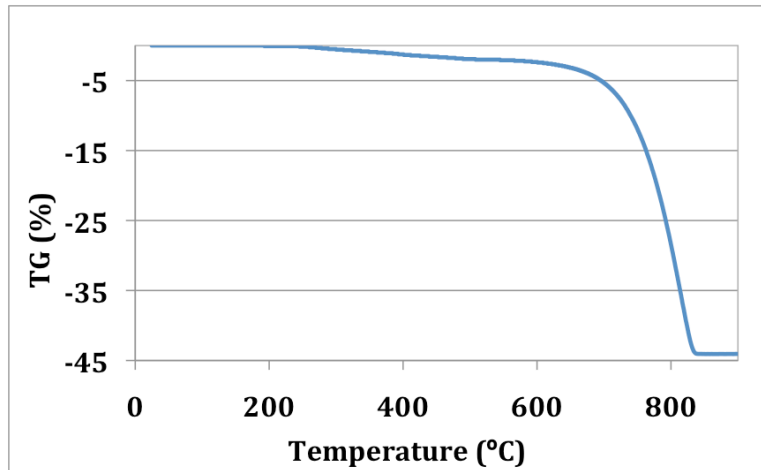
Figure 5 – Thermogram of PCC0

Figure 6 shows the thermogram of a PCC that has been modified with TEOS. A weight decrease between 0℃ and 200℃ can be observed, which corresponds to about 3% water of total weight. This was expected, as silica is very hygroscopic [44]. As for PCC0 there is a weight loss between 200℃ and 580℃, which corresponds to the additives used for PCC synthesis, and from 580℃ on degradation of CaCO₃ begins. The total weight loss of modified PCC (35%) is lower comparatively to unmodified PCC (44%), as silica does not melt up to a temperature of 1713℃ [45].
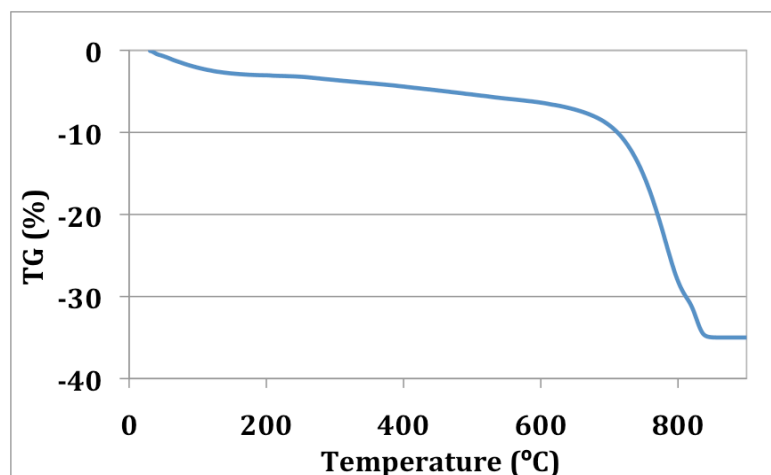
Figure 6 - Thermogram of PCC28

The quantity of silica (wt%) on the particle surface has been determined from the thermogravimetric plots using the following equation [24]:

28

$$100 - [(\text{weight loss from } 580°C \text{ to } 900°C) \times 100.1/44.0] - [(\text{weight loss from } 30°C \text{ to } 200°C)] - [\text{PCC additives percentage}].$$

The term [weight loss from 580°C to 900°C) x 100.1/44.0] corresponds to the relative amount of $CaCO_3$, taking into account the decomposition of $CaCO_3$ (100.1 g/mol) into CaO and CO_2 (44 g/mol). The weight loss between 30°C and 200°C is due to water release, and the quantity of PCC additives in wt% was already determined for the unmodified PCC and used for the calculation of the amount of additives for the modified PCC. As the weight fraction of PCC is now lower due to the silica, the amount of additives was only 3.31 %. The amount of silica was calculated to be 28.1 %. Therefore, this PCC is from hereon called PCC28.
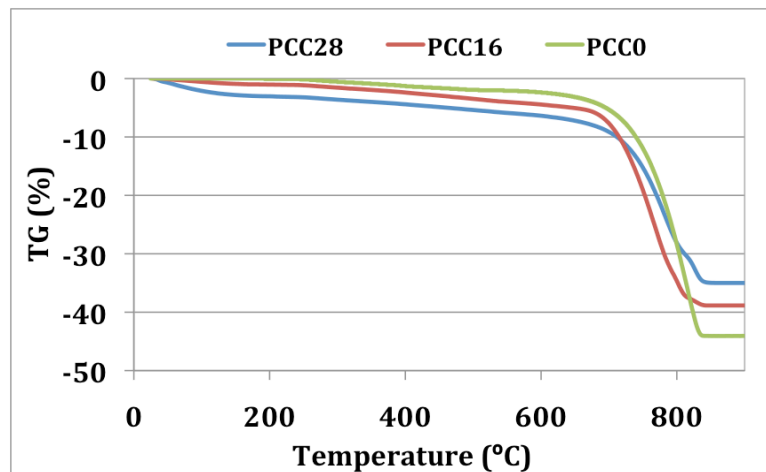
Figure 7 – Thermograms of PCC0, PCC16 and PCC28

Figure 7 shows the thermograms of PCC0, PCC28 and a PCC that has been modified in a previous study with an ammonia concentration of 0.1 mol/dm³. The silica content of this PCC was determined to be 15.6% and the weight loss corresponding to water (until 200°C) of this PCC was only 1%. That means that with a lower ammonia concentration the deposited amount of silica and therefore the amount of water also decrease, as already been published [24]. The PCC containing 15.6% is from now on called PCC16. It was used in this study to compare the influences of different silica amounts on the particle properties and retention and paper properties. This comparison can be helpful to determine the optimum silica content for later applications.

Figure 8 shows the PCC particles without any modification. The characteristic scalenohedral shape of the particles with a high degree of aggregation can be verified.
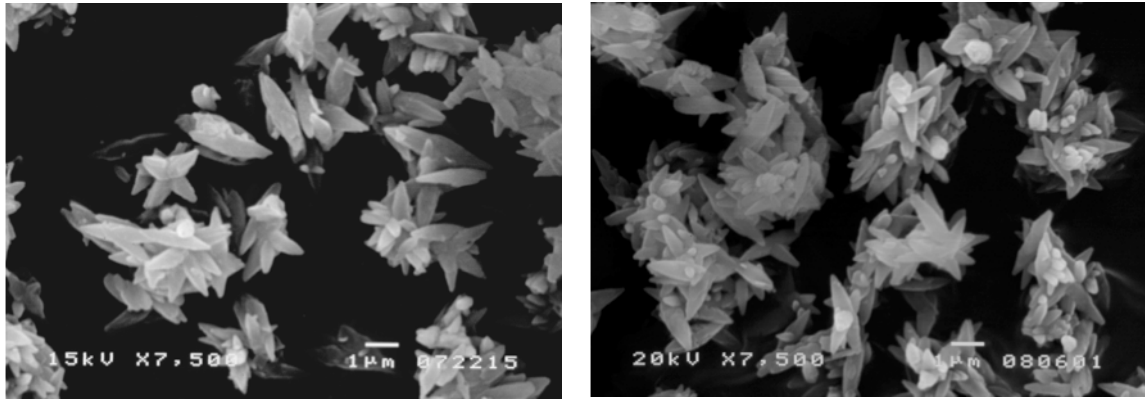
Figure 8 - SEM images of PCC0

Figure 9 shows the modified PCC with 15.6% silica and the scalenohedral shape of the particles is not as well defined as without silica. It appears that the silica forms a film on the PCC surface and spheres at some spots. The level of aggregation is also very high.
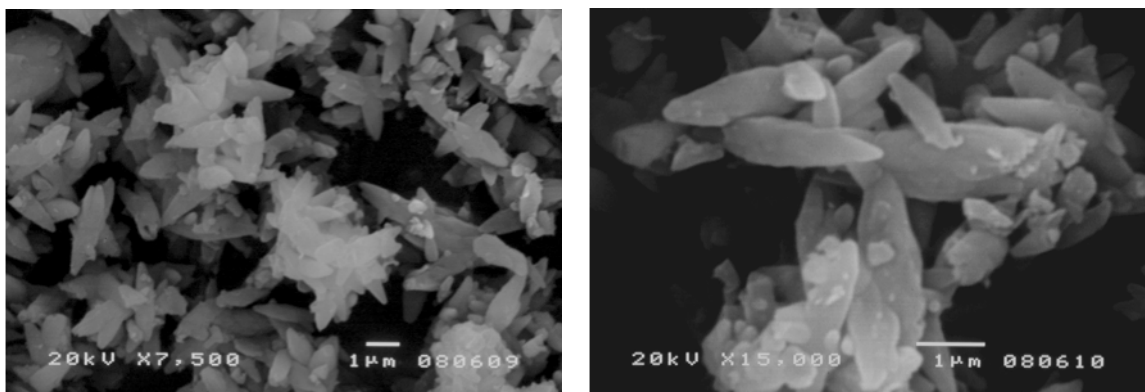
Figure 9 – SEM images of PCC16

With silica content of 28.1%, the scalenohedral shape is even less defined, already not showing the typical (star-like) aggregation shape of PCC (Figure 10). With these scanning electron microscopy images, the results of the thermograms can be confirmed. With increasing ammonia concentration, the silica content increases, and the silica forms a dense film on the particle surfaces.
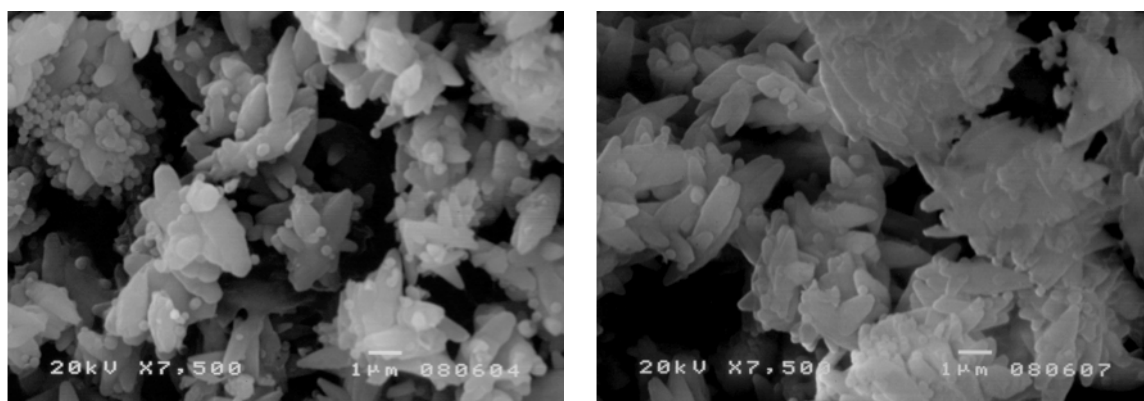
Figure 10 – SEM images of PCC28

Elemental Analysis

Unmodified PCC (PCC0) and PCC28 have been characterized in terms of their elemental composition and the results are shown in Table 7.

Table 7 – Elemental Analysis of PCC0 and PCC28

	%N	%C	%H	%S
PCC0	<100 ppm	11.166	0.833	0.040
PCC28	0.263	8.555	1.261	0.016

After the PCC modification with silica, traces of nitrogen (0.26%) were determined in the samples with 28% silica, which are assumed to be traces that come from ammonia. 11% of carbon in PCC0 were expected, as the molecular mass of $CaCO_3$ is about 100 g/mol with carbon having a molecular mass of 12 g/mol. The percentage of carbon is less in the modified PCC28, since there is 28% silica . Therefore, the percentage of carbon is quite similar to the expected 8.7% (0.72 x 12 = 8.7%). Hydrogen increased from 0.83 to 1.26% after

modification, which can either be a deposit from ammonia or from adsorbed water on the surface due to the hygroscopicity of silica. For both samples, the sulfur amount is neglectable. Due to equipment constrains, the quantity of oxygen could not be determined with this method.

Laser diffraction

The particle size measurements were done using Targon® as dispersant. A different dispersant from Malvern has been tried, but the results showed a very high particle size, which lead to the assumption that the dispersant was not efficient. Using Targon the particle size was more in accordance with expected and visual observation via SEM. Table 8 shows the results of PCC's particle size before and after modification.

Table 8 – Particle size of PCC's

	PCC 0	PCC16	PCC28	PCC29
Particle size (µm)	4.589	5.347	8.134	6.802

As expected, especially after observing the scanning electron microscopy images, the particle size increases with increasing amount of silica on the filler surface. The increase in size between PCC0 and PCC16 is of 15.6 %, whereas the increase between PCC0 and PCC28 is much higher (77%). This value seems very high and only one measurement was done due to little amounts of PCC. For comparison, the particle size of an earlier modified PCC with 29% (6.802 µm) is also shown in Table 8. This particle size corresponds to a particle increase of 48% comparatively to PCC0. Therefore, when measuring the particle size of PCC28, the suspension must not have been very well dispersed, because PCC28 and PCC29 should give similar results and 77% size increase appears to be very high.

Figure 11 shows the size distribution curves. As it can be seen, all samples have similar bimodal shape distributions and the average particle size increases with increasing silica content. Furthermore, the fraction of smaller sizes also decreases with increasing d_{50} size.

Zeta Potential

The Zeta-Potential of the PCC became very negative after modification, being most negative for the highest silica content (Table 9).

Table 9 – Zeta Potential of PCC's

	PCC 0	PCC16	PCC28
Zeta Potential (mV)	6.9	-33.7	-39.8
pH	8.5	7.9	8.2

Xu *et al* [46] measured the zeta potential of silica powder in water and plotted the zeta potential values over pH. For a pH of 7.9, the zeta potential of silica was approximately -94 mV and for a pH of 8.2 almost -100mV. Therefore a decrease of zeta potential after silica modification was expected. The unmodified PCC barely has any charge, which means it will not be retained in the fiber matrix through chemical bonding but rather through physical entanglement. Turning negative after modification can be an advantage, as cationic starch and polymers can interact with the PCC and retain it via electrostatic interactions. Nevertheless, negatively charged polymers will also be tried out for retention trials, as a dual system with cationic starch.

Figure 12 shows the zeta potential distribution curves for each PCC sample. The curves of the modified PCC samples are broader than the curve of PCC0, which implies a higher range of zeta potential. This means that the modified PCC particles are less homogeneous, as a consequence of the surface modification treatment that will unlikely be completely evenly distributed at the surface.
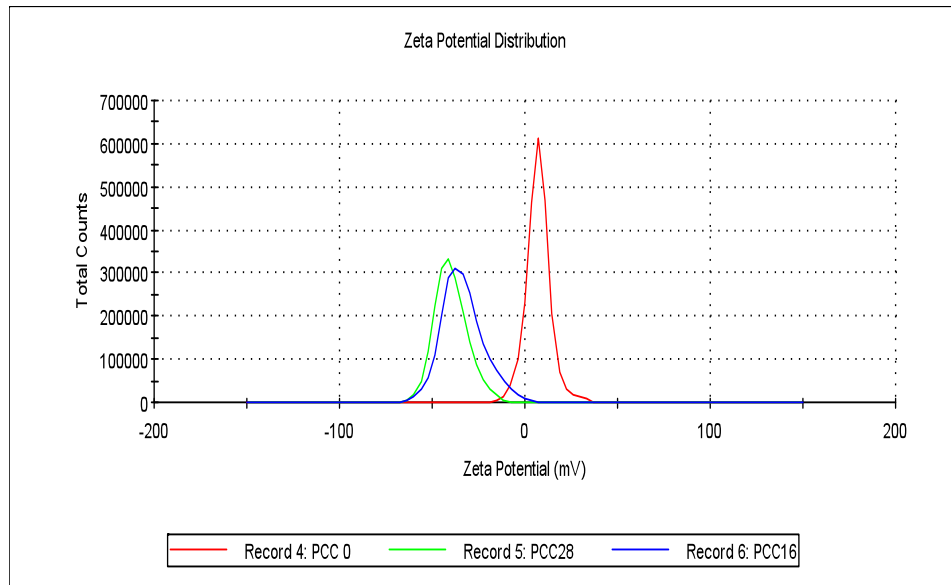
Figure 12 – Zeta Potential distribution of PCC0, PCC16 and PCC28

Brightness

The brightness measurements of the particles, which have only been done for PCC0 and PCC28 due to insufficient amounts of PCC16, show that with increasing silica content an increase in brightness can be verified (Table 10), as expected.

Table 10 – Brightness of PCC particles

	PCC 0	PCC16	PCC28
Brightness R457 (%)	91.0	-	95.9

4.2 Retention and Drainage

Drainage tests have been performed with PCC0 and PCC28 using the polymers Percol, E2++++, Z0, T1, X0, an amphoteric polymer and two metallic salts. Unfortunately, after obtaining the fiber mat, the ash content was performed at a furnace temperature of 600°C. At that temperature, the degradation of $CaCO_3$ has already started (see section 3.2.2). Nevertheless, the results obtained although not accurate, allow for a comparison between all polymers used. Based on these results (shown in Appendix 3, Table 21), Percol, E2++++ and Z0 were selected for the repetition of the drainage tests (with ash content determination at 525°C) and eventually their further usage, as they lead to the highest filler retention in the fiber mat.

Figure 13 shows the drainage curve for fiber with PCC28, starch, ASA and Percol (duplicate). The test starts at a vacuum of 300mbar. The vacuum drop from 0s to point A results in the initial rapid flow of water through the screen (free drainage). Point A is considered to be the point, where the fabric is covered with a layer of fibers, resulting in an increase of vacuum between point A and B because of fiber build-up. At point B the vacuum starts to drop again, as air starts passing through the fiber mat. Point B is the drainage time, also called "dry line". The final vacuum at point C can be related to the porosity of the sheet.
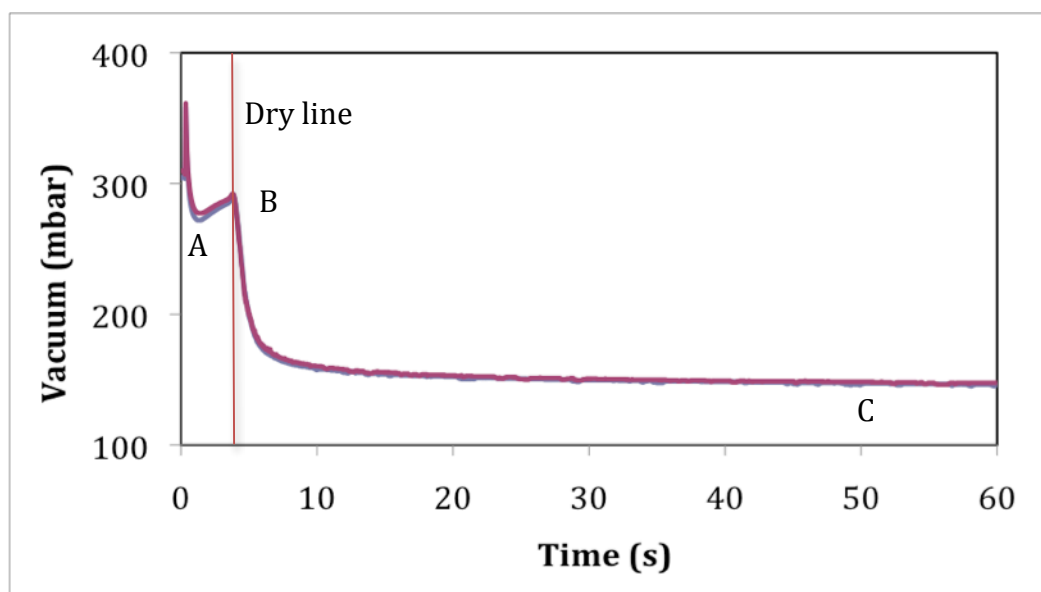
Figure 13 – Drainage curve from DDA Analyzer

Table 11 shows the drainage times (Point B) for the three PCC's and the different fiber mat compositions.

Sample	PCC0 (s)	PCC16 (s)	PCC28 (s)
Fiber	5.2	5.2	5.2
Fiber + PCC	4.8	7.1	6.2
Fiber + PCC+Starch+ASA	5.5	5.6	5.6
Fiber + PCC + Starch + ASA + Percol	4.7	4.7	4.6
Fiber + PCC + Starch + ASA + E2++++	4.0	5.1	3.4
Fiber + PCC + Starch + ASA + Z0	16.7	12.1	16.8

As already shown in the thermograms, the PCC loses weight up to 580°C without degradation, due to water (especially for silicated PCC) and additives (from $CaCO_3$ precipitation). Therefore, it is necessary to determine the "solid content" of PCC. This was determined by doing a cycle in the furnace for each PCC sample at 525°C during 16 hours. These results are shown in Table 12, and for the calculation of retention, the amount of PCC added was corrected taking into account these yields:

Table 12 – Yield of PCC samples

PCC0 (%)	PCC16 (%)	PCC28 (%)
98.7	95.4	91.6

The results of the retention in the Dynamic Drainage Analyzer are shown in Table 13. For all PCC samples, retention increases with the addition of additives, being the highest for the complete series of additives (starch, ASA and polymer), as expected.

Table 13 – Retention results of drainage tests

Sample	PCC0 (%)	PCC16 (%)	PCC28 (%)
Fiber + PCC	83.1	84.4	71.1
Fiber + PCC+Starch+ASA	83.5	87.3	84.0
Fiber + PCC + Starch + ASA + Percol	93.9	91.9	91.2
Fiber + PCC + Starch + ASA + E2++++	90.2	89.9	87.1
Fiber + PCC + Starch + ASA + Z0	96.1	92.7	90.1

For PCC0 and PCC16, the highest retention of 96% and 93% respectively can be achieved using Z0 as a polymer. The fact Z0 provides the best retention result would encourage the use of this polymer for handsheet forming, but it had to be excluded due to the high drainage times of 16.7 and 12.1 s respectively (Table 11). Drainage times in that order of magnitude (3x higher) would lead to a necessary decrease in paper machine speed to remove the water from the paper web, detrimentally affecting machine runability, which is not an option. For PCC28 retention of 91% could be achieved with Percol and therefore is the best choice for this sample, resulting in a reasonable drainage time of 4.6 s. Also, for PCC0 and PCC16, good filler retention could be achieved with Percol with equal drainage times. The polymer E2++++ gave lower retentions for all PCC samples (when compared to Z0 and Percol), but as it leads to a lower drainage time, it was not excluded. From these tests, the polymers Percol and E2++++ have been chosen to continue research. However, only handsheets with Percol were produced in this study, while handsheets with E2++++ will only be produced in a future study.

4.3 Paper Properties

Filler Retention

Typically, one handsheet of approximately 1.6 g was placed into the furnace for the determination of filler retention. In these cases, the retention was calculated by dividing the ash content by the amount of PCC added (after correction taking into account the yield of Table 12). In some cases, different amounts of paper

with unknown quantities of PCC were placed into the furnace and the retained filler amount had to be determined in a different way, assuming the total retention of solids to be 100%. In these cases, the following equation was used:

Equation 3 – Calculation of filler retention

$$retention\ (\%) = \frac{ash\ (g)}{(paper\ (g) * added\ PCC\ (g)\ (corrected)\ /\ 1.6\ g)}.$$

The retention results are shown in Table 14. The results marked with * were calculated using Equation 3. Series 2, 4, 5 and 6 (Table 5) could not have been performed with PCC16, as there was not enough of it.

Table 14 - Retention results of handsheets

PCC	Series #	Retention (%)	Filler content (%)
PCC0	1	58	12.26
	2	66	13.68
	3	67	13.71
	4	81/82*	15.99
	6	64	13.22
PCC16	1	62	11.59
	3	69	13.75
PCC28	1	51	10.05
	2	52	10.27
	3	57	11.19
	4	71/78*	14.33
	5	78/85*	15.42

Unmodified PCC (PCC0) has a very small negative zeta potential, and therefore their retention in the paper is due mostly to physical entanglement in the fiber matrix and the Percol is used as a bridging agent between the fibers. Since the modified PCCs have higher (negative) zeta, it is expected (without the use of a

retention agent) that their affinity towards fibers decreases, and this decrease should be higher with the higher degree of substitution / deposition. In fact, it is observable that PCC16 has a better retention than PCC0 for normal amount of Percol used, but PCC28 had the worst retention. This could mean that the amount of Percol being used was not sufficient to overcome the repellant forces between fibers and PCC28. Therefore, an increase of up to 50% in Percol used was evaluated, resulting in retention increases of 15, 11 and 11% for PCC0, PCC16 and PCC28 respectively. Higher retention gains were expected for modified PCC, and one possible explanation for not observing this is that the Percol added is being preferentially consumed by the fibers. When added to the former, Percol is added when the water reaches the upper sensor. Since the agitation is done by bubbling air from the bottom up, and since the filler is much denser than the rest, the probability of having proper mixing of all components (mainly fibers, Percol and PCC) is slim. Therefore an experiment was done, where Percol was added to the beaker (at a consistency of 0.4% instead of 0.02% in the former) with a reaction time of 5 seconds, during which the agitation was done with a magnetic stirrer. The formation of flocs was immediately observed. Unfortunately, there was not enough PCC16 to perform these experiments, but the results for PCC0 and PCC28 show a huge increase in filler retention, especially for the latter that increased 67%. This confirms the aforementioned hypothesis that PCC28 has a zeta potential too high thus hindering its retention when the Percol is added at too low of a consistency with inefficient mixing.

Although the target filler content was 20%, since the PCC was never fully retained, its percentage on the handsheets was always lower. Since the hydrodynamics of a handsheet former are drastically different from those in a paper machine, the filler content in handsheets is always lower than in machine made paper.

Structural Properties

The structural properties of the different handsheets series produced with and without different PCCs are given in Table 15.

For PCC0, the amount of filler (between 12 and 16%) does not seem to affect any of the structural properties of the handsheets. In order to draw any conclusion when using different PCCs, handsheets comparison must be made for similar filler content. Therefore, handsheets with similar filler content are highlighted with the same colors.

Table 15 – Structural Properties of handsheets

PCC	Series	Filler content (%)	Grammage (g/m²)	Bulk (cm³/g)	Permeability (100ml/s)	Roughness (ml/min)
⋮	F	0	69.3	1.45	9.2	107
	FA	0	70.9	1.44	3.1	197
PCC0	1	12.3	78.2	1.63	2.9	217
	2	13.7	78.2	1.58	3.1	227
	3	13.7	80.3	1.63	3.5	246
	4	16.0	85.0	1.64	2.8	227
	6	13.2	79.9	1.64	3.9	227
PCC16	1	11.6	80.6	1.54	2.6	184
PCC28	1	10.1	77.4	1.58	3.4	202
	3	11.2	79.2	1.58	4.2	206
	4	14.3	83.4	1.58	2.2	226
	5	15.4	84.1	2.21	2.3	225

Comparing PCC16 series 1 with PCC28 series 3 (with 11.4 ± 0.2 % filler – in orange), one can see that air permeability is the only structural property that is significantly different. However, the 4.2 Gurley seconds obtained for PCC28 series 3 is a result of only two averaged measurements and therefore may be an outlier.

All handsheets produced with PCC have higher bulk than the ones without even though they have higher grammage. Since bulk is the inverse of apparent density (bulk = thickness/grammage), for a given thickness the increase in grammage reduces bulk. However, as expected, the incorporation of PCC (especially scalenohedral [47]) increases thickness by roughly 25-28%, which more than

compensates the increase in grammage (14%). This results in a bulkier handsheet, which is advantageous from a properties point of view (particularly stiffness).

The use of silicated PCC (comparing PCC28 series 5 with PCC0 series 4 in green) translates into a higher handsheet bulk, which is expected since PCC28 is bigger than PCC0. However, even considering an increase of 77% in filler size (which is unlikely as discussed previously – see Section 4.1, this should only account for a bulk increase of roughly 12% (77% x 15.4% filler content) and not 35%, as it is observed. This suggests that the PCC is occupying more space between fibers instead of the void between them and it could be evidence that PCC is actually promoting fiber-PCC-fiber bonds.

Optical properties

The optical properties of the different handsheets series produced with and without different PCCs are given in Table 16.

As expected for each PCC, as the filler content increases, so does the brightness of the handsheet. However, unexpectedly, the gain in brightness from adding PCC to handsheets (compared with handsheets made out of fiber and additives) is very minute. Also, the addition of additives alone seems to have improved brightness considerably, which is also not expected since the addition of ASA typically lowers the brightness of paper. The opacity and light scattering coefficient behave as expected, increasing with the addition of PCC.

When comparing PCCs with different silica amounts, only two comparisons are possible and highlighted in the table. For PCC content of 15.7 ± 0.3 % (in green) the modified PCC seems to impart a slightly lower opacity and lower light scattering, whereas brightness remains unaffected, although it was expected to increase, since PCC28 had a higher brightness by itself. This behavior of these 3 optical properties can be explained by the previous hypothesis that PCC is occupying more space between fibers instead of matrix voids, thus shielded from light.

Table 16 – Optical Properties of handsheets

PCC	Series	Filler content (%)	Opacity (%)	Brightness (%)	Light Scattering Coefficient (m²/kg)
⋮	F	0	76.9	76.8	32
	FA	0	78.9	84.8	33
PCC0	1	12.3	86.3	86.8	51
	2	13.7	90	85.7	56
	3	13.7	90.5	86.2	58
	4	16.0	89.2	87.9	57
	6	13.2	90.6	86.2	58
PCC16	1	11.6	86.5	87.0	50
PCC28	1	10.1	84.3	86.0	45
	3	11.2	94.3	-	58
	4	14.3	85.9	86.8	46
	5	15.4	86.7	87.1	48

The results regarding PCC28 series 3 are odd and do not match with the results for the other series of PCC28 and are probably the result of a fluke. Furthermore, the unavailability of brightness results makes its comparison with PCC16 unworthy.

Mechanical properties

The mechanical properties of the different handsheets series produced with and without different PCCs are given in Table 17.

The first important observation is that for each PCC with the same silica amount, the filler content (always in the range of 10 to 16%) does not seem to significantly affect any of the mechanical properties. On the other hand ALL mechanical properties are higher when silicated PCC is used even if at higher filler content (see Table 18). Furthermore, the highest improvement in

mechanical properties seems to be achieved with PCC16. This indicates that there is an optimum amount of silica on the surface of PCC somewhere between 0 and 28%. For example, at PCC content between 11.2 and 12.3% (series 1 for PCC0 and PCC16 and series 3 for PCC28 – in orange), the tensile index for PCC16 is 50% higher than that of PCC0 and 40% higher than that of PCC28. In Table 18, the data regarding the mechanical properties is rearranged to emphasize the gain when compared to PCC0 for the same filler content (± 0.6%).

Table 17 – Mechanical Properties of handsheets

PCC	Series	Filler content (%)	Tensile index (N.m/g)	Burst index (kPa.m^2/g)	Tear index (mN.m^2/g)	Stiffness (kN/m)	Internal Resistance (J/m^2)
⋮	F	0	62.3	3.97	8.8	562	270
	FA	0	48.1	3.81	9.6	521	437
PCC0	1	12.3	36.4	2.06	6.9	469	228
	2	13.7	37.8	2.17	-	495	242
	3	13.7	34.3	1.82	-	477	221
	4	16.0	35.0	1.95	7.1	515	215
	6	13.2	33.7	1.96	-	457	268
PCC16	1	11.6	54.7	3.49	7.9	563	364
PCC28	1	10.1	40.8	2.34	7.3	516	256
	3	11.2	39	-	-	502	292
	4	14.3	38.5	2.24	7.5	525	263
	5	15.4	38.5	2.21	7.4	526	243

Unfortunately, there was not enough filler or time to produce more PCC with silica amounts between 0 and 28% in order to confirm and further identify the optimum amount of silica adsorption onto the surface to the mineral filler.

Filler content (%)	PCC	Tensile index (%)	Burst index (%)	Tear index (%)	Stiffness (%)	Internal Resistance (%)
11.7	PCC16	150	169	114	120	160
	PCC28	108	-	-	107	128
13.7	PCC28	109	113	---	110	108
15.7	PCC28	110	113	104	102	113

For handsheets containing only fiber, tensile strength is a function of fiber strength and inter-fiber bond strength. Certain additives (strength agents) improve the bonding between fibers, thus augmenting the bonding strength and tensile strength (although that was not seen in this work). As aforementioned in the introduction, the incorporation of fillers will disrupt some inter-fiber bonds thus imparting bond strength and tensile. With the addition of silica moieties on the surface of PCC, hydrogen bonds can now be established between fibers and filler. Therefore, tensile strength becomes now dependent on fiber strength, inter-fiber bond strength, filler-fiber bond strength and the amount of filler-fiber bonds (or ratio of filler-fiber to fiber-fiber bonds). Therefore, it is legitimate to conclude that there must be an optimum amount of silica on the surface of PCC, which translates into an optimum tensile strength.

If an unmodified PCC is used, then inter-fiber bonds are simply disrupted. On the other hand, if silicated PCC is used, instead of just losing inter-fiber bonds, these are replaced by filler-fiber bonds and therefore overall bonding strength increases. However, assuming that filler-fiber bonds are weaker than inter-fiber bonds (which is very likely since the fibers are much bigger than filler and therefore inter-fiber bonds act in a much longer distance), then as the amount of filler content and / or silica deposition increases, the amount of replaced inter-fiber bonds may be too high and the overall bonding strength decreases.

From the mechanical properties of the handsheets, it is possible to conclude that the use of silicated PCC improved ALL mechanical properties, even at slightly

higher filler loading. Other properties were not detrimentally affected, with perhaps the exception of opacity that seems to slightly decrease. Another interesting conclusion is that it seems to exist an optimum amount of silica deposition on the filler surface, as 16% silica content seems to result in the best properties.

5 Conclusions

The present study had the main objective of developing a silica modified PCC that could improve its properties from a filler point of view, such as retention in paper and the improvement of mechanical properties by promoting filler-to-fiber bonds. Another objective was to evaluate the efficiency of the modification. As previously reported [24], it is not only possible to deposit silica particles onto the surface of PCC, but it is also possible to control their quantity by controlling the reagent concentration during the sol-gel process. The quantity of deposited PCC was determined using thermogravimetric analysis and SEM images were used to visually verify the presence of silica and its influence on the shape of the filler particles. An increase in particle size was observed with increasing silica deposition as expected. For silica content of 28-29 % the increase in size was in the range of 48 to 77%. This broad range of size can be explained by the difficulty in properly dispersing the samples, as they have a high tendency to flocculate and form aggregates. Upon modification the zeta potential of PCC shifted from slightly positive (7mV) to strongly negative (-40 mV), and this "increase" would be more pronounce to higher silica amounts. This behavior was expected as pure silica has a zeta potential of -100 mV [46] and it should lead to decreased affinity towards fiber when no retention aid is used. On the other hand, when cationic retention aids are used, it is expected that their retention increases, due to increased interaction between filler-polymer-fiber. Therefore the choice of polymer to use is crucial. From the drainage and retention tests performed using three polymers, Percol, E2++++ and Z0, the first showed to have the best compromise between retention and drainage time and was therefore chosen for use during handsheet production in order to evaluate its impact in paper properties.

Since there is an enormous difference in the consistency and grammage used for handsheet production and DDA tests, the retention of filler was re-evaluated using handsheets. The addition of retention aid in the handsheet former proved to be inefficient since retentions below 60% were achieved, whereas in the DDA the retention was always higher than 90%. In order to maximize the retention of

filler, two variables were changed: the amount of Percol and the procedure of addition. By increasing its amount, the retention of filler improved only slightly with better results for the unmodified PCC. The addition of the retention aid to a higher consistency furnish had a very significant increase in retaining the filler, which was more pronounced for PCC28, reaching 85%. Therefore, the addition of Percol should always be done to fiber suspensions of higher consistencies.

The use of silicated PCC conferred higher bulk to handsheets. The increase observed was significantly higher than what was expected due to the fact that silicated PCC is bulkier than unmodified PCC. Therefore, another fact must be responsible for this increase. The hypothesis that silicated PCC is participating in filler-fiber bonds can justify this increase, as this would increase the amount of filler particles entrapped between two fibers instead of simply "filling" the voids in the fiber matrix. This would also explain the decrease in opacity and light scattering coefficient observed for silicated PCC, since filler particles would be shielded from light by the fibers. This would also explain why brightness did not increase even though silicated PCC is brighter than unmodified PCC.

Physical testing of handsheets further confirms this hypothesis, as the use of silicated PCC improved ALL mechanical properties even at slightly higher filler loading. Another interesting conclusion is that optimum silica deposition on the filler surface is between 0 and 28%. In fact, for a 16% silicated PCC, tensile index increased up to 50% when compared to unmodified PCC. This is a remarkable result that confirms that modified PCC content can either be increased, while maintaining the same mechanical properties, or maintained, thus increasing the mechanical properties of papers.

6 Future Work

In this work, studies with PCCs containing three different amounts of silica (0, 16 and 28% (w/w silica/PCC)) on the surface have been done. Mechanical properties of the handsheets were best for the 16% modified PCC, and decreased for 28% of silica. Therefore, optimum conditions for handsheet properties must be between 0 and 28% of silica. For future work, new modified PCC samples with 10 and 20% of silica should be prepared. Additionally, PCC with 15% should be prepared again, to verify the first results of retention and strength properties of the handsheets and to evaluate the reproducibility of the PCC and handsheet results.

Furthermore, as concluded in this study, the polymer should always be added into the beaker and a contact time in the beaker of at least 5s should be guaranteed. Additionally, as concluded from the results obtained with the Dynamic Drainage Analyzer, branched polyacrylamide E2++++ is a good alternative for retention aid and therefore handsheets are to be prepared using it in order to evaluate, if this polymer is in fact a good alternative to Percol for the silica modified PCCs. For all steps, the formation of each series and their measurements should be repeated various times, as several results in this study have not been able to be reproduced, and to confirm results that have already been obtained.

When the optimum silica amount for retention and paper properties has been determined, and the choice between the polymer for the silica modified PCCs has been made, trials should be done increasing the filler content in the handsheets with the same grammage of 80 g/m^2 as in this study, for comparison. It is expected, that for higher modified PCC contents similar paper properties as for handsheets with lower unmodified PCC contents can be achieved.

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List of Abbreviations

AKD	Alkyl Ketene Dimer
APAM	Anionic PAM
ASA	Alkyl Succinic Anhydride
CPAM	Cationic PAM
DADMAC	Diallyldimethylammonium chloride
DDA	Dynamic Drainage Analyzer
ECF	Elemental Chlorine Free
EN	European Norm
F	Fiber
FA	Fiber + Additives
GCC	Ground Calcium Carbonate
ISO	International Standard Organization
PCC	Precipitaded Calcium Carbonate
PAM	Polyacrylamide
SEM	Scanning Electron Microscopy
TAPPI	Technical Association of the Pulp and Paper Industry
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric Analysis
Wt	Weight

Appendix 1

Preparation of suspensions for DDA and handsheet production

Starch suspension with ASA:

1. Heat distilled water to a temperature of 60℃
2. Mix 20 g dry starch with ca. 250 ml of the heated water
3. Add ca. 10 mg of enzyme (alpha-amylase) with a micropipette
4. Heat the mixture fast to 80℃ (vapor of coffee machine) and maintain for 5 minutes at that temperature
5. Add 3.3 ml of zinc sulfate to deactivate the enzymes and stop the reaction
6. Increase the temperature up to 90-92℃ and maintain during 15 minutes
7. Add 2 g of ASA solution (5 mg of ASA for 50 mg of Starch)
8. Add water to a final volume of ca. 500 ml
9. Cool suspension down to ca. 50℃ and maintain temperature during usage
10. Calculate concentration (water evaporates) and amount to be added

Percol:

1. Heat distilled water to a temperature of 60℃
2. Mix 0.1 g dry polymer with ca. 100 ml of the heated water
3. Stirr and let homogenize, under constant heating of around 60 – 80℃
4. Add water to final volume of 400 ml and stop heating
5. Add 4 ml to DDA

E2++++:

1. Mix 0.25 g polymer solution (40 % solids) with 400 ml cold water
2. Magnetic stirring for at least 30 min
3. Add 4 ml to DDA

Z0, T1, X0:

1. Mix 0.1 g dry polymer with 400 ml cold water
2. Magnetic stirring
3. Add 4 ml to DDA

Appendix 2

Settings for the DDA equipment:

Table 19 – DDA Settings

	Speed
Preparation time	300
Stirrer left time	-10
Amount furnish	500
Vacuum	300
Max. exp. time	60

Table 20 - DDA Settings: Stirrer Speeds

	Speed	Set time
1	0	0
2	800	-300
3	0	0
4	0	9999
5	0	9999

Appendix 3

Results of Drainage tests and retention determined at 600°C furnace temperature:

Table 21 – Results of retention (DDA) determined at 600°C

Sample	PCC0 (%)	PCC28 (%)
Fiber + PCC + Starch + ASA + Percol	83	73
Fiber + PCC + Starch + ASA + Aluminum sulfate	83	65
Fiber + PCC + Starch + ASA + Iron sulfate	83	69
Fiber + PCC + Starch + ASA + X0	---	62
Fiber + PCC + Starch + ASA + T1	90	72
Fiber + PCC + Starch + ASA + Z0	90	81
Fiber + PCC + Starch + ASA + Amphoteric B	72	67
Fiber + PCC + Starch + ASA + E2++++	84	77

Appendix 4

Air resistance (Gurley)

Time necessary for a certain volume of air to pass through a certain area of paper (constant pressure), in s/100ml

Bulk

Volume per weight unit, in cm^3/g

Burst index

Ratio between burst strength and grammage, in $kPa.m^2/g$

Grammage

Quotient between mass and area of a sample, g/m^2

Internal Resistance

Energy required to delaminate a sheet of paper in the Z direction (a measurement of bond strength between the layers)

Scott-Bond method: the sheet is delaminated under the action of a pendulum with controlled mass and speed, in J/m^2

Opacity

Ratio between reflectance factor of a single sheet against a completely black background (R0) and the reflectance factor of a set of opaque sheets (R00)

Opacity (%) = R0x100/R00

Permeability

Air volume that passes through 1 m^2 of paper area per 1 Pa in 1 s, in $ml/(m^2.Pa.s)$

Roughness (Bendtsen)

Air flow that passes between a circular measuring head and paper surface (ml/min)

Specific Light Scattering Coefficient

Measurement of capacity of paper to scatter light, in m^2/kg

Theory of Kubelka-Munk:

$$SLSC[m^2/kg] = \frac{R_\infty}{w(1 - R_\infty^2)} \cdot \ln \frac{R_\infty(1 - R_\infty R_0)}{R_\infty - R_0}$$

with w – grammage; R_∞ – intrinsic diffuse reflectance factor; R0 - reflectance of a layer with ideal black background

Tear Index

Ratio between tear strength and grammage, in mNm^2/g

Tensile Index

Ratio between tensile strength and grammage, in Nm/g