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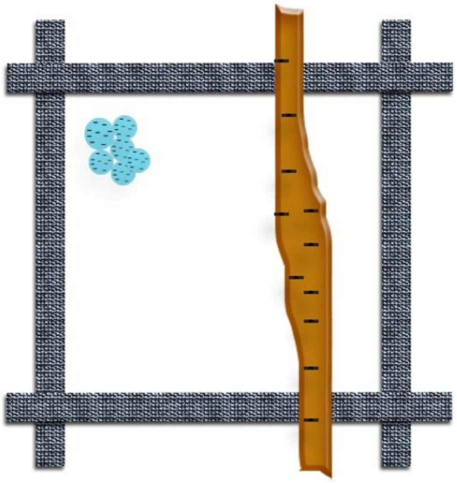

The Effect of Pre-flocculation of Fillers on Paper Strength

Master of Science Thesis [in the Master Degree Programme, Materials and Nanotechnology]

MARCUS PETERSSON

Department of Chemical and Biological Engineering
Division of Applied Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

Producing paper at the lowest possible cost has for a long time been an ambition for papermakers. Cheaper paper can be accomplished by exchanging the more expensive cellulose fibres for less expensive materials, fillers. In doing this, some desirable properties of papers can be enhanced while others, such as strength, will be negatively affected. To circumvent the detrimental effect of increased filler content, much development work has been done on aggregating fillers prior to integration into the paper. Aggregation of fillers can also enhance retention and dewatering of papermaking processes, which is desirable for both economic and environmental reasons.

In this work, the aim was to see if the paper strength could be maintained even when higher filler contents were integrated into the paper. The approach was to pre-flocculate filler particles of precipitated calcium carbonate (PCC), with a three component model system; two polycations and one binder. The binder, carboxymethyl cellulose (CMC), and one of the polycations, polyaluminium chloride (PAC), were the same throughout the work. The amount of the binder and type of the other polycation were varied so that the properties of the produced flocs could be regulated.

The size of the produced flocs was mainly studied with Static Light Scattering (SLS), in a Mastersizer. The paper sheets were produced in a dynamic sheet former (DSF) with three different filler contents ca; 27, 33 and 37%. The strength of the produced sheets was assessed by tensile strength, z-strength and Scott-bond measurements.

The results showed that the tensile strength for a paper was correlated to the size of the filler aggregates from the pre-flocculation. The z-strength, on the other hand, was seemingly not dependent on floc size, but rather showed a correlation to the amount of binder addition.

Sammanfattning

Att tillverka papper till minsta möjliga kostnad har sedan länge varit en ambition för papperstillverkare. Billigare papper kan framställas då dyrare cellulosafibrer ersätts av billigare material, fyllmedel. Fyllmedel kan bidra till att förstärka en del önskvärda egenskaper hos pappret men egenskaper såsom styrka kan bli lidande. Ett sätt att undvika den negativa effekten av fyllmedel är att flockulera fyllmedelspartiklar till större aggregat innan de tillsätts till mälden. Att förflockulera fyllmedel kan även bidra till förbättrade processvillkor; till exempel retention och avvattning kan underlättas. Förbättrade retentions- och avvattningsförhållanden kan ge besparingar både ekonomiskt och miljömässigt.

Inom ramarna för detta arbete eftersträvades att bevara pappersstyrkan med hjälp av förflockulering även då fyllmedelshalten ökades. Tillvägagångssättet var att förflockulera fälld kalciumkarbonat (PCC) med ett modellsystem innehållande tre komponenter; ett bindemedel och två polykatjoner. Som bindemedel användes karboxymetylcellulosa (CMC). För att styra egenskaperna hos de bildade flockarna, ändrades mängden bindemedel och även typen av den ena polykatjonen. Den andra polykatjonen har varit den samma genom hela arbetet, polyaluminiumklorid (PAC).

Statisk ljusspridning (SLS) användes för att studera storleken på de bildade flockar, vilket gjordes med hjälp av en Mastersizer. Papperslabbark tillverkades med en dynamisk arkformare (DSF), där tre olika fyllmedelshalter 27, 33 och 37 % användes. Dragstyrka, z-styrka och Scott-bond var de styrkor som mättes i de tillverkade pappersarken.

Resultaten i detta arbete visade att dragstyrkan styrdes av flockarnas storlek. Större fyllmedelsflockar främjade en högre styrka. Z-styrkan visade sig däremot inte vara lika beroende av flockstorlek, utan mer av bindemedelstillsats.

Preface

This diploma work has been performed at Eka Chemicals in Bohus, and is the concluding part of the Master program Materials and Nanotechnology. The work has been located at the Product RD&I department at Eka and was supervised by Daniel Person, Senior Specialist at the company. The thesis is the last part of my education in Chemical Engineering at Chalmers University of Technology.

I would like to thank Daniel Person at Eka Chemicals who supervised me during the work and made the project possible and enjoyable. I would also like to thank Michael Persson and Håkan Fägersten and the rest of the co-workers at Eka Product RD&I, who have made this work educative and entertaining. Last but not at least I would like to thank Krister Holmberg at Chalmers for being the examiner for this work.

Contents

Introduction

In the forming section of a paper machine, there is a big size difference between the larger fibres and the smaller fines and fillers. The smaller matter in the furnish (the matter that will constitute the paper after dewatering) is considerably smaller than the holes in the wire. To maintain the smaller components on the wire, some kind of aggregation to larger flocs is needed. There are two possible ways to achieve this; either by agglomeration of the fines and filler particles to macro-particles or by binding the fines and fillers to the long fibres (Klass & Sikora, 2007). A risk when binding the fines and fillers directly to the fibres is that fibre-fibre bonds will be affected. Fewer fibre-fibre interactions will have a negative effect on the paper strength. The other approach is to pre-flocculate fillers and in some cases fines prior to the addition to the stock which can contribute to both better processing conditions and enhanced properties for the final paper product.

Paper properties that can be enhanced by pre-flocculation of fillers are especially the mechanical ones. When fillers are pre-flocculated, the number of particle entities will decrease and the size of the aggregates will increase. The strength of papers is determined by the fibre strength, the fibre-fibre interactions and the processing conditions. Fewer and larger particle entities that are a result of pre-flocculation will have less impairing influence on fibre-fibre interactions, and thus on strength.

In the work behind this thesis, the approach has been to pre-flocculate fillers with a three component model system, containing one binder and two polycations. The binder chosen for the system was a pure, well-defined and highly charged carboxymethyl cellulose (CMC). One of the polycations was polyaluminium chloride while the other one was varied. The idea with varying one of the polycations both in amount and type was to regulate the properties of the filler flocs produced. The amount of binder was also varied to regulate filler properties. The type of filler used in this project was Precipitated calcium carbonate (PCC). Attempts were made to correlate size and strength of filler flocs made with the model system to the strength of the produced paper. If it proved possible to correlate size and strength of filler flocs to strength of produced paper, improvements of paper strength can be made easier in future work. New flocculants can then be tested and evaluated on filler slurries. This will make it easier to find well-functional flocculants, since they can be tested without the time-consuming papermaking and -testing.

The technique of choice for measuring size of filler flocs was static light scattering. A few other possible techniques for characterization of the flocs were also tried e.g. rheology, turbidity, UV-Vis and flow cytometry but SLS was the fastest, most informative and most consistent method. Evaluation of how the flocs were able to withstand different kinds of shear forces was done by measuring the floc size before and after shearing of the sample in various ways, e.g. by mixing in an Ultra-Turrax (UT) or dynamic drainage jar (DDJ), by propeller stirring in an ordinary beaker, circulation in the Mastersizer or passage through a dynamic sheet former (DSF).

Investigations were made of how well the strength of the paper sheets was preserved with pre-treatment of fillers when higher filler contents were adopted. The thickness, weight and strength of the sheets were measured. The strength evaluation was conducted by e.g. tensile strength, z-strength and Scott-bond measurements. The aim was to create an equally strong paper with pre-flocculation at 37% filler content as nontreated filler at 27%. The use of less wood fibres would lead to savings both economically and environmentally.

Background

In this section, the background of the project is introduced.

The furnish

When controlling and regulating processes in papermaking, it is an advantage to have some understanding of the composition and properties of the components in the furnish. A furnish can consist of a wide range of components, e.g. wood fibres, fibre fines, fillers, electrolytes, surface-active molecules and sizing molecules. Interaction between different components can be desirable or non-desirable and thus should be controlled to achieve the required performance. The suspended particles in the furnish are often negatively charged (Scott, 1996). The charges on cellulosic fibres arise mainly from carboxylate groups which are created on the hemicellulose xylan. The xylan is integrated in the cellulose structure (Norell, Johansson, & Persson, 1999). The negative charge on fillers will originate from the ionization of the filler/water interface or from adsorption of negatively charged compounds on the surfaces of the filler (Scott, 1996).

Flocculation

The literature describes four types of polymer induced flocculation; macromolecule bridging, charge neutralization, patch flocculation (Porubska, Alince, & van de Ven, 2002) and network flocculation.

The effectiveness of a polyelectrolyte retention aid system depends on several different factors; partly on the flocculation characteristic but also on the suspended particles and the suspending medium. The properties of the polyelectrolyte that are likely to be important in the flocculation mechanism are molecular weight, structure, charge density and concentration. For the suspended particles, properties such as size and charge density are of great interest. The pH, conductivity and ionic charge are believed to be important for the suspending medium (Ovenden, Xiao, & Wiseman, 2000)

Coagulation

Coagulation or charge neutralization in papermaking occurs when added (poly-)electrolytes neutralize the charge on oppositely charged components, thus taking away the repulsive forces that separates them. An effective coagulation is reached when the distance between the suspended particles are so short that a polymer can create bridges between two particles (Gallagher, 1990) Coagulation without additional bridging polymers is weak and takes place in a narrow span of electrolyte addition. A too high addition will create oppositely charged components and redispersion will occur. The coagulation aids are low molecular weight highly cationic compounds that do not reach out from the electrical double layer (Norell, Johansson, & Persson, 1999). In Figure 1, a schematic illustration of coagulation is shown.

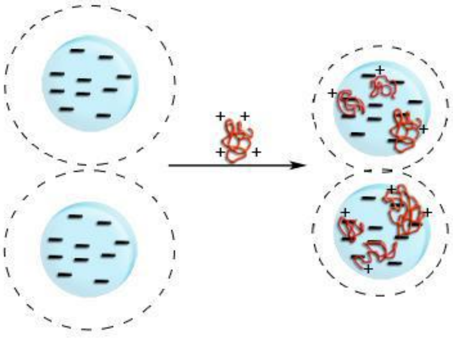


Figure 1. Coagulation between two equally charged particles can occur with an oppositely charge polymer.

Bridging flocculation

To achieve bridging between two particles with equal sign of their net charges, the flocculants have to be able to reach beyond the electrical double layer of the particles. To accomplish this, a polymer with high molecular weight and low charge density is preferably used (Shin, Changman, Kyoun, & Mah, 1997). If the polymer chains are too short they will not be able to link the two particles, due to the long distance repulsive forces. The literature draw a rough line at one million Dalton in molecular weight and under this value the charge neutralization begins to dominate over bridging (Herrington & Gilla, 1987). A highly charged polymer will lead to a flat conformation on the oppositely charged particle surface and no segments of the polymer chain will able to reach beyond the electrical double layer. Flocs built up by bridging are relatively strong, but too high shear forces will break up the flocs and degrade the polymer. The damaged polymers are likely too short to be able to create reflocculation through bridging once more (Norell, Johansson, & Persson, 1999). In Figure 2, a schematic illustration of bridging flocculation is shown.

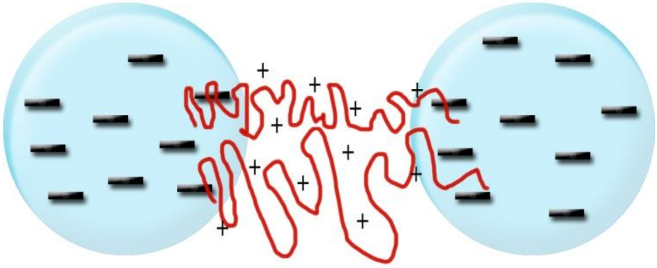


Figure 2. Bridging flocculation between two negatively charged particles with a positively charged polymer.

Patch flocculation

The patch mechanism is created by covering patches of the (often) negatively charged surfaces with a positively charged component. The patch flocculation in comparison with coagulation must not neutralize the charge of the particle, but just create an oppositely charged patch that can interact with areas on non-covered parts of other particles. The patching is preferably made by a compound with moderate charge density and relatively low molecular weight (Taweewat, Hubbe, Heitmann, & Venditti, 2004). Flocs interacting through patching are more sensitive to shear than the stronger bridging mechanism (Shin, Changman, Kyoun, & Mah, 1997). On the other hand, when the patching flocs are separated by too high shear, no degradation of the flocculants will occur, so reflocculation is possible (Norell, Johansson, & Persson, 1999). Figure 3, shows an illustration of patch flocculation.

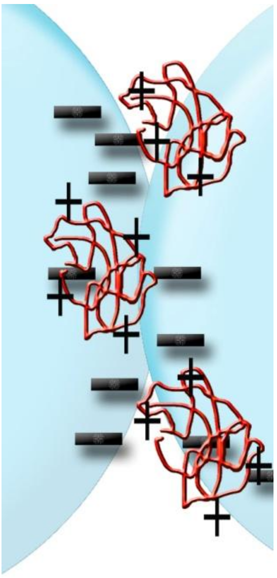


Figure 3. Patch flocculation between two negatively charged particles with positively charged polymer.

Network flocculation

Network flocculation can be induced by electrostatic interaction or by hydrogen bonding between two interacting components. The system often contains a high molecular weight polymer together with a cross-linking component. The cross-linking component can be a simple ion, an aluminium salt or a polymer and will then interact with the high molecular weight polymer by either electrostatic interactions or by hydrogen bonds (Lindström & Glad-Nordmark, 1984). The formed network structure will capture the particles and thereby flocculate them. In Figure 4, a schematic illustration of network flocculation is shown.

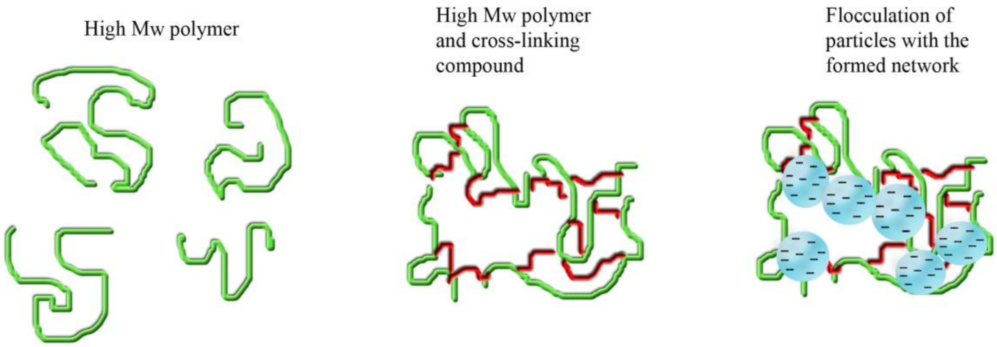


Figure 4 Network flocculation between a high Mw polymer and a cross-linking compound.

Flocculation systems

The types of interactions that will occur between suspended particles are of course depending on the particles but also on the flocculation system. For enhancing retention and dewatering a variety of different flocculation system are available. In the following section, four different types of flocculation systems that are used as retention aids are described.

Single-component retention aids

The single-component systems often consist of polymers but can also consist of highly charged particles. If particles are used, the flocculation mechanism will either be coagulation or patching. With a single-polymer system it is also possible to create bridging flocculation. The bridging polymer should then have a low charge density and a high molecular weight. Too high charge density will lead to a flat conformation of the polymer on the particle surface. Various kinds of polymers have been used in chemical retention flocculation in papermaking; examples of polymers used are Polyacrylamides (PAM), polyethylenimine (PEI), polyamines, polyamidoamines, polyethylene oxide (PEO), poly-diallyldimethyl-ammonium chloride (p-DADMAC) and modified starch (Shin, Changman, Kyoun, & Mah, 1997)

Dual-component retention aids

Dual-component systems generally use both the effect of patch and bridging flocculation (Petzold, Mende, Lunkwitz, Schwarz, & Buchhammer, 2003). This contributes to the ability to withstand higher shear forces than single-component retention aids (Wågberg & Lindström, 1987). Dual polymer systems are often based on a cationic polymer together with an anionic. The classical way of addition is to first add the cationic polymer to the furnish and thus create positively charged patches on the dispersed particles. Later an anionic polymer with high molecular weight is added to form bridges between dispersed components. The cationic polymer is usually starch, polyamine or modified polyamide amine while the anionic polymer is commonly polyacrylamide (Lindström, Hallgren, & Hedborg, 1989).

Microparticle retention aids

The aim of microparticle systems is to achieve more shear resistant flocs. The microparticle system exhibit a reflocculation mechanism that is more pronounced than for the single- and dual-polymer retention aids. The system generally consists of a high molecular weight cationic polymer together with an anionic microparticle. The cationic polymer is often starch or polyacrylamide and the anionic particles can be colloidal silica or clay. The proposed mechanism for microparticle systems is that the cationic polymer binds to surfaces of the suspended particles, and then the anionic microparticles interacts via a charge mechanism with the polymer chains and link them together (Clémencon & Geril, 1999). Microparticle systems have been shown to be less sensitive to flocculant overdosage but require a higher dose. Microparticle systems have proven to have several benefits over other retention systems such as faster dewatering in the press section and porosity in the final paper (Wågberg, Mirjam, Inger, & Swerin, 1996). Agne Swerin et al (Swerin, Sjödin, & Ödberg, 1993) have also shown that microparticle systems are less affected by the addition sequence of the two flocculants than a dual polymer system. The most commonly used microparticle system utilizes colloidal silica as the anionic particle together with a cationic polymer (starch or PAM). Another common anionic particle used is bentonite which can be up to 300nm long and very thin, approximately 1nm (Klass & Sikora, 2007). It has been shown that bentonite can interact with both charged and uncharged sites on cationic PAM, in contrast to anionic silica to which only charged groups will form interactions (Swerin, Sjödin, & Ödberg, 1993).

Cationic microparticle

When microparticle systems are used, the most common concept is to use a negatively charged particle together with a cationic polymer. But it is also possible to do the opposite, i.e. to use a cationic particle and an anionic polymer. In this approach, the aim is to let the cationic particle bind to the negatively charged filler particles. The negatively charged polymer can then connect the positively charged particles and thereby flocculate the fillers. The advantage with this approach is that particles cannot adopt another conformation and will thus not lie flat on the filler surface, which can be a risk when polymers are adsorbed to the filler. Because of the stable form of the particles and their size they will not as easily as polymers migrate in to cracks and holes on surfaces (Mirza, Conyngham, & Covarrubias, 2002).

Retention and drainage

Retention is a measure of the amount of a given substance in the final product compared to the amount of the substance in an earlier step in the process (Scott, 1996). In papermaking processes, commonly used terms are first-pass retention (FPR), machine retention and system retention (Norell, Johansson, & Persson, 1999).

First-pass retention or wire retention is the most commonly used parameter and is referred to when retention is mentioned in this work. First-pass retention is defined as how much of suspension component that is retained after the wire section compared to the amount prior to the headbox (Norell, Johansson, & Persson, 1999). In Figure 5, an illustration of the size of the holes in the wire compared to the size of the fibres and the fillers is shown.

An ideal retention system should at minimum dosage flocculate filler and fines without providing a too extensive fibre-fibre flocculation and be shear resistance without affecting the sheet formation (Blanco, Negro, Fuente, & Tijero, 2005).

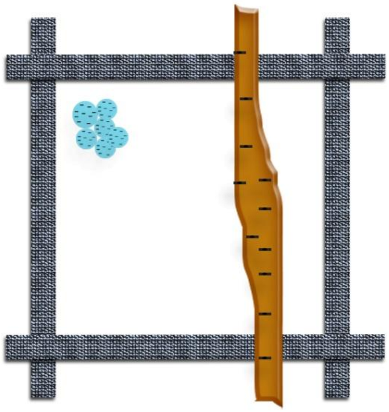


Figure 5. Wire holes compared to the size of fibres and fillers.

Drainage or dewatering is substantial for papermaking, since a furnish can consist of more than 99.5% water before the forming section. Dewatering is both expensive and time consuming so an easy dewatering can both lead to economical and production rate benefits. Retention aids often also improve the drainage of a system. Water flow between fibres becomes easier when fillers and fines are aggregated to larger particles and attachment of the agglomerates to longer fibres will also help to improve water flow.   (Seppänen, Ström, & Elftonson, 2000) (Blanco, Negro, Fuente, & Tijero, 2005)

There is a wide range of retention and drainage systems on the market and continuous improvement of existing systems are on-going. A lot of effort is put into trying to develop new systems to enhance the retention and drainage even further. The first retention aids that were adopted by the paper manufactures were systems based on alum (Norell, Johansson, & Persson, 1999). Systems based on alum were well-functioning for acidic papermaking but the effect declined with increasing pH. The reason is that alum can carry a high positive charge at low pH but loses this ability as the pH increases. The charge on alum is important due to that fibres, fillers and fines often are negatively charged in the fibre suspension (Porubska, Alince, & van de Ven, 2002) (Shin, Changman, Kyoun, & Mah, 1997), and the positively charged alum helps to decrease the repulsive electrostatic forces between the components in the furnish. When an increasing amount of paper mills in the eighties started to adopt neutral to alkali papermaking processes the need for new retention systems grew. Micro- and nanoparticle systems were introduced to the market around the same time period, and they have proved to have advantage over the old systems containing single- or dual polymers (Norell, Johansson, & Persson, 1999). Today, most paper mills use a microparticulate system for retention and drainage control (Svedberg & Lindström, 2010).

Retention and drainage can also be enhanced by pre-flocculation of fillers to larger aggregates. The improvement of retention and drainage together with the better strength properties of papers when fillers are pre-treated has lead to that some of the recent development has focused on pre-flocculation of fillers, where the fillers are aggregated before being added to the stock. In pre-flocculation, the aim is to be able to increase the filler content without a significant degeneration of the paper properties. With increased filler content, the raw material cost will go down, as less wood fibres will be used. With increased filler content, savings can also be made due to lower dewatering costs. Because high filled papers are easier to dewater (Esser, Hähnle, & Adalbert von Vadkerthy, 2009). Pre-flocculation of fillers will provide larger aggregates, the larger aggregates are easier to maintain in the web, and thus relatively less retention chemicals are needed. If fillers are flocculated in the fibre suspension there is a risk for fibre-fibre flocculation as well. When the fibre-fibre flocculation is too extensive there will be a large difference in composition between different areas in the paper web, i.e. poor formation of the paper sheet. The areas with fewer fibres will be more sensitive and will more easily break under stress. With agglomeration before mixing in the filler, the aim is to achieve higher filler levels and at the same time good formation of the paper product.

It is also important from both an economical and environmental perspective to minimize the use of fresh water in the papermaking process. Higher closure of the white water system requires a well-functioning retention system, to prevent circulation of chemicals and materials in the system (Norman, 2005). The larger pre-flocculated aggregates are less prone to get trapped in the white water circulation system, which lowers the demands on the retention system when higher closure is adopted.

Fillers

Fillers are solid particles that are insoluble and are added to the paper process to enhance paper sheet optical properties and to reduce cost (Gaudreault, Di Cesare, Weitz, & van de Ven, 2009). A filler should fulfil some other requirements as well to be well functional, e.g. a high degree of whiteness, a high refractive index, low solubility in water, small particle size and a low specific gravity (Wilson, 2006). There exists a wide range of fillers, both natural and synthetic. Paper properties that can be positively influenced by addition of fillers are mainly optical properties, but others such as smoothness, printability, dimensional stability and sheet formation can also be improved (Gaudreault, Di Cesare, Weitz, & van de Ven, 2009). Introduction of fillers into paper can also imply unwanted effects, such as reduced mechanical strength, wire abrasion, lower total retention of solid compounds, increased two-sidedness, reduced stiffness, and increased dusting (LI, Collis, & Pelton, 2002). The most commonly used fillers in papermaking are: kaolin clay, calcium carbonate, titanium dioxide, talc, silica and silicate (Gaudreault, Di Cesare, Weitz, & van de Ven, 2009).

Calcium carbonate

In the late eighties when an increasing amount of paper mills changed their operating conditions from acidic to alkaline, a large increase in the use of $CaCO_3$ followed. Papermaking processes that are operating under acidic conditions cannot use calcium carbonate as a filler because calcium carbonate will dissolve at low pH. The use of $CaCO_3$ has also been triggered by the high brightness of the mineral. Calcium carbonates used in papermaking are divided into three categories; chalk, precipitated (PCC) and ground (GCC) calcium carbonate (Thorn & On Au, 2009).

Precipitated Calcium Carbonate (PCC)

PCC is a bright mineral and can be of very high purity. Precipitated calcium carbonate can be produced in different forms, e.g. scalenohedral, rhombohedral and in aragonite structures. For papermaking the scalenohedral form is the most common PCC used (Gaudreault, Di Cesare, Weitz, & van de Ven, 2009). Almost all PCCs are made with the milk of lime process, which can be divided into three steps.

The first step is heating of calcium carbonate to produce quicklime (CaO) and carbon dioxide (CO_2).

In the second step, the lime is added to water and thus forms calcium hydroxide ($Ca(OH)_2$).

In the third and last step, the calcium hydroxide will be reacted with carbon dioxide to create calcium carbonate, the formed carbonate is insoluble in water and precipitates.

This process is made for two reasons; firstly to take away impurities and secondly to control the shape of the formed carbonate. What type of PCC that is produced depends on factors such as reaction time, temperature, agitation, pressure, rate of carbon dioxide addition and post-crystallization processing (Specialty Minerals Inc, 2011). It has been shown that the form of PCC can have a large impact on the properties of the final paper product. Prismatic PCC has for example a lower negative effect on strength than scalenohedral PCC (Lindström & Florén, 1987).

Flocculation of fillers

Retention flocculants are added to the paper making systems to aggregate fillers, fines, fibres and colloidal particles in the stock (Shin, Changman, Kyoun, & Mah, 1997), and thus maintain the compounds in the web. Pre-flocculation agents on the other hand are added to flocculate filler particles prior to the addition to the stock. Pre-flocculation of fillers will make it easier to maintain the fillers in the web because of the larger size of the aggregates, and thus lower the requirements on the retention system. The pre-flocculation should also enhance the strength properties of the paper product.

Pre-flocculation of filler

A high filler content in the paper will as mentioned earlier introduce a wide range of possible advantages but unfortunately also some negative effects will arise as well. This can to some extent be counteracted by pre-treatment of the filler. The goal with pre-treatment is to achieve porous aggregates of filler particles, before they are added to the fibre suspension. Aggregates of fillers will not interfere with fibre-fibre bonding to the same extent that non-flocculated filler does, because of the larger size and thus smaller amount of particles. A porous structure of the aggregates will also enhance optical and printing properties (Seppänen, Ström, & Elftonson, 2000). At the same time as it is desirable to create open flocs, the flocs must also withstand the high shear forces that are present in paper machines (Gaudreault, Di Cesare, Weitz, & van de Ven, 2009).

Filler effect on paper strength

There are three different strength directions of a paper, the machine direction (MD), the cross direction (CD) and the out-of-plane direction (ZD). Paper is stronger and stiffer in the plane than out of the plane due to that fibres are oriented in the paper direction. The mechanical properties of a paper in the plane direction are dependent on both the fibre-fibre interaction (strength and concentrations of bonds) and the fibre strength in the axial direction. The strength in the ZD is mainly dependent on fibre-fibre interactions. The inherent fibre properties are not so important for the ZD strength because few fibres are oriented in that direction. When fillers are added to the paper, the strength of the paper will be negatively affected because fillers generally do not bind as strongly to fibres as fibres can do to each other. Higher filler contents in the paper will lead to more disturbances of the fibre-fibre interaction and thus a lower strength. The aim with pre-flocculation is to decrease the number of particles by agglomeration of the small particles to larger flocs. This will lead to fewer particle entities that can disturb the fibre-fibre interactions and thus a better strength of the paper is maintained. The strength of a paper will also be affected by papermaking conditions such as the pressing, drying and forming technique (Fellers, Ankerfors, Girlanda, & Lucisano, 2007).

Eklund at al. (Eklund, 1991) state that fillers can be incorporated in a fibre structure in three different ways, see Figure 6, and will have different impact to the paper depending on how it is integrated.

1. **Expansion:** Fillers will expand the fibre network and thus lower its density. The expansion of the fibre network will improve the light scattering properties of the paper. Unfortunately, the filler particles will interfere with the fibre-fibre interactions and as a result, mechanical properties will be lowered.
2. **As filling:** Fillers will end up in the open spaces between the fibres, and will not interfere with fibre-fibre interactions. Mechanical properties will therefore be unaffected by the filler addition but the light scattering will increase. The density of the paper will increase thanks to the filler addition and no volume expansion of the fibre network.
3. **Insertion:** The fibre-fibre interaction can be affected by the insertion of filler in between them, lowering the mechanical properties as a consequence. The insertion of filler will on the other hand not affect the overall light scattering (Fellers & Andersson, 2009).

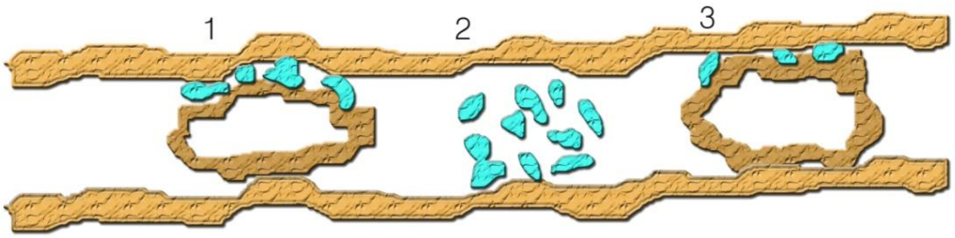


Figure 6. How fillers can be incorporated in a fibre structure (based on a figure from (Fellers, Ankerfors, Girlanda, & Lucisano, 2007)

Theoretical studies of paper strength

A few attempts have been made to correlate the paper strength to the properties of fibres and fillers and the bonds between them. A well accepted basic theory is that the paper strength is dependent on fibre strength and bond strength. But when fillers are incorporated into the fibre network, new problems arise. The loss in fibre-fibre bonds and the creation of new filler-fibre bonds have to be taken into consideration.

Page theory

Page has developed one of the most accepted theories for calculating tensile strength. The equation suggested by Page take fibre strength and bonding ability into consideration, but properties like formation, fibre shape, fibre length distribution and failure stress of the bonds are not taken into account.

where

Because of the complexity of describing interaction between fibres that have different properties, and also the difference in papermaking conditions, the Page theory is only valid in ideal cases. Page theory has shown to give good correlation between properties of straight fibres and tensile index of papers dried under restrained conditions (Fellers, 2005)

Modified Page theory

According to Yoon (Yoon, 2007) the tensile strength of papers containing only fibres have been theoretical studied, but theoretical studies of the tensile strength when fillers are incorporated are more limited. Theoretical studies of the case where fillers are pre-treated were non-existent before the work of Yoon (Yoon, 2007).

A modification of the Page theory has been developed to treat papers containing fillers (Yoon, 2007). It starts with the simplified Page equation

where

T = tensile strength of paper

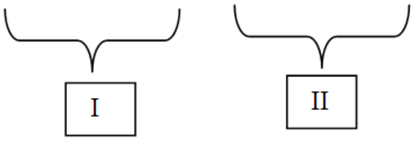
Z= zero-span tensile strength of paper

C = collection of constants of fibre characteristics for a given pulp

b = shear bond strength per unit bonded area

RBA = relative bonded area of the sheet

The term b, multiplied by the relative bonded area has been proven to have a linear relation to the z-strength. In (Yoon, 2007) it is assumed that fillers will affect the tensile strength proportionally to the surface area of the fillers. They have expressed the shear bond strength per unit bonded area (b), in two terms; one that describes specific bond strength between available surface area of fillers and fibres (I), and one describing the same for fibres–fibre interaction (II).



where:

A= fibre strength term from the page equation

C= collection of the constants for a given pulp

b_c =filler/fibre specific shear bond strength per unit area

b_f = fibre/fibre specific shear bond strength per unit area

S_c= specific surface area of filler

S_f = specific surface area of the fibre

x = mass fraction of filler in paper

k=constant related to filler available to interfere with fibre-fibre interactions.

As mentioned above the z-strength (ZDT) has a linear correlation to b*RBA, which gives:

Equation 4, can then be rewritten for the calculation of a dimensionless z-strength (Yoon, 2007):

where

$\zeta =$ / (ratio of filler-fibre specific bond strength)
$\Delta =$ / (ratio of specific surface areas)

If the dimensionless z-strength is plotted against the mass fraction of filler with different values of ζ and Δ the following curves will be obtained, Figure 7.

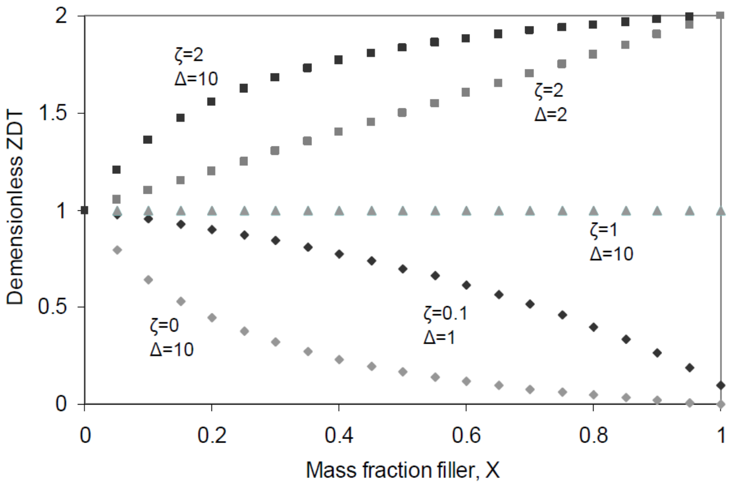


Figure 7. ZTD (Dimensionless) as a function of mass fraction for different ζ and Δ. (Yoon, 2007)

When ζ is equal to one, the filler-fibre interactions will be as strong as the fibre-fibre interactions, and the dimensionless z-strength will then be unaffected by filler addition. If ζ is larger than one, the filler-fibre interactions are stronger than the fibre-fibre. Most common is when filler-fibres interactions are weaker than fibre-fibre interactions, and thus a ζ smaller than one. When ζ is smaller than one, filler addition will have a negative effect on the z-strength.

Materials and methods

Investigations were made of how well the strength of the paper sheets was preserved with pre-treatment of fillers when higher filler content were adopted. Pre-treatment of the fillers were made with a three component model system, containing one binder and two polycations. The binder chosen for the system was a pure, well-defined and highly charged CMC. One of the polycations was PAC while the other one was varied. The idea with varying one of the polycations both in amount and type was to regulate the properties of the filler flocs produced. The size of the filler flocs were measured with a Mastersizer.

Evaluation of how the flocs were able to withstand different kinds of shear forces was done by measuring the floc size before and after shearing of the sample in various ways, e.g. by mixing in an Ultra-Turrax, in a dynamic drainage jar, by propeller stirring in an ordinary beaker, circulation in the Mastersizer or passage through a dynamic sheet former (DSF).

Paper sheets were produced in a dynamic sheet former with three different filler contents ca: 27, 33 and 37%. The strength evaluation of the paper sheets was conducted by e.g. tensile strength, z-strength and Scott-bond measurement. In the following section the methods and the materials that have been used during this work are described in more detail, and also how the filler flocs and the papers sheets were made.

Dynamic Drainage Jar (DDJ)

The dynamic drainage jar was invented by Kenneth W. Britt in 1973, and the purpose was to simulate furnish hydrodynamics in a paper machine. The DDJ has been widely used for retention testing but also for testing of drainage. The system is built up by a jar with baffles on the inside of the walls. The material of the jar is PMMA (Plexiglas). At the bottom of the jar is a wire mesh screen, a support screen and a valve that controls the outflow from the jar. Inside the jar is an impeller, and the impeller speed can be regulated so that the forces acting on the sample can be controlled (Penniman, 2004). The essential parts of the DDJ are shown in Figure 8.

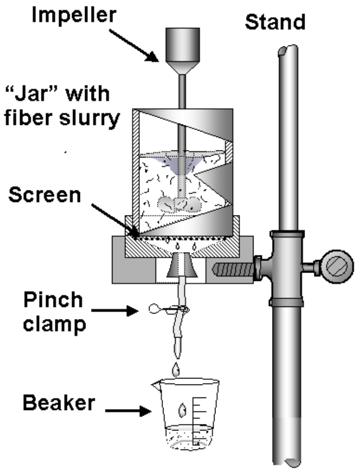


Figure 8. Illustration showing the essential parts of a DDJ (Hubbe, 2002)

Static light scattering

One way of determining the size of particles is to use a light scattering technique. Depending on the size and form of particles, they will scatter light differently. By analyzing the light passing through and light scattered by the particles it is possible to calculate their size.

In this diploma work, a Mastersizer MicroPlus from Malvern has been used for the size determination of filler flocs. The Mastersizer uses a static light scattering technique for size determination (Amzon, 2011). The size range that can be studied is quite large, from 0.05 µm to 550 µm, and the studied matter shall be in wet form. The sample is placed in a beaker of a volume of 600 to 1000 ml, and it is also possible to subject the sample for ultrasonication. It is possible to regulate the stirring speed of the sample and the ultrasonic probe (Malvern Instruments, 2011).

Particle Charge Detector (PCD)

The PCD measures how much charge that is carried by particles but it is also possible to investigate polymers. The PCD uses an indirect technique to measure the charge of an unknown sample, by measurements of the amount of counter charged polyelectrolyte needed for neutralization. The machine records oscillation of the counter-ions to the polyelectrolyte adsorbed to the walls of the container when a shear is applied to the sample. If there are counter-ions around the studied polyelectrolyte, the machine will titrate an oppositely charged polymer (based on the charge of the studied samples). When the titrated polymer neutralizes the charge of the sample, no gathering of counter ions at the wall will occur. By knowing the charge and amount of titrated polymer, it is possible to calculate either charge or concentration on the sample depending on what´s known and unknown in the sample (Fischer & Böckenhoff, 2001).

In this work, a PCD machine from Mütek (PCD-03) has been used, and the used titrand was p-DADMAC with the concentration 0.0001 eq/l.

Homogenizer or Ultra-Turrax (UT)

The essential parts in the Ultra-Turrax are a rotor and a stator and in both the rotor and the stator gaps are incorporated. The rotor rotates very fast and causes the suspension to be sucked in axially. The suspension will then be forced out to the surroundings by the gaps, see Figure 9. This change in direction will create a very high acceleration of the particles. The acceleration will create shear and thrust forces on the particles. This together with the high turbulence between the rotor and stator will disperse particles (IKA).

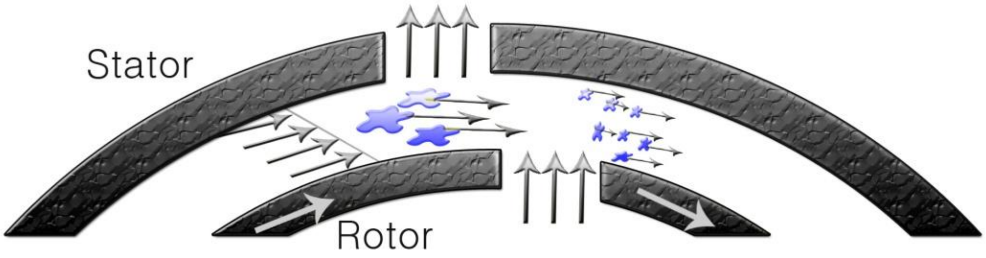


Figure 9. Forces in the Ultra-Turrax (based on figure from (IKA)).

Total organic carbon (TOC)

The TOC method used in this work is provided by LANGE. For this technique, the sample should have a pH value in the range of 3-10 and both the sample and the reagents should have a temperature around room temperature. The detection range for the used method (LANGE LCK 386) is between 30-300 mg/l and the measuring sequence will take approximately two hours.

In the TOC-method, LCK 386, the first step was to transfer 1 ml of sample into a digestion cuvette. The cuvette was then shaken for five minutes in a TOC-X5 shaker, without cap. The indicator cuvette was opened and a double-threaded cap with a membrane was mounted instead. The digestion cuvette was mounted on the other side of the double-threaded cap, and the combination was heated for two hours at 100°C. When the cuvette combination had cooled down to room temperature, the indicator side of cuvette combination was placed in a spectrophotometer, XION 500.

The principle is to first take away the total amount of inorganic carbon from the sample (TIC), this is done with the TOC-X5 shaker. The TOC will then be oxidized to CO_2. The CO_2 will then pass the membrane between from the digestion cuvette to the indicator cuvette. The color of the indicator cuvette will shift due to the CO_2. The change in color is detected by the photometer, XION 500.

Slurry preparation

All the slurries were made in the same way, if no comments are added in specific cases. The preparation has been made with help of a propeller and a 500 ml plastic beaker. The pure PCC suspension with a filler content of ca 20% by weight, was first added to the beaker at a low stirring speed. Later, the binder was added at a rotation speed of 700 rpm and mixed for one minute. The polycations were premixed together with water, the water is added so that the sought concentration of the slurry can be reached; 10%. The water mixture was prepared with a magnetic stirrer. The mixture of water and the polycations are then added to the filler/binder mixture and the speed of the propeller is increased to 1000 rpm for one minute.

Sheet forming

The sheets have been formed in a dynamic sheet former, manufactured by Techpap. Of each fibre-filler composition, a long sheet is produced, which can be divided into three lab sheets with the dimensions 16 * 22 cm. The furnish is first poured into the container followed by the filler slurry during rapid stirring. The retention system that is used in this work is Compozil (C-PAM (PL 1510) and anionic particles (NP 442)) together with PAC. Starch (Perlbond 970) was added to improve the strength of the produced papers. The sheets are pressed directly after being shaped and then dried under restrained conditions for 8 minutes.

Testing of paper strength

To evaluate how the flocculation systems affect the strength of the paper made, standard testing methods have been used. Three different kinds of test methods have been used; Scott-bond, z-strength and tensile testing. The tensile tests have been used both for the machine direction (MD) and for the cross direction (CD). The strength in the MD will be higher than that in CD since more fibres are aligned in the MD.

Scott-bond

The Scott-bond method measures the internal bonding of a paper sheet in the z-direction. The sample is held in place by double adhesive tapes between a rigid foundation and an L-shaped metal piece. When the pendulum hits the L-shaped metal, some of the energy will be absorbed by the paper sample before it breaks, see Figure 10. The loss in height of the pendulum can be recalculated to this absorbed energy (Fellers, Paper physics, 2005).

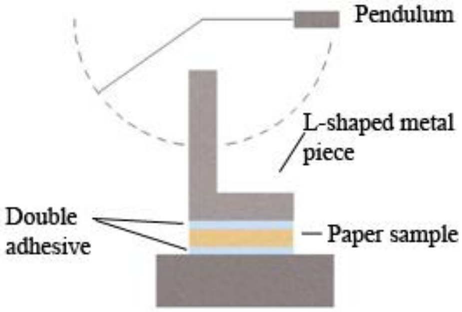


Figure 10. Scott-bond tester gives the energy absorbed by the paper sample, in loss of height of the pendulum.

Z-strength

The z-strength measuring technique tests the delamination resistance of paper sheets. The sample is held in place by two strips of double adhesive tape. Two pistons, one from above and one from beneath, applies a pressure on the sample. The applied pressure will make the pistons stick to the adhesive tape. The pistons will then move away from the paper sheet and the resulting force will split the paper in the z-direction, Figure 11. The force that is required for splitting the paper is a measure of how strongly the paper is held together in the thickness direction (Fellers, 2005).

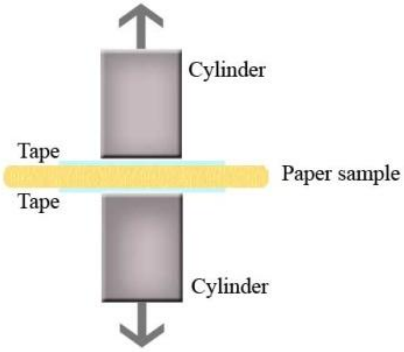


Figure 11. Z-strength with the tape method.

Differences between Z-strength measurements based on tape versus laminate

A new method for determining the z-strength of paper has been developed by Innventia AB. The new method should be more suitable for strong and thin papers than the original double adhesive tape method. The new method uses a laminating process instead of tape. The tape method according to Fellers et al (Fellers & Andersson, 2009) gives uncertain values above 500 kpa and has an upper limit around 1000 kpa. The tape method is also less appropriate for thin papers, because of penetration of the tape into the fibre structure. The new lamination method creates very strong bonds to the paper surface, up to 7000 kpa. This gives better possibilities to test strong papers (Fellers & Andersson, 2009).

Tensile testing

The tensile test determines how well the fibres are bound together and the fibre strength. Fibres with several bonding sites will have a higher strength than fibres with fewer. The test is performed by placing a paper strip with known length, grammage and width between two fixed positions and pulling in the length direction of the strip with a known force, see Figure 12.

Figure 12. Tensile strength of a paper strip.

The specific index stress of the sample can then be calculated with the formula

where F (N) is the applied force and w (g/m^2) is the grammage of the sample and b (m) is the width. The strain can be calculated as the elongation of the sample divided by the original length

If one plots the stress against the strain, a number of useful properties of the sample can be read out from the graph, e.g. tensile stiffness, tensile index, strain at break and tensile energy absorption (TEA) (Fellers, 2005).

Materials

Binder

The binder used in this work was a CMC, Akucell 0305, selected as a model binder, since it´s a high purity, well defined and highly charged polysaccharide. Akucell 0305 has a molecular weight of 140 000 g/mol and the degree of substitution is between 0.80-0.90 (BRENNTAG SPECIALTIES, Inc., 2007) . Figure 13 shows the repeating unit in the CMC structure.

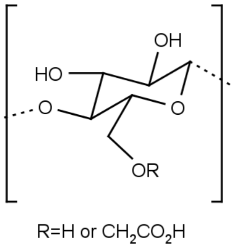


Figure 13. The repeating unit in the CMC polymer

Polycations

Because both the binder and the filler in our case are negatively charged and thus will experience electrostatic repulsion to each other, polycations have been used. The polycations will lower the repulsion between the binder and the filler, and greater interaction can occur. If the network flocculation type is desirable the polycations should also be able to cross-link the CMC binder.

One of the polycations has been fixed while the other one has been varied. The fixed cationic compound is polyaluminium chloride (PAC 8210). Both the composition and the molecular weight have been varied for the other polycations. In Table 1, a list of the tested polycations is shown.

Tabel 1. Information of the polycations used

Compound	Abbreviation	Molecular weight
Polyamine	PA1	Low
Polyamine	PA2	Low/Medium
Polyamine	PA3	Medium/High
Polyamine	PA4	High
Polyethylene imine	PEI1	Low
Polyethylene imine	PEI2	High
Polydiallyldimethylammonium chloride	p-DADMAC1	Low/Medium
Polydiallyldimethylammonium chloride	p-DADMAC2	Medium/High

Pulp

The pulp that has been used when paper sheets were produced in the DSF is a mixture of 20% softwood and 80% hardwood. The Canadian Standard Freeness of the pulp was around 320ml. The pulp is stored in the fridge at a consistency of ca 30 %. The same day as the sheets were to be made, the pulp was diluted to approximately 5%. The pH of the pulp was checked and the conductivity was increased to approximately 1500 µS/cm by addition of calcium chloride (0.1 g/l of furnish) and sodium sulphate (up to 1500 µS/cm). The solids content was also checked after dilution to get a more exact value.

Results and Discussion

The aim of this project was to investigate how different pre-treatments of fillers could preserve paper strength at higher filler content. The adopted approach was to look at a flocculating system containing three different polyelectrolytes; a negatively charged binder and two polycations. The idea was to try to find correlations between properties of the pre-formed filler flocs and the strength of the final paper product.

Determination of amount of polycations

The amounts of the polycations appropriate for neutralization of the binder were determined with the help of a PCD machine. The aim was to find a charge concentration on the PCC supernatant after addition of polyelectrolytes that was close to that of the supernatant of pure PCC. The charge on pure PCC can differ with time and was therefore tested each time as a reference. The charge of the supernatant of pure PCC was often quite consistent and was slightly negative. To measure the charge on the different slurries, centrifugation was carried out prior to the measurement. 10 g of the supernatant was used in each measurement.

The charge neutralization was made to prevent complications in the papermaking process. If the net charge on the filler slurry differs too much from the original system, new problems can arise in the complex processes that are operating when papers are produced. It is well documented that free CMC in papermaking process will cause processing problems. An additional problem that can occur if the amount of free polymer is large is migration of polymers to the surface of the paper produced. The migration to the surface can give elevated z-strength in laboratory scale, which is not likely to occur in the rapid industrial production.

The PCD measurements gave an indication if there were any free polymers in the solution. Unfortunately, the PCD can only detect charges, so if there were free polymer complexes in the solution that had been charge neutralized, detection with the PCD is not possible. As a complement to the PCD, TOC measurements were conducted. TOC will measure the amount of organic carbon in the studied matter and will therefore detect neutralized polymer complexes. TOC measurements indicated that less than 1% of the added polymers were present in the supernatant for slurries with optimized charge. The conclusions from the TOC and the PCD measurements are that the vast majority of the added polymer will be associated with the filler particles in the model system studied.

Floc size dependence on preparation conditions

Some experiments were made with different mixing speeds during preparation of the slurries. This was done to study the effect of rotation speed on the floc size. The first experiments were carried out with two different polycations, PA2 and PA4, but with the same amount of CMC, 10kg/t. The slurries were made at 200 and 1000 rpm in a beaker with a propeller. The results can be seen in Figure 14. Here, one can see that the smaller flocs made by PA2 are less sensitive to rotation speed than the lager flocs produced with PA4.

The size of the created flocs was investigated by a Mastersizer, during two minutes.

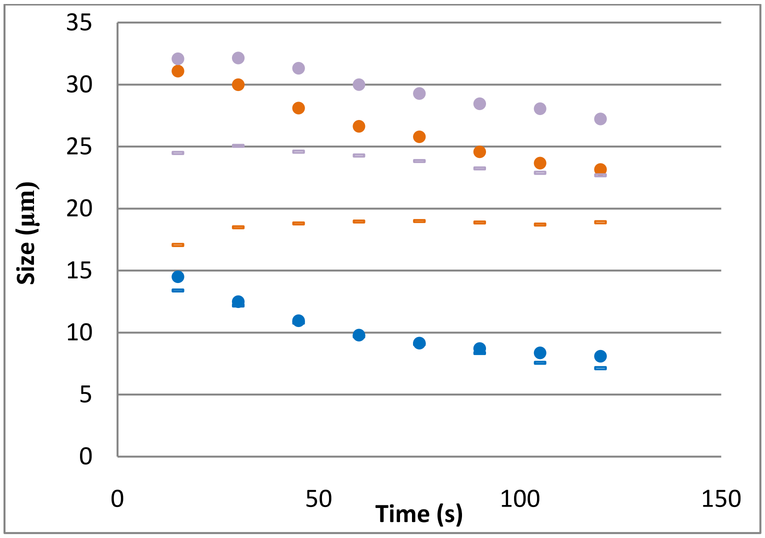


Figure 14. Floc sizes of filler at different conditions, ● = 10kg/t CMC with PA2 at 200 rpm in a beaker, ▬ = 10kg/t CMC with PA2 at 1000 rpm in a beaker, ● = 10kg/t CMC with PA4 at 200 rpm in a beaker, ▬ =10kg/t CMC with PA4 at 1000 rpm in a beaker, ● = 10kg/t CMC with PA4 at 300 rpm in a DDJ, ▬ =10kg/t CMC with PA4 at 2000 rpm in a DDJ.

The sensitivity of the flocs with PA4 was also tested in a DDJ with two different speeds, 300 and 2000 rpm. The result from this experiment is also shown in Figure 14, and it can be concluded that the size of the flocs is larger when made at a lower speed. It also looks like the size of the flocs for the two different speeds are approaching the same value in the Mastersizer.

According to the result, it looks like that the rotation speed had only a minor impact on the size of flocs shaped. For the smaller flocs, the difference in size was almost negligible for the different rotation speeds. The larger flocs showed a slightly higher dependence on the speed when made. But the sizes after two minutes in the Mastersizer were almost equal for flocs produced at two different speeds. This is logical, because larger flocs will be subjected to higher shear forces, due to their size. Bonds that are weak can therefore survive better when they are incorporated in the smaller flocs. The weak bonds will be broken up if they are in the larger flocs, and will thus be more sensitive to the conditions when they are made.

Filler floc strength

During a two minute period, it was monitored how the shear forces in the Mastersizer affected the filler flocs. Mastersizer experiments were also made on flocs that had been subjected to forces applied by a ultra-turrax, a dynamic sheet former or by a dynamic drainage jar, to further investigate how sensitive the flocs were to the applied shear forces. In Figure 15, one can see the effect from the Mastersizer but also the effect from UT and DDJ on filler floc size, for three different CMC additions. The slope of the curves shows how the floc sizes are changed with time in the Mastersizer. From Figure 15, it is also possible to see that the DDJ forces have a small effect on floc size, it even seems like the size of the flocs increases after the sample has been subjected to DDJ stirring. It is also shown that the UT forces are quite strong and will decrease the size of the flocs drastically.

The DDJ treatment sustained for two minutes at a speed of 1500 rpm and the filler slurries were diluted ten times to fill the one litre jar. The UT treatment was also conducted for two minutes at level 3, which is equal to 16 000 1/min, slurries were diluted three times before the UT treatment.

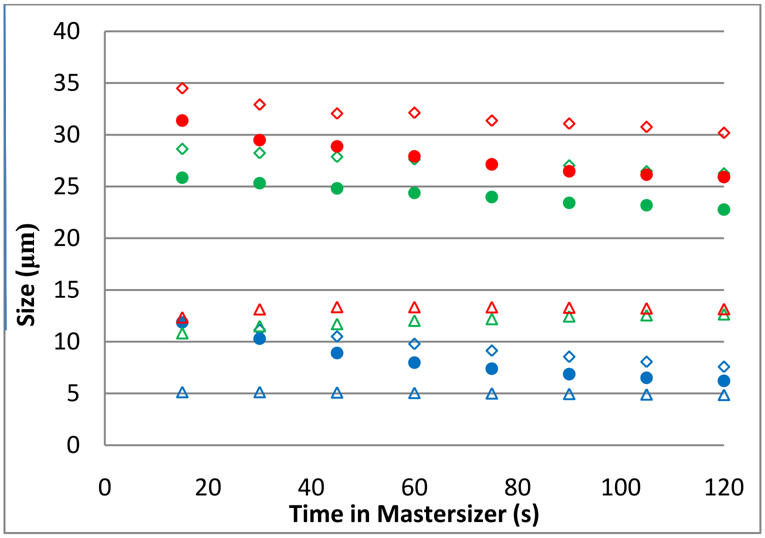


Figure 15. Size of filler flocs in a 120 second span, ● ◊ Δ = 10kg/t CMC with PA2, ● ◊ Δ = 15kg/t CMC with PA2 and ● ◊ Δ = 20kg/t CMC with PA2. ● = no-treatment, ◊ = after DDJ and Δ = after UT.

Magnitude of forces created by the DSF

In order to investigate how big forces that were present in the sheet forming equipment and how the flocs were affected by this, the influence of one pass through the DSF was also checked. This was done mainly to see how big the flocs were after the DSF machine which is an indication of the size in the final paper product. Another reason was to see how large the forces were in the machine, compared to the other techniques that were tested before, e.g. mixing in beaker, DDJ, UT and Mastersizer, to see if the forces in these experiments were of comparable magnitude. In Figure 16, the behaviour in the Mastersizer for four different slurries is shown before and after treatment in the DSF. The difference between the four slurries is the amount of added binder; 10, 15, 20 or 25 kg/t CMC. From the Figure, it is reasonable to say that the forces in the DSF are moderate, lower than forces applied by the UT. The behaviour of the flocs is similar to the behaviour in the Mastersizer and thus it is probable that the shear forces in the DSF are of the same magnitude as the forces created in the Mastersizer. This experiment was conducted at two separate occasions, with the same outcome.

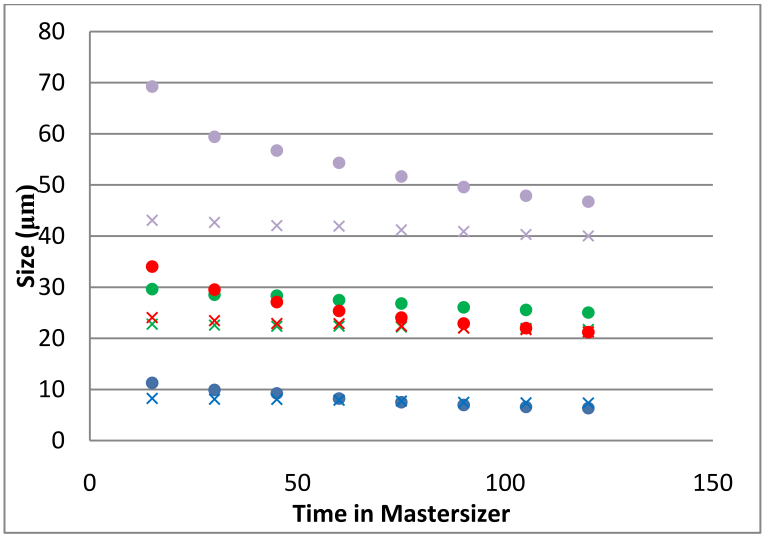


Figure 16. Size of filler flocs before and after subjected to forces by the DSF, all with the polycation PA2 ● =10kg/t CMC before DSF, x =10kg/t CMC after DSF, ● =15kg/t CMC before DSF, x =15kg/t CMC after DSF,● =20kg/t CMC before DSF, x =20kg/t CMC after DSF, ● =25kg/t CMC before DSF, x =25kg/t CMC after DSF.

Improvement of strength by pre-treatment of filler

These experiments were conducted to investigate how different amounts of chemicals affected the properties of filler flocs such as size and strength. Different amounts of CMC together with PAC and PA2 were used. The amount of PAC was fixed as mentioned earlier, but PA2 was varied in amount to match the increased amount of CMC. The adopted approach to find the right charge balance when the amount of CMC was increased was to make slurries with different amounts of PA2. The slurries were then centrifuged and charge measurements were made on the supernatant.

In table 2, the required amount of the polycation, PA2, needed to neutralize the amount of CMC added is shown, based on the PCD measurements.

Table 2. The required amount of PA2 needed to neutralize the amount of CMC added

Amount of CMC (kg/t)	Required amount of PA2 (kg/t)
10	5
15	14
20	17

The filler was incorporated in the paper sheets with the help of the DSF. Strength measurements showed that a higher addition of chemicals gave a higher strength. In Figure 17-19, the different strength measurements are shown.

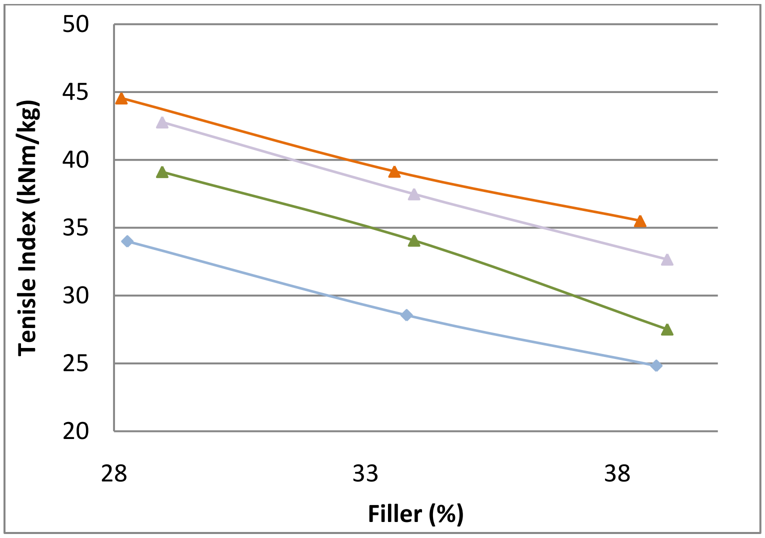


Figure 17. Tensile strength at different filler content ▲ = 10kg/t CMC with PA2, ▲ = 15kg/t CMC with PA2, ▲= 20 kg/t CMC with PA2, blue diamonds are without any pre-treatment.

The tensile strength values that are reported in this report are a geometric mean values of the tensile strength in the machine direction and the cross direction.

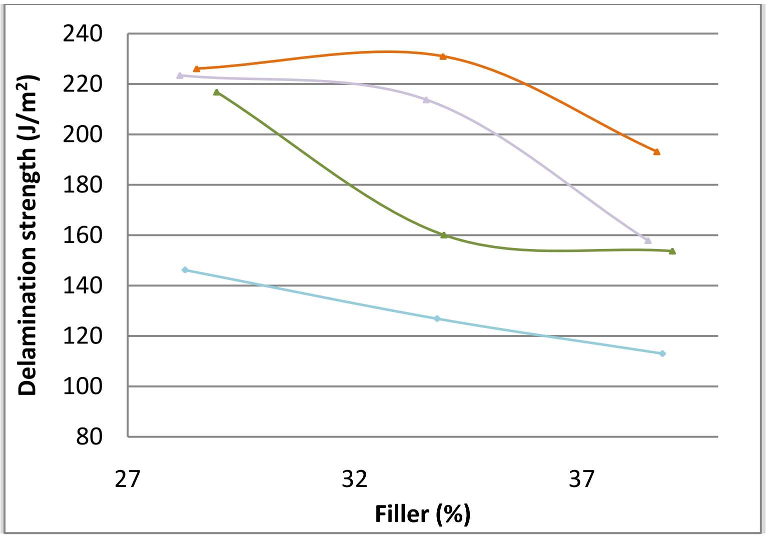


Figure 18. Scott-bond at different filler content, ▲= 10kg/t CMC with PA2, ▲= 15kg/t CMC with PA2, ▲= 20 kg/t CMC with PA2, blue diamonds are without any pre-treatment.

The values from the Scott-bond measurements should not be paid too much attention to, because of the uncertainty in the method. Few data points were measured and a very large variance in the results was obtained.

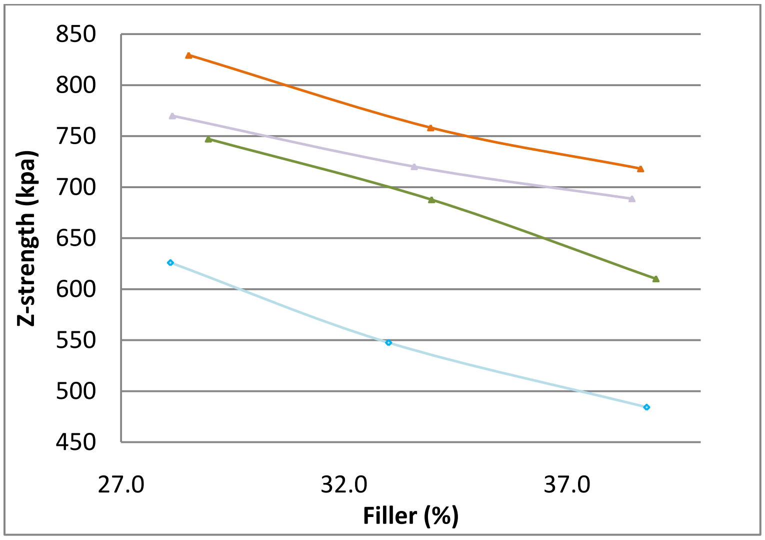


Figure 19. Z-strength at different filler content , ▲= 10kg/t CMC with PA2, ▲= 15kg/t CMC with PA2, ▲= 20 kg/t CMC with PA2, blue diamonds are without any pre-treatment.

The slurries were also tested in the Mastersizer before the DSF. This was done with the intention to find a correlation between the strength of the paper and the size and / or the strength of the filler flocs incorporated in the paper. In Figure 20, the sizes of the flocs are shown for a two minute measurement in the Mastersizer.

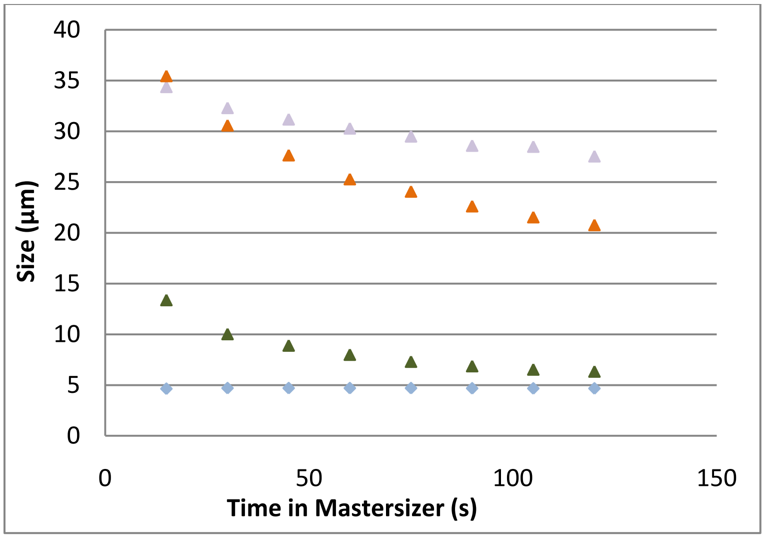


Figure 20. Size on filler flocs studied in a 120 seconds interval in a Mastersizer ▲ = 10kg/t CMC with PA2, ▲ = 15kg/t CMC with PA2, ▲= 20 kg/t CMC with PA2, blue diamonds are without pre-treatment.

From Figure 20, it is possible to see that more polymer addition gave rise to larger filler flocs at the beginning of the measurement. The data indicate that the flocs produced with 15kg/t CMC are less sensitive to shear forces in the Mastersizer than flocs produced with 20kg/t CMC. The size of flocs produced with 15kg/t will pass the size of the flocs produced with 20kg/t CMC between 15 and 30 seconds in the Mastersizer. This behaviour is rather unexpected but a possible explanation can be that the charge balance is more accurate at 15kg/t CMC, and that this will produce more stable flocs. All the three different strength measuring methods, tensile, (Figure 17), z-strength (Figure 18) and Scott-bond (Figure 19) showed that more chemical addition gave higher strength. With this knowledge, the aim was to see whether at an addition of 10kg/t CMC, a stronger paper could be made by exchanging PA2 for other polycations.

Different polycations

To test if the system with 10kg/t CMC could be improved by exchanging the polycation, PA2, different polycations were investigated. The tested polycations were; polyamine, poly-DADMAC and polyethylenimine. Eight different slurries were tested, all with different sizes on the produced flocs; four of the slurries were made with PA, two with p-DADMAC and two with PEI with different molecular weights. The results from the size measurements can be seen in Figure 21.

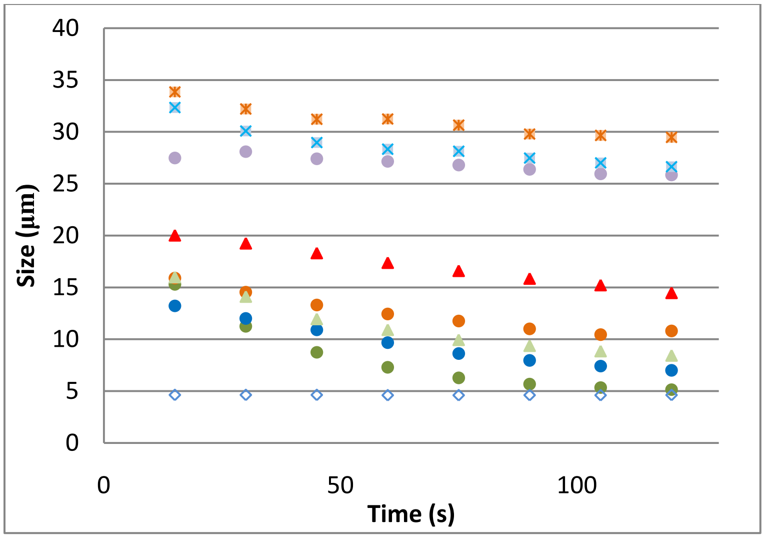


Figure 21. Size on filler flocs in a range of 120 seconds in the Mastersizer, ◊ = no treatment, 10/kg/t CMC with, ● = PA1, ● = PA2, ● = PA3, ● = PA4, ▲= p-DADMAC1, ▲= p-DADMAC2, ✖ = PEI1, ✖ = PEI2.

The PEI with the high molecular weight produced the largest filler flocs followed by the PEI with the lower molecular weight. The results show that a higher molecular weight of the polycations gave larger flocs, and this was valid for all three of the studied polymers. The strength measurements are shown in Figure 22 and 23, where it looks like tensile strength follows the size very consistently while the z-strength has a not so clear correlation if any.

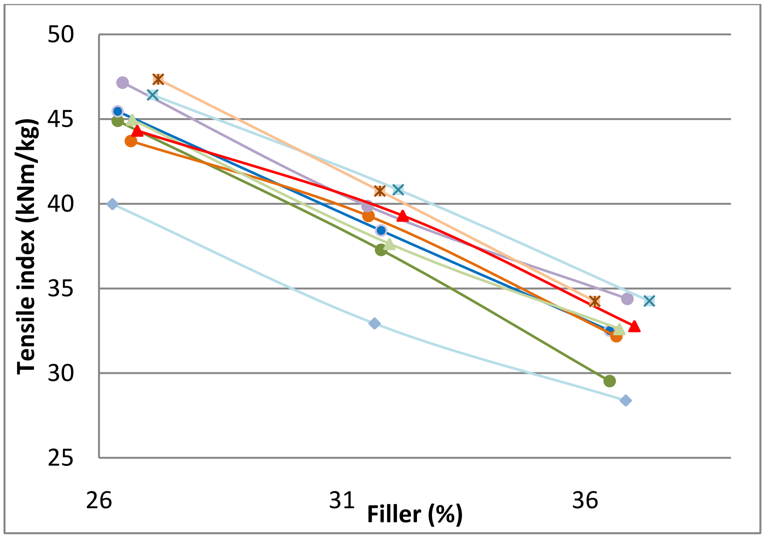


Figure 22. Tensile strength at different filler content, ◆= no treatment, 10/kg/t CMC with, ● = PA1, ● = PA2, ● = PA3, ● = PA4, ▲= p-DADMAC1, ▲= p-DADMAC2, ✖ =PEI1, ✖ = PEI2.

The fact is that the tensile measurements gave the same result that was obtained earlier, higher strength for larger flocs. This is also consistent with what is expected, based on literature studies, where it is reported that larger and fewer aggregates will interfere less with fibre-fibre interactions and therefore preserve strength better.

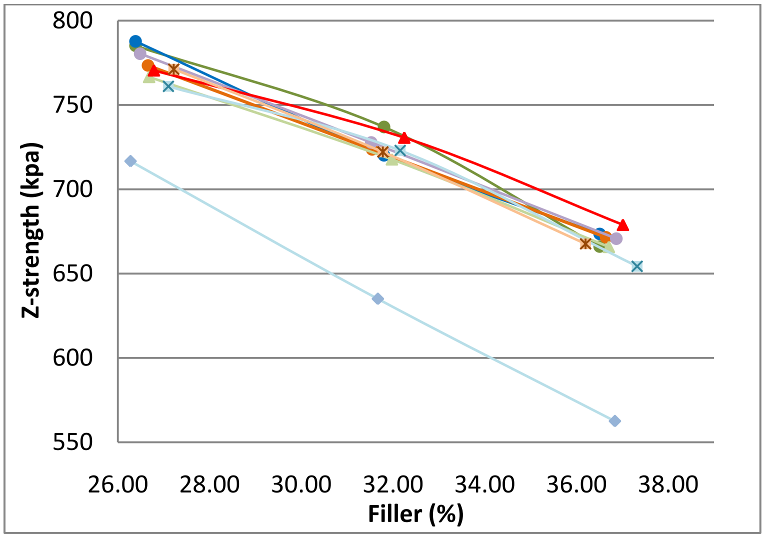


Figure 23. Z-strength at different filler content, ◆= no treatment, 10/kg/t CMC with, ● = PA1, ● = PA2, ● = PA3, ● = PA4, ▲ = p-DADMAC1, ▲ = p-DADMAC2, ⊠ =PEI1, ⊠ = PEI2.

From the z-strength measurements shown in Figure 23, it is hard to see a correlation to the size of the flocs. All of the papers produced in this experiment are quite close in strength (except the reference) but the size of the flocs differs. In all the cases were the filler is pre-treated, 10kg/t CMC has been used. This indicates that z-strength correlates to amount of added binder.

Size and binder effect on paper strength

The experiments so far have shown that a higher binder addition gives larger flocs and also that the produced paper will have better strength properties. To investigate whether the increased strength depends on whether filler flocs are fewer in amount and thus will interfere less with fibre-fibre interaction , or if the increased strength arises from the fact that more active polymers are added and as such contribute to the higher strength. To test this, three different slurries were made with three different amounts of CMC, 15, 20 and 25 kg/t. The floc size of the 15 and 20 kg/t samples had in previous experiments shown to be approximately the same after the DSF, see Figure 16. The size of the flocs produced with 25kg/t addition of CMC, were larger after they had been subjected to forces by the DSF, than the two lower amounts, 15kg/t and 20kg/t, see Figure 16. To get the 25kg/t to the same size as the other two, shear forces on the flocs were applied before the DSF machine. One minute of shearing by UT at the lowest level was enough to get approximately the same size after the DSF as the other two compositions. The filler flocs were then integrated in paper sheets and the strengths were evaluated. Different correlations could be seen from the strength measurements; from the tensile test it looks like the strength was the same for the three different additions but for the z-strength, higher addition gave a higher strength.

The results can be seen in Figure 24 and 25, indicating that the tensile strength is mostly influenced by the size of the filler flocs. This can be explained by the theory that fewer particle entities will disturb the fibre-fibre interaction less. Larger particle aggregates will of course lead to fewer particle entities. Z-strength measurements indicate that size was not significant for paper strength in that direction. The z-strength seemed to be more dependent on the amount of added chemicals. A rational explanation could not be found but after consultation with Christer Fellers at Innventia AB, we considered to try another method for measuring z-strength. According to articles written by Fellers and co-workers, our z-strength measurement method is not appropriate for strong and thin papers. The method that we used was not able to give true values above approximately 500 kpa, and the papers that we made had a higher strength than that. The trends of the data from our measuring technique should be the same, but the absolute values should be very uncertain and could not be trusted. In order to investigate if the trends from our measurements were maintained in the lamination method at Innventia, samples were sent to Stockholm for further analysis.

The results from the measurements conducted by Innventia, showed that our method gave the same trend as Innventia's method did. The absolute values were lower for our tape-method which was expected. In the article written by Fellers et al. z-laminate is plotted against z-tape and a trendline has been drawn (Fellers & Andersson, 2009). Our obtained data are not on that line, but rather close.

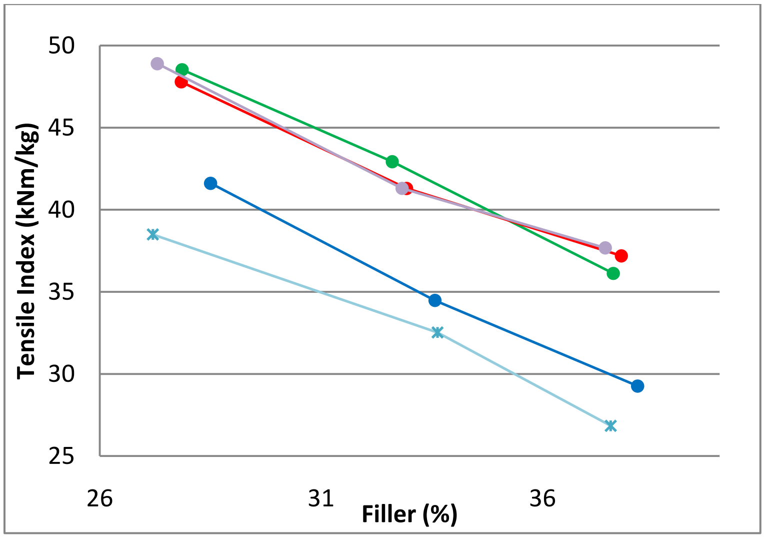


Figure 24. Tensile strength at different filler content, ●=10kg/t CMC with PA2, ●=15kg/t CMC with PA2, ● =20kg/t CMC with PA2, ● =25kg/t CMC with PA2, ✳= no treatment.

In Figure 24 and 25, 10kg/t CMC is also shown. Both the tensile strength and the z-strength indicated a lower strength for the flocs produced with 10kg/t CMC. This was expected, since the size these filler flocs were smaller than the other three, and had also had less addition of binder.

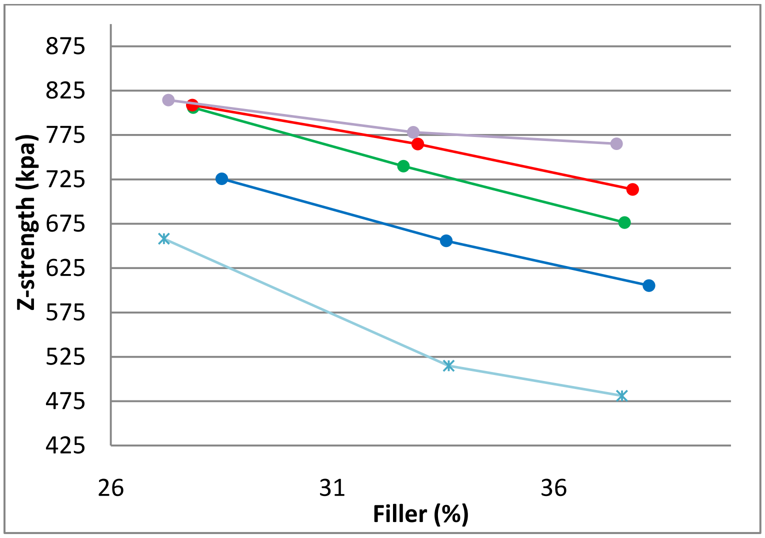
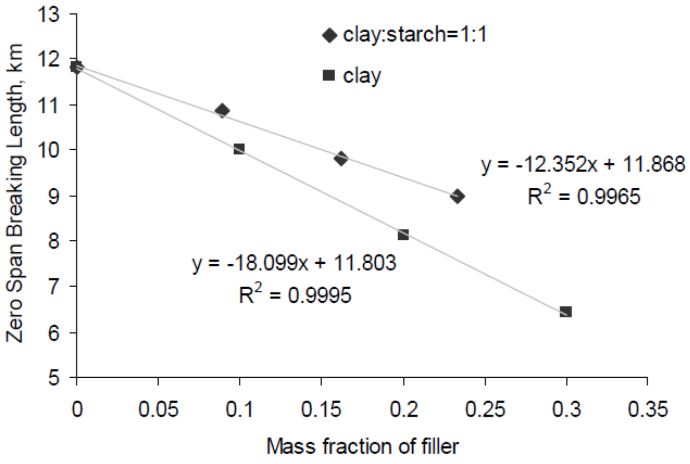


Figure 25. Z-strength at different filler content, ● =10kg/t CMC with PA2, ● =15kg/t CMC with PA2, ● =20kg/t CMC with PA2, ● =25kg/t CMC with PA2, ✳= no treatment.

Conclusions

The results obtained in this work have shown that the tensile strength and the z-strength did have a clear correlation. If the Page theory is studied, it looks like the z-strength and tensile strength should have a correlation. This because of that the zero-span tensile index,   (equation 1) or Z (equation 2), should measure strength of individual fibres. The strength of the fibres should not be affected by filler addition. Yoon (Yoon, 2007) on the other hand, showed that the zero-span tensile index can be affected by both filler addition and pre-treatment of fillers, Figure 26. The lack of correlation between the two strengths can then to some extent be explained by the modified Page theory. Unfortunately the modified Page theory can not explain our results, since the trend shown in Figure 26, are in opposite direction to your results.



Figur 26. Effect of filler addition, both treated and nontreated, for zero span breaking length (Yoon, 2007)

The main flocculation mechanism operating in this model system is believed to be network flocculation. This is based on that the polycation, PA has in previous work (Holmgren, 2010) been proven to have a poor adsorption to the PCC particles. The PA and the other polycation, PAC, are likely to flocculate CMC. The addition sequence of chemicals makes it probable that the polycations will interact with free CMC.

All the strength measurements have shown that the strength of a paper is negatively affected by a higher filler addition. According to Figure 7, the filler-fibre interactions in our system are thus weaker than the fibre-fibre interactions, $\zeta < 1$.

No clear correlation was found between the filler floc strength and the properties of the produced paper. A possible explanation for this can be that the forces in the dynamic sheet former were quite small, and therefore did not affect the filler flocs significantly. The strength of formed filler flocs is likely more important in real industrial paper machines, where the forces are much higher.

The results have shown that it is possible to regulate properties of filler flocs; both their size and their strength can be varied. In this work, the properties of the filler flocs have been controlled by both addition of more binder and by changing the cationic polymer.

The size of the filler flocs have been shown to be very important for the tensile strength of the paper. Larger flocs promoted a higher tensile strength. The z-strength of a paper has been shown to be rather independent of the filler floc size. Higher z-strength values were shown to be more favored by an increased amount of added binder.

The processing conditions when the filler flocs were made had little influence, especially for smaller filler flocs.

The double adhesive tape method for measuring the z-strength used in this work was shown to work well when comparing paper sheets. The absolute values obtained, on the other hand, were too low, compared to the lamination method used at Innventia. In this work, the focus has been on comparing sheets with different pre-treatments of the fillers, thus the tape method was appropriate.

Future work

The maximum sizes of flocs that still will provide papers with an acceptable formation haven’t been found. It would therefore be interesting to see how big the flocs can be before the paper properties will suffer.

To validate the achieved results herein, sheet forming using flocs produced with the same chemical addition but with different sizes would be desirable. One could systematically decrease the size of some of the flocs with the help of an Ultra-Turrax or other type of shear force. The tensile strength of the produced papers should then be affected, but the z-strength of the papers with the flocs with the different sizes should give the same value.

It would be interesting to conduct further experiments on the three component flocculating system used in this work, to more accurate decide which flocculating mechanism that is operating. A way of achieving this is to study the rheological response of the system when different additions of polymers are used, either with fillers or without.

More polycations should also be tested with the same conditions as used in this work, where size and strength of the flocs formed are measured and compared with the ones in this work. Different kinds of binders can also be tested and evaluated.

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