HYDROPHOBIC SURFACE SIZING OF TESTLINER

Misla Lagus
Faculty of Science and Engineering
Åbo Akademi University
2019

ÅBO AKADEMI – FACULTY OF SCIENCE AND ENGINEERING

Abstract

Subject: Surface sizing of testliner

Author: Misla Lagus

Title of work: Hydrophobic surface sizing of testliner

Supervisor: Martti Toivakka

Assistant supervisor: Kimmo Huhtala

Abstract

The demand for inexpensive, sustainable packaging is rising continuously, and surface sizing of testliner is gaining importance. In this study, the effect of sizing method, base paper properties, and surface sizing agent (SSA) properties on starch pickup, paper strength, and sizing effect were examined.

The starch pickup was shown to depend on surface size solids content and base paper porosity. The strength of the base paper was tied to the porosity, a more porous base paper was weaker, as expected. Surface sized paper strength depended on the base paper strength and the starch amount added.

Differences in sizing effect were witnessed both between different SSAs and between different base papers. Wettability and starch absorption of base paper affected the sizing effect. SSA particle size, SSA hydrophobicity, and poly aluminum chloride (PAC) usage also affected the sizing effect.

Keywords: surface sizing, testliner, packaging, surface sizing agent, base paper properties, hydrophobicity, sizing effect

Date: 13.3.2019

Pages: 72

ÅBO AKADEMI – FAKULTETEN FÖR NATURVETENSKAPER OCH TEKNOLOGI

Abstrakt

Ämne: Ytlimning av testliner	
Författare: Misla Lagus	
Arbetets titel: Vattenavstötande ytlimning av testliner	
Handledare: Martti Toivakka	Biträdande handledare: Kimmo Huhtala

Abstrakt
Efterfrågan på billiga, hållbara förpackningar stiger kontinuerligt, och ytlimning av testliner blir samtidigt allt viktigare. I denna studie undersöktes effekten som baspapprets egenskaper, ytlimningsmedlets egenskaper och ytlimningsmetoden har på stärkelseupptagningen, pappersstyrkan och ytlimningseffekten.

Stärkelselösningens torrhalt och baspapprets porositet påverkade stärkelseupptagningen. Porositeten påverkade baspapprets styrka, ett mer poröst papper var svagare, som förutsett. Både baspapprets styrka och stärkelsemängden påverkade det ytlimmade papprets styrka.

Skillnader i ytlimningseffekten kunde ses både mellan de olika baspappren och mellan de olika ytlimningsmedlen. Ytlimningseffekten påverkades av baspapprets vätbarhet och stärkelseabsorption. Ytlimningsmedlets partikelstorlek, ytlimningsmedlets hydrofobitet och användningen av poly aluminiumklorid hade också inverkan på ytlimningseffekten.

Nyckelord: ytlimning, testliner, förpackning, ytlimningsmedel, baspappersegenskaper, hydrofobitet, limningseffekt

Datum: 13.3.2019	Sidantal: 72

Acknowledgements

First and foremost I would like to thank my assistant supervisor Kimmo Huhtala for guiding the work, for listening to my ideas and suggestions, for motivating me to finish writing the thesis, and most of all for always asking me to aim a little bit higher.

Sheryl Hildén, Kai Dahlskog and Jussi Salonen, thank you for our insightful conversations and for sharing your industry knowledge.

I would like to thank Mia Ahokas for providing invaluable insight and advice during the writing process.

Sanna Salonen, thanks for your innovative ideas and advice on laboratory practicalities.

I would further like to thank everyone working at CH-Polymers laboratory facilities in Raisio. I will always be grateful for how every one of you have shared your expertise and knowledge with me without restraint. Special thanks to Taru Ojala-Lehtonen and Minna Lamminen for your continued friendship, and for teaching me most of the laboratory analyses.

I would like to thank Professor Martti Toivakka and Assistant Professor Mari Nurmi for trusting me to complete this master’s thesis and for the final touches.

I am also grateful to everyone involved in sending base paper samples from the participating paper mills and to Business Finland Oy (former TEKES) for providing funding for the work inside the BIOBIND project.

Table of contents

List of tables and figures

List of abbreviations

AKD	Alkyl ketene dimer
ASA	Alkenyl succinic anhydride
CD	Cross direction
COD	Chemical oxygen demand
DWR	Dynamic water retention
FWA	Fluorescent whitening agent
KL	Kraftliner
MD	Machine direction
PAC	Poly-aluminum chloride
PPS	Parker print-surf
SAE	Styrene acrylic ester
SCT	Short-span compression test
SMA	Styrene methacrylate
SSA	Surface sizing agent
T_g	Glass-transition temperature
TL	Testliner

Introduction

The focus of this thesis is hydrophobization of testliner through surface sizing. It is a relevant topic because corrugated boxes are low-cost, sustainable packaging materials that are being used more and more because of the prevalence of online shopping. Packaging materials are also gaining more traction in the paper industry as the market share of graphical papers continues to decline. The use of recycled fiber-based testliner is further rising compared to virgin-fiber based kraftliner because recycling of paper and board has never been practiced in Europe to the degree it is today, with the Americas and Asia following the trend (CEPI, 2016; Holik, 2013; ERPC, 2016).

Surface sizing, or applying starch and surface sizing agent (SSA) to the paper surface, is an old process. The application on testliners is nevertheless complex because of the large number of changing parameters in the hydrophobization. Previously, and in some cases currently, hydrophobization of liners would be achieved through internal sizing, i.e., adding the sizing agents to the wet end of the paper machine. However, especially recycled testliner fibers can contain a wide range of paper chemistries that may complicate the wet end internal sizing process, leading to deposits and costly shutdowns. Surface sizing allows for a simplification of the wet end, prevention of the uneconomical application of sizing agents to the inside of the paper is, and precise fine-tuning of the surface properties (Bajpai, 2015; Zeng, 2013).

The exact mechanisms for hydrophobization in surface sizing are currently not well understood, and laboratory studies seldom correlate well with practical on-machine tests. Furthermore, there is no SSA that would provide the same level of hydrophobization on all testliners. Through a better understanding of the surface sizing process, wasteful SSA application amounts could be avoided, and SSA's could be developed more efficiently. A reliable laboratory method would facilitate SSA development further and improve performance prediction possibilities.

In this thesis, the goal is to increase our understanding of the hydrophobization in testliner surface sizing. In Chapters 1 through 4, the surface sizing process and relevant materials are discussed from a literature point of view. The methods and materials used in this study are presented in Chapters 5 and 6. The results of the thesis are covered in Chapters 7 to 10, starting with observed differences in sizing effect and continuing to the effect of surface sizing method, base paper and SSA parameters on sizing effect.

I LITERATURE REVIEW

The focus of this work is hydrophobization in surface sizing of testliner. In order to introduce the surface sizing process, the following literature review covers surface size application methods, starch, surface sizing agents (SSA), and testliner base paper. Relevant theories of hydrophobization and water penetration are also introduced.

1. Surface size application method

The surface sizing operation is placed in the middle of the drying section of the paper machine. A solution of starch, surface sizing agent and potential additives is applied to the surface of the paper web, using either a pond type size press, metered film press, or a novel method presented in the following chapter. The three surface size ingredients and the application method can be varied, comprising the endless individual configurations of each paper machine. Further, the pickup and efficiency of the surface size is dependent on concentration (solids content), starch type, temperature, viscosity, pH, sheet moisture, internal sizing and its development, and machine speed (Hagiopol, Johnson, 2012).

1.1. Pond type size press

The pond type size press, or flooded size press, is the older and nowadays less used of the two most common surface size application methods. The paper web passes between two rotating cylinders with a pond of surface size between them (Figure 1). Wet pickup in the pond type size press is usually 30-50% of the paper weight, i.e., 300 to 500 kg/t. Typically, the pond size press is run at approximately 10% solids, corresponding to 30-50 kg/t dry pickup (Holik, 2013; Maurer, 2009; Gess, Rodriguez, 2005).

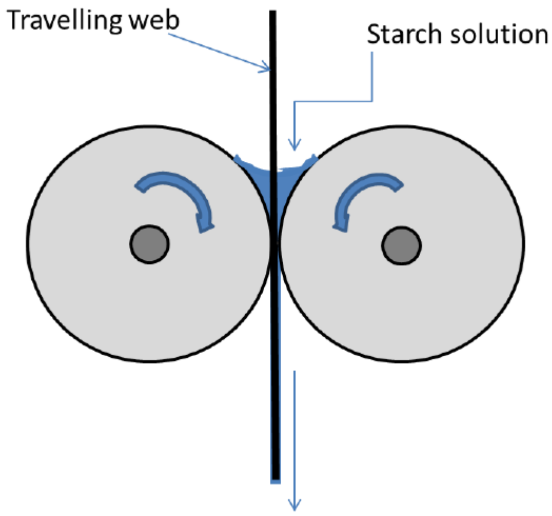

Figure 1. Pond type size press (Andersson, Ridgway & Gane, 2013)

Surface size is transferred to the paper through wetting and capillary transfer in the pond, and pressure penetration in the nip. Wetting and capillary transfer are mainly controlled by the formation and chemical properties of the paper. The formation includes porosity, basis weight, density, surface smoothness, moisture content, and temperature. Increased porosity increases the pickup, and a rougher surface raises pickup when more liquid is metered through the nip. Chemical properties depend on the raw material and the presence and development of internal sizing. The internal sizing influences the fiber surface energy, limiting the capillary transfer of surface size, thus shifting the transfer mechanism towards pressure penetration. Without internal sizing, the starch pickup is mostly dependent on pore wall wetting. The low solids content in the pond type size press means that the paper is rewetted considerably, and the absence of internal sizing may lead to web breaks especially at slower speeds (Maurer, 2009; Gane, 2001; Holik, 2013; Andersson, Ridgway & Gane, 2013; Gess, Rodriguez, 2005).

Pressure penetration in the nip is hydrodynamic force-dependent. The hydrodynamic force, and thus pickup, increases with softer, larger size press rolls, higher nip pressure, and faster machine speed. When machine speed is increased the transfer mechanism will shift from mainly pond interactions to more pressure penetration. During the change, starch pickup will pass through a minimum before the hydrodynamic pressure increases (Holik, 2013; Maurer, 2009).

Other than the pickup, the holdout of surface size should be considered. The added surface sizing agents are designed to make the surface of the paper hydrophobic, a higher level of holdout is often desired to prevent the wasteful application of SSA to the middle of the liner. However, surface size starch contributes to the strength of the paper, and holdout should be optimized for both strength development and hydrophobization depending on the requirements. The holdout is generally increased by lower paper porosity and higher molecular weight or viscosity of starch (Maurer, 2009; Gess, Rodriguez, 2005).

Problems and defects in pond size presses can occur because of web detachment from the rolls and pond instability. Upon leaving the size press nip, the paper web must be pulled apart from one of the size press rolls. To prevent defects, the starch viscosity, roll diameter, web tension and web take-off angle should be optimized. At high machine speeds, high turbulence may occur in the pond causing instability, e.g. splashing. Stability problems can be alleviated with foils dipped into the pond on each side, and by using bigger roll diameters (Maurer, 2009; Gane, 2001; Holik, 2013).

Pond size press pigmentation has been studied showing promising results of decreased drying energy demand, reduction in fluorescent whitening agent (FWA) addition amount, and better holdout at the surface due to higher solids content. However, metered size press pigmentation has been found more efficient for fiber reduction (Wygant, Lucidi & Kendrick, 2009).

1.2. Metered film press

The metered film press is the other of the two most common surface size application methods and is widely used today. It was developed to reduce the splashing and rewetting problems with the pond-type size press. Instead of passing the paper through a pond where starch is picked up, a set amount of starch is metered on an applicator roll and pressed into the paper (Maurer, 2009; Lehtinen et al., 2000). There are two widely used methods of starch metering which will be presented next.

The gate roll film press

In the gate roll film press, the starch amount is metered by film splitting between three rolls: the metering (= gate) roll, the transfer roll, and the applicator roll. The metering roll is in contact with a starch pond, from where a film is picked up. The film is split once in the nip between metering and transfer roll, and a second time between transfer and applicator roll. The residual film is pressed onto the paper in a nip between the applicator roll and the backing roll. If the starch is applied on both sides of the paper, either a simultaneous or tandem configuration can be chosen. In a simultaneous gate roll film press, the backing roll is the applicator roll for the other side. In a tandem gate roll film press, the other side of the paper is treated in a separate station after the first one (Maurer, 2009).

Pond instability and splashing are common problems with the gate roll film press. They can be controlled by running the metering roll at slow speeds, or by using higher solids content and higher viscosity starches. The higher solids content, in turn, allows paper webs of a higher moisture content to be sized without risk of web breakage, reducing drying energy and time both before and after the film press. These advantages can enable higher machine speeds, further increasing the machine efficiency (Maurer, 2009).

Rod metered film press

In a rod metered film press (Figure 2) surface size starch is applied to the metering roll with a short dwell coater or a pond, and a rod meters the starch to the preferred film thickness. Surface size pickup is controlled by machine speed, surface size viscosity, film split between paper and roll, and roll hardness. Film split between metering rod and roll, rod profiling, and rod pressure are also relevant (Holik, 2013; Maurer, 2009).

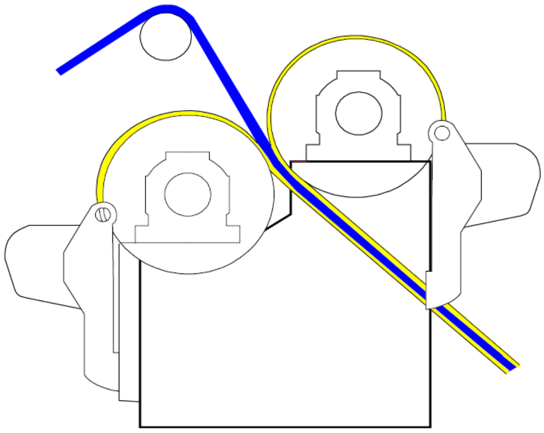

Figure 2. Two-sided metered size press (Forsström, 2003)

The method has the same advantages over pond type size presses as the gate roll film press, i.e., the higher solids content of the starch allows a reduction in drying energy. Solids contents up to 30% have been studied and shown to be runnable, giving a higher holdout of starch, resulting in decreased paper porosity, decreased oil absorption, decreased internal strength of paper, and increased surface strength and bending stiffness. However, the effect of higher viscosity starch on the SSA efficiency has not been evaluated (Lipponen, 2005).

Sources of problems with metered film presses are starch viscosity and film splitting behavior. Low viscosity starch may lead to fluid spraying in the metering. In the film splits between rolls and between roll and paper, misting and orange peel pattern can occur. For the roll-paper split, the problem may be prevented by bringing the film-splitting closer to the roll (Maurer, 2009).

Metered film press pigmentation has been studied with promising results. Fiber content could be reduced in the final product for savings in fiber price, and the size press could be used as a precoating device. However, adding pigments to the surface size adds viscoelastic behavior to the “sizing color”, and the formulations need optimized rheology and water retention for runnability (Gane, 2001; Wygant, Kendrick & Walter, 2008).

1.3. Novel and alternative methods

New methods for surface size application that have been introduced are calender water boxes, spray application, and foam application. In the calender water boxes, the starch is usually diluted and applied at a low level with lubricants. Surface strength of the paper is increased, and fiber swelling after coating is limited (Maurer, 2009). Spray application may become more important in the future, with possible benefits including higher starch solids contents, no wearing parts and easy control of surface size amount (Holik, 2013; Valmet, 2017). Adding foaming agents to the surface size and applying it as a foam keeps the surface size efficiently on the surface of the paper. The advantages could be lower coat weights needed and higher solids contents, but the foaming agent may also hinder the performance of the SSA (Sievänen, 2010).

2. Surface size

The surface size applied to the paper consists of starch, surface sizing agent (SSA) and potential additives. The SSA decreases water absorbency, the starch increases the strength of the paper, and together they improve printability by controlling ink penetration (Zeng, 2013). In this work, hydrophobization is the focus point. Strength is, however, a far too important part of the surface sizing result to be ignored, and thus the following chapter will cover both starch and surface sizing agents, other additives will be introduced briefly.

2.1. Starch

Starch is a naturally occurring biopolymer which is present in a variety of plants. For use in the paper industry, the main raw materials are corn, potato, wheat and tapioca. In the plants, starch exists as semi-crystalline granules consisting of two polymers of D-glucose units, amylose (20-30%) and amylopectin (70-80%), both built up with α-1,4-bonds (Figure 3). Amylose is the smaller of the two, despite being present at only 20-30 mass-% there are about 150 times as many linear amylose molecules as larger branched amylopectin molecules. The ratio of the two constituents, branch points in amylopectin, and granule size of the starch depend on the source (Holik, 2013).

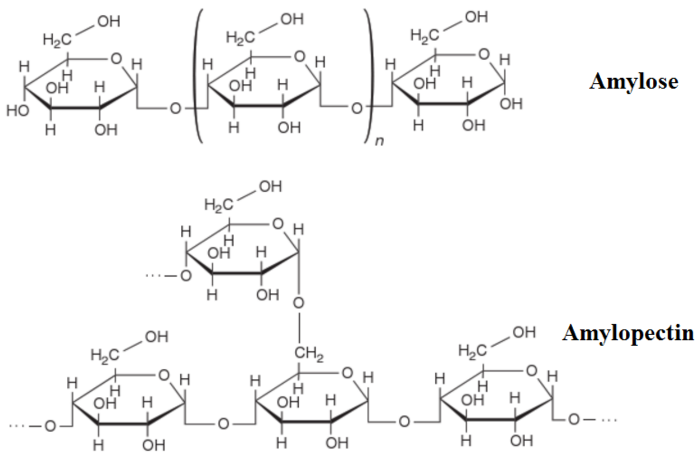

Figure 3. Amylose and amylopectin chemical structure (modified from Holik, 2013)

2.1.1. Starch in the paper industry

In the paper machine, starch can be added to the wet end, sprayed on the forming wire, and added as surface size. It is by weight the third most used material after cellulose fibers and mineral pigments in papermaking and paper conversion (Maurer, 2009).

Wet end starch

Wet end starch is typically added at levels up to 1.5% of cationic starch or up to 5% of starch with a cationic polymer. Higher addition levels can disrupt the charge balance in the wet end. The strength of the paper is improved when the free hydroxy groups in the starch interact with fiber surface cellulose, participating in hydrogen bonds. Retention and formation are improved when the gel-like starch network encapsulates particles and fines. Cationic starch is retained efficiently due to ionic interactions with the anionic fibers, while anionic or native starch needs to be used with a cationic polymer, like polyvinylamine, which improves retention by forming aggregates or through precipitation. Anionic starch can also be used in conjunction with cationic starch to stabilize the charge balance (Maurer, 2009; Holik, 2013).

Spray starch

Spray starch is sometimes added to the paper web on the forming wire at addition levels of up to 20% of the dry product. The starch is usually unmodified and uncooked; it is assumed that cooking and gelling take place throughout the drying process. Benefits of spray starch include retention where it is sprayed (surface or between layers), improved bonding between layers, lower manufacturing costs, and increased strength. However, when making recycled linerboard at high machine speeds the starch may not have enough time to penetrate into the sheet and gelatinize, causing plugged wires and accumulation of starch in discharges (Maurer, 2009; Holik, 2013; Ryu, Lee, 2007).

Surface size starch

Surface size starch is added to the paper at the size press or film press for pick up levels of 30-70 kg dry starch per ton of paper, usually about 40 kg/t. The starch binds large vessels and loose fibers with hydrogen bonds, increasing the strength of the paper up to 60%. Stiffness, dimensional stability, and air leak density are also improved. Native starch is not suitable due to high viscosity and tendency to retrograde; the starch must be modified or converted either by the supplier or at the paper mill before use (Zeng, 2013; Maurer, 2009; Holik, 2013).

2.1.2. Dispersion and conversion

Native starch is rarely used in surface sizing because of the high molecular weight and corresponding high viscosity. It is either converted, modified, or both to control the viscosity, charge and bonding ability. Starch is usually supplied dry in package or bulk container to avoid transporting water. Dispersion and conversion are done on-site at the paper mill. Common conversion methods include enzymatic conversion, thermal conversion, thermos-chemical conversion and acid hydrolysis. Chemical modification (usually oxidation, hydroxyethylation or cationization) can be done either at the supplier or the paper mill (Holik, 2013; Gane, 2001; Maurer, 2009).

Dispersion

Dispersion is carried out by heating the starch during agitation for a set amount of time, either continuously or in a batch process. The starch granules swell, and the semi-crystalline structure breaks up, forming a gel-like network. Minimum requirements are 20 minutes at a temperature of 95 ºC, but granular fractions will persist in the starch suspension. Jet cooking with pressurized steam at higher temperatures (120-140 ºC) disperses most residues. Excess steam and pressurized release of starch can increase dispersion efficiency further, lowering the viscosity. Jet cooking is especially popular with pre-modified starches (Gess, Rodriguez, 2005; Maurer, 2009; Holik, 2013).

Conversion

Conversion lowers the molecular weight and viscosity of the starch to ease the application. Thermal conversion happens during efficient thermal dispersion or jet cooking, heat and shear disperse the starch for complete hydration and lower viscosity.

Thermo-chemical conversion combines thermal conversion with chemical modification (Holik, 2013; Gane, 2001; Gess, Rodriguez, 2005).

In enzymatic conversion, enzymes are added to the starch dispersion in a batch or continuous process. The enzymes break down the starch under controlled pH, agitation and heating until the desired viscosity is achieved, then the temperature is increased rapidly to kill the enzyme. The method is simple and inexpensive, but reproducibility is low which can lead to variations in viscosity (Gess, Rodriguez, 2005; Maurer, 2009).

Acid hydrolyzed starch is depolymerized with acids, e.g. hydrochloric acid. The method is inexpensive, but the resulting depolymerized starch has an unstable viscosity and is sensitive to retrogradation, and therefore temperature and pH control is required (Maurer, 2009).

2.1.3. Retrogradation

During cooling and storage, the semi-crystalline structure of starch may recover in a process called retrogradation. Amylose aggregates form particles, while amylopectin forms a gel where linear parts of the molecules align. The retrogradation of amylose can start if dilute starch is kept at a temperature of 67-90 ºC, and amylopectin can start thickening below 55 ºC. Retrogradation is facilitated by starch molecular weights between 6500 and 160 000, slightly acidic pH (6.5), high amylose content, destabilizing ions (for example aluminum and calcium), contamination, well-dispersed starch and hydrolyzed starch (Maurer, 2009).

To avoid retrogradation, the temperature of dispersed (cooked) starch should be kept at 60-65 ºC or above 95 ºC. Starch modification by oxidation or esterification can reduce retrogradation, and preservatives can be used to prevent microbial action that lowers the pH. Redispersion of amylose particles requires breaking of bonds at high temperatures (115-120 ºC), whereas for amylopectin a temperature of 55 ºC is sufficient to dissolve the gel (Maurer, 2009).

2.1.4. Modification

Chemical modification of starch is increasingly popular, in 2009 about two-thirds of the starch used in size press application was modified (Maurer, 2009). The higher cost of modified starch compared to native on-site converted starch probably limits the use in testliner production, however, the benefits may outweigh the cost. Advantages of modified starches include improved stability, lower viscosity, retrogradation resistance, improved film formation and binding properties. The most common methods for modification are oxidation (oxidized starch) and derivatization (ethylated starch and cationic starch). Cationic starch has superior retaining and fixing properties, while anionic starches are compatible with a range of additives, including FWAs (Maurer, 2009; Jonhed, 2006).

Oxidized (anionic) starch

Oxidized starch is produced by reacting starch with sodium hypochlorite or peroxide (or less commonly with ozone or sodium periodate). The hydroxyl groups in starch are transformed to carboxyl groups, and starch is depolymerized through ring-opening. Starch properties (e.g. viscosity) can be controlled by adjusting the reaction conditions or by choice of raw material (different amylose to amylopectin ratio) (Gess, Rodriguez, 2005; Vanier et al., 2017; Jonhed, 2006).

Oxidized starch has improved water holding, film formation, film strength, and film integrity properties compared to native starch, giving the final paper high surface strength and improved ink holdout. The new bulky carboxyl groups hinder retrogradation sterically, reducing the gelatinization temperature. In surface sizing, oxidized starches have been shown to penetrate deep in the paper structure and decrease opacity (Gess, Rodriguez, 2005; Jonhed, 2006; Lee et al., 2002).

The anionic character of the starch influences the interaction with other papermaking substances. Broke recycling brings the anionic starch to the wet end, where it prevents pigment and cellulose agglomeration through efficient dispersion, and reduces retention. This leads to anionic trash in the effluent water and increased chemical oxygen demand (COD). To combat the retention problem, slightly oxidized starch, i.e., bleached starch, has been developed for surface sizing. Bleached starch is produced with a low degree of oxidation (carboxyl content less than 0,3%) and partial crosslinking. However, the dispersing properties of anionic starch still worsen retention and, therefore, the use of anionic starch in surface sizing is generally declining (Lee et al., 2002; Jonhed, 2006; Gess, Rodriguez, 2005; Maurer, 2009).

Cationic starch

Cationic starch is produced by a nucleophilic substitution reaction with tertiary or quaternary amines. The reaction with tertiary amines requires acidic pH, but quaternary amines work across acid to alkaline pH values. Hydroxyethylated cationic starch is produced for specialty products (Maurer, 2009).

In surface sizing, cationic starch has been found to increase the holdout of the surface size on the paper surface. The higher holdout, in turn, improves opacity, brightness, print gloss, and ink print density (Shirazi et al., 2005; Lee et al., 2002).

The primary advantage of cationic starch over anionic and nonionic starch is improved binding and retention ability. The cationic starch interacts with the anionic fibers ionically, which produces stronger binding compared to hydrogen bonds. During broke processing, the cationic starch binds fillers and fines, reducing the suspended solids and COD of the wastewater significantly. Because of environmental regulations and discharge limits, the use of cationic starch in surface sizing is rapidly growing (Lee et al., 2002; Maurer, 2009; Jonhed, 2006).

2.2. Sizing agent

The purpose of sizing is to make paper water resistant to some degree. In general, the mechanism is to coat the hydrophilic fibers with hydrophobic sizing agents. The sizing agents can be either amphipathic molecules, having one hydrophilic and one hydrophobic part, or highly hydrophobic molecules. The sizing agents can be applied to the paper either in internal sizing, in surface sizing, or in a combination of the two. In internal sizing, the sizing agent is added to the paper stock at the wet end of the paper machine, while surface sizing agents are added to the starch at the size press. The sizing agents can be characterized according to application method (internal or surface) and functioning principle (reactive or non-reactive). Reactive sizing agents form a chemical or physical bond with the cellulose fibers during drying, characterized by a developing hydrophobicity. Non-reactive sizing agents need a high level of hydrophobicity to make the paper moisture resistant without the bond to the fibers, but the hydrophobicity effect is instant (Holik, 2013; Hagiopol, Johnson, 2012).

2.2.1. Internal sizing agents

The most important property for internal sizing agents is the retention. Otherwise, the sizing agent will flow out with the effluents. Reactive internal sizing agents form a bond with cellulose and are thus readily retained. Cationic non-reactive sizing agents are attracted to the anionic fibers because of their charge, but anionic or non-ionic non-reactive internal sizing agents need a retention aid. Other than retention, the hydrophobic character, molecular weight, molecular orientation, glass-transition temperature (T_g), paper surface friction and pH compatibility are all essential factors for the hydrophobization process (Hagiopol, Johnson, 2012).

The three most popular internal sizing agents are all reactive: rosin, AKD (alkyl ketene dimer) and ASA (alkenyl succinic anhydride) (Figure 4) (Hagiopol, Johnson, 2012).

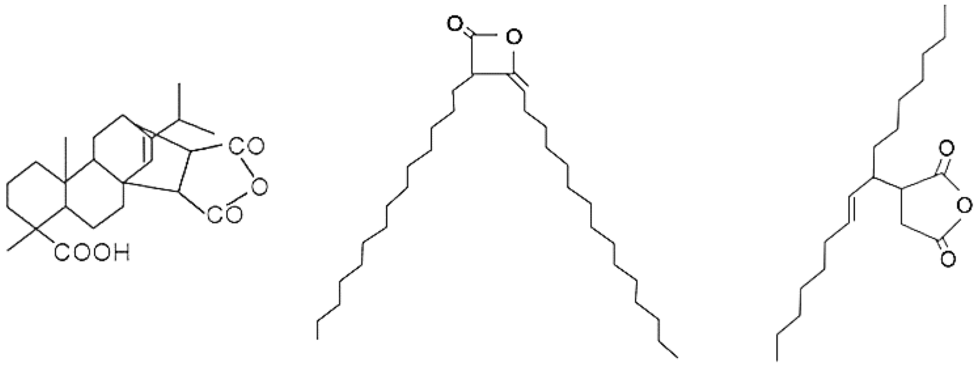

Figure 4. Structure of internal sizing agents. From left to right: fortified rosin, AKD and ASA (modified from Holik, 2013)

One of the oldest sizing agents, rosin is extracted from resin that occurs naturally in trees. Extraction is carried out from the black liquor in the pulping process. Rosin requires an acidic pH to be effective, limiting the use of calcium carbonate pigments because of dissolution. Rosin is anionic and needs alum (aluminum sulfate, $Al_2(SO_4)_3$) to bind to the fibers. Later, rosin sizing agents have been modified, reacted further (using either the double bond or the carboxyl group), and saponified to produce a range of rosin-based sizing agents with increased hydrophobicity (e.g., fortified rosin) (Hagiopol, Johnson, 2012; Zeng, 2013).

AKD and ASA were invented after rosin sizing for alkaline and neutral papermaking. They quickly became popular because the pH allowed calcium carbonate pigment to be used. AKD and ASA are highly reactive with cellulose fibers, but also with the surrounding water, which can quickly “kill” the sizing agent through hydrolysis. AKD creates sticky by-products in the hydrolysis reaction, lowering machine efficiency. The reactive sizing agents are nonpolar, and thus need emulsifiers and stabilizers to be water soluble (Figure 5). Emulsion stability issues are common, especially ASA hydrolyzes fast and must be dispersed right before use. AKD size needs a high temperature curing at drying and grade-dependent curing times to impart hydrophobicity. ASA size is more reactive than AKD and does not require curing, but elevated stock temperatures and higher pH increase efficiency (Hagiopol, Johnson, 2012; Holik, 2013; Zeng, 2013).

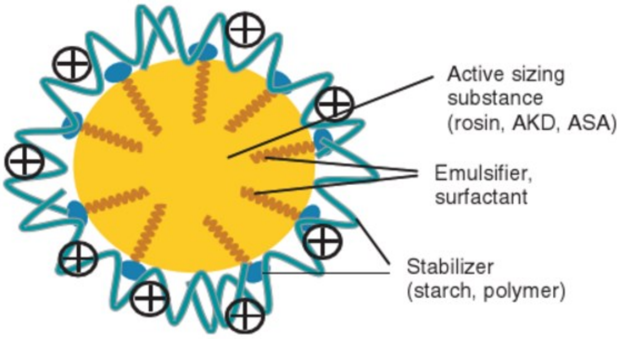

Figure 5. Sizing agent particle in emulsion (Holik, 2013)

There are many other polymeric internal sizing agents, and new ones are being researched continuously to combat the problems of dispersion stability, retention and hydrolysis reactions. Common synthesis methods for non-reactive sizing agents are to add hydrophobic tails or cationic charges to existing polymers. Reactive sizing agents can be synthesized utilizing cellulose-reactive groups, for example, epoxy groups, aziridines, carbamoyl chloride groups, succinic anhydride groups, and ketene dimer groups (Hagiopol, Johnson, 2012; Gess, Rodriguez, 2005).

2.2.2. Surface sizing agents (SSA)

Surface sizing agents (SSA) are applied with the starch on the surface of paper. Thus, wasteful application to the inside of the paper sheet is prevented. The paper machine wet end chemistry is also simplified because of the exclusion of sizing agents. Surface sizing agents are usually non-reactive, i.e., they do not participate in reactions that alter their molecular structure when applied to the paper. To be effective, SSAs need a high degree of hydrophobicity and a high coverage on the paper sheet. The hydrophobicity needs to be balanced with hydrophilic character to enable the mixing of SSA with starch, and thus the SSA particles are amphipathic (they contain one hydrophobic and one hydrophilic part). Stabilizers are used to prevent agglomeration of the amphipathic particles, and to prevent foaming of the surface size, both of which decrease coverage on the paper (Hagiopol, Johnson, 2012; Holik, 2013).

A high degree of coverage is essential to provide hydrophobicity. Adequate coverage is assured by adjusting the SSA T_g, minimum film-formation temperature (MFFT) and the paper machine drying conditions to allow the SSA particles to spread on paper surface. A film is usually not formed, instead a lattice of hydrophobic SSA particles and hydrophilic starch. The efficiency can further be improved by increasing the hydrophobic character of the SSA, decreasing particle size (more coverage for same SSA dosage) and using different types and amounts of stabilizers to prevent agglomeration in the surface size and excessive penetration in the paper sheet. For example, zirconium salts have been used as complexing agents to prevent penetration of the SSA (Pandian, van Calcar & Wolff, 1994; Hagiopol, Johnson, 2012).

There is a multitude of SSA chemistries available for virtually all types of papermaking conditions. Some internal sizing agents can also be applied as SSA. For example, while AKD has been used in surface sizing, it is only stable for a couple of hours at starch temperatures (about 60 °C). The most common SSAs are polymeric SSAs, usually with a styrene base to provide hydrophobicity. While the polymeric SSAs are mostly used in surface sizing, they may also be used as internal sizing agents or in combination with traditional internal sizing chemistry (Gess, Rodriguez, 2005; Holik, 2013).

A polymeric SSA is commonly synthesized by emulsion copolymerization, usually through a free radical polymerization that starts with homogeneous nucleation. Essential factors for the synthesis are reaching the target T_g, control of the particle size distribution, and control of the stabilizer type and concentration. Glass-transition temperature can be estimated theoretically taking into account the ratio of monomers and the monomer's individual T_g. Particle size can be controlled by adjusting the number of nuclei at the beginning of the reaction and ensuring their protection. The polymer composition is influenced by the process type and the monomer ratio. The structure is influenced by T_g and composition (homogeneous or, e.g., core-shell). The chemical composition distribution can be affected by reaction conversion, monomer ratio, and monomer reactivity. The copolymer will orientate so that the more water-soluble co-monomer is oriented towards the particle surface (Hagiopol, Johnson, 2012).

The two main, widely used groups of polymeric SSA are styrene-maleic anhydride copolymers (SMA) and styrene-acrylic ester copolymers (SAE) (Figure 6) (Hagiopol, Johnson, 2012; Holik, 2013).

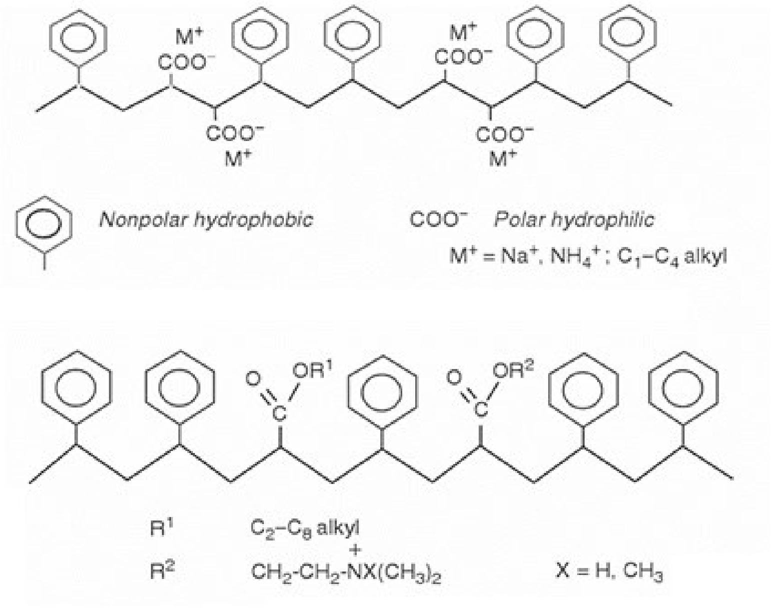

Figure 6. Structure of SMA (top) and SAE (bottom) (modified from Holik, 2013)

2.3. Other surface size additives

Other than SSA, prevalent additives in the surface size starch are preservatives for the starch, promoters, defoamers, fillers, and pigments, FWAs, co-binders and other functional additives, for example, to improve printability (Holik, 2013).

Promoters in surface sizing are usually aluminum compounds, e.g., poly aluminum chloride (PAC). Promoters can be used with rosin sizing or ASA sizing to fixate the molecules to the fibers, but SMA SSA hydrophobization performance has also been reported to increase. Aluminum has a high cationic charge which gives it high affinity toward the fibers, as well as the anionic sizing agents. Fines and fillers will also be retained with aluminum, preventing SSA particles absorption only in the fillers and fines (Holik, 2013).

2.4. Improving print quality with surface sizing

Pigment addition to the size press has been shown to increase paper smoothness, improve optical properties, increase density and stiffness, and improve printability. The pigment can be used to replace some of the fiber in the paper, the size press can act as a precoater, and FWA demand can be reduced (Wygant, Kendrick & Walter, 2008).

When pigments are added, the surface size solids content increases considerably, up to 60%. A high pigment loading may require additional binders and rheology modifiers in addition to starch to improve runnability (Maurer, 2009).

Fluorescent whitening agents (FWAs) are usually added at the size press to prevent wasteful application in the bulk of the paper. The FWAs improve opacity and whiteness of the paper (Holik, 2013).

3. Testliner base paper

The following chapter introduces testliners and the paper machines used to produce liner in general.

3.1. Testliner

Testliners are produced in grammages of around 70-450 g/m^2 globally (in Europe 70-130 g/m^2) with maximum machine speeds above 1500 m/min. The speeds have been increased through improved designs to achieve high annual production for low basis weight paper grades. The paper machines for liner production usually have one or two layer gap formers or one to multi-ply Fourdriniers. The multi-layer design enables production of white top liners or high-performance liners with kraft pulp additions in the top layer and also works to decrease sheet two-sidedness (Holik, 2013).

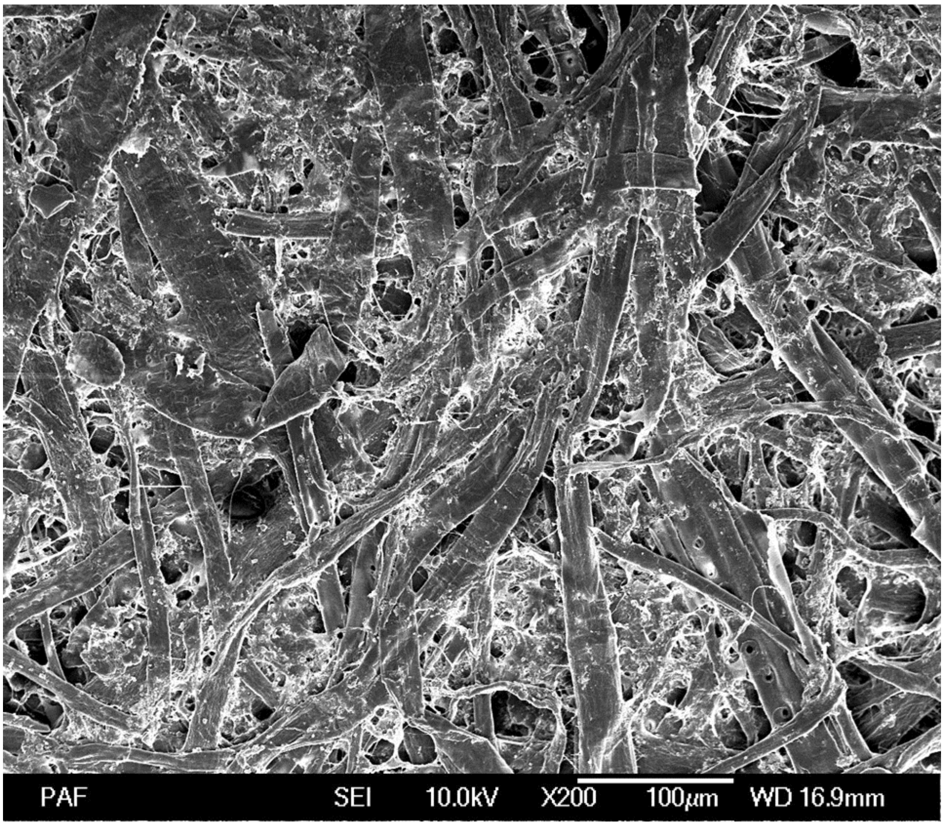

Figure 7. Structure of an unsized European testliner

3.2. Raw material

Testliner paper grades are entirely based upon recycled, secondary fibers giving a structure shown in Figure 7. The fibers are usually sourced from old corrugated containers, but recycled newsprint and graphical paper may also occur. Fibers are reused on average 3.5 times in Europe. (ERPC, 2016) For each reuse, the fiber properties deteriorate, thereby making the paper weaker (Holik, 2013).

The strength decrease is a combination of decreased fiber strength and decreased interfiber bonding. Recycling treatment seems to have a higher impact on interfiber bonding through a decrease in surface bonding potential, and the first recycling cycle results in the largest decrease in paper strength. Repeated drying and rewatering also impact the fibers in the paper, which poses a problem for samples studied in laboratory scale (Nazhad et al., 2008; Khantayanuwong, 2002).

Recycled secondary fibers are not as absorbent as virgin fibers. Fiber treatment, e.g., refining and sorting, is the primary way to increase the absorbency of the paper for more efficient starch pickup in the paper. Internal sizing will also impact how the surface size penetrates the paper or stays at the surface (Holik, 2013).

More fines in paper furnish increase the density of the paper and have an impact on porosity. Fines naturally fill up pores as well as pull fibers closer together decreasing the thickness of the sheet. Fibrils contain a tenfold surface area compared to flake-like fines. The presence of fines on the paper surface can be significant for SSA performance (Sirviö, Nurminen, 2004).

3.3. Papermaking process

Recycled paper stock processing

Because of the already subpar properties, it is crucial to process the recovered paper stock properly before it ends up in the paper machine chest. Processing consists of repulping, separation, treatment of fibers, and treatment of contaminants. Repulping is an energy-intensive mechanical process of disintegrating the stock to individual fibers. These fibers then need to be separated from contaminants, for example, studs from used boxboard. Separation techniques include screens, hydrocyclones, and flotation cells. Then, the clean fibers are treated with refiners and in some cases bleach, and finally, chemicals are added to reduce or negate the effect of residual contaminants. The processed stock is fed to the paper machine headbox through the approach flow system, where all components of the stock are mixed, metered and supplied continuously. From the headbox, the suspension is distributed onto the wire, where the formation of the paper web takes place (Höke, Höke & Schabel, 2010; Holik, 2013).

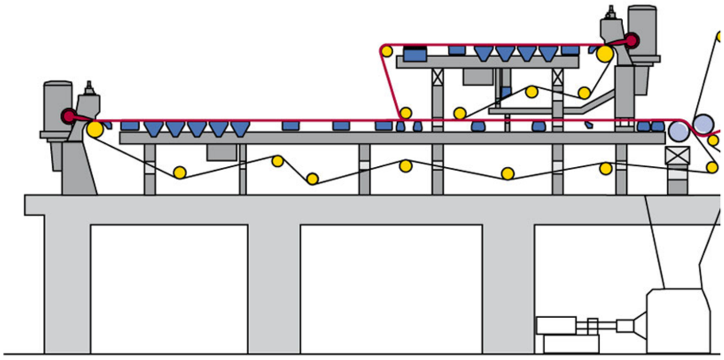

Figure 8. Two-ply Fourdrinier/hybrid forming section schematic (MultiLayer machine,Voith)

Formation

Different wire configurations impact the final paper structure, which further will have an impact on surface size penetration and performance. For testliners, standard configurations are the Fourdrinier, the gap former and the hybrid former. The Fourdrinier is a long planar wire where almost all dewatering happens on the bottom side, leading to a pronouncedly two-sided paper with higher compaction of fibers on the wire side, leaving fines and filler at the top. However, shoeboxes can disturb this two-sidedness with centrifugal force. A gap former wire means that the fiber suspension is a jet delivered between two wires and the dewatering is equal to both sides. The paper will have high symmetry with fillers and fines in the middle. However, pressure pulses can be used to mix the distribution. A hybrid former is a Fourdrinier wire with a second wire loop on top. The two wires are adjoined after some dewatering has already taken place before the press section (Figure 8). This configuration gives higher Z-direction symmetry than the Fourdrinier and also increases the drainage efficiency (Forsström, 2003; Holik, 2013).

Pressing, drying and calendering

After formation, the paper enters the press section where the sheet passes through several press nips where more water is pressed out mechanically. Paper is densified, porosity decreases, fillers and fines are carried to the surface with the water and paper roughness is affected. The surface densification affects liquid (and starch) absorption properties (Holik, 2013).

Dryers evaporate the rest of the water by heat, and after this, the surface size is usually applied to the paper web. Coating takes place after surface sizing if it is required, and finally the paper may be calendered to increase its smoothness (Holik, 2013).

4. Hydrophobization and water penetration theory

The goal of hydrophobic surface sizing is to increase the water repellence of the paper surface, i.e. to control water interaction with the paper surface. The interaction depends on the fiber surface chemistry, or interfacial energies (γ), and on the paper microstructure (Holik, 2013). Paper microstructure is often modelled as a collection of capillaries, although in reality the situation is far more complex.

Droplet contact angles (θ) indicate whether the paper is easily wettable ($\theta < 90^{\circ}$, $\cos\theta > 0$) or liquid repellent ($\theta > 90^{\circ}$, $\cos\theta < 0$). The contact angle is a result of interfacial energies according to the Young's equation:

$$\cos\theta = \frac{\gamma_{paper-air} - \gamma_{paper-liquid}}{\gamma_{liquid-air}}$$

When the interfacial energy between the air and the paper is lower than the interfacial energy between paper and water, it is energetically favorable for the paper to have an interface with air rather than with water, and the paper is hydrophobic. The sizing agent should thus either decrease the surface free energy ($\gamma_{paper-air}$) or increase the interfacial energy ($\gamma_{paper-liquid}$) (Holik, 2013).

The influence of paper microstructure for wetting driven capillary absorption can be described by the simplified Washburn equation

$$h \approx \frac{1}{r} \times \cos\theta,$$

where r is the radius of the capillaries, h is the water penetration depth into the paper and θ is the contact angle. According to the simplified Washburn equation, the water penetrates deeper into the structure the smaller the capillary radius, if the paper is easily wettable ($\theta < 90^{\circ}$, $\cos\theta > 0$) (Holik, 2013).

In surface sizing, especially when carried out by conventional size presses, the starch is forced into the paper by the nip pressure during application. This pressure penetration is controlled not by the surface energetics but rather by the driving pressure, the compressed pore structure of the paper (permeability) and the starch viscosity.

II EXPERIMENTAL PART

The objective of this thesis was to determine what properties of the base paper, the sizing agent, or the sizing process have an impact on the sizing effect, measured as paper surface hydrophobicity (Cobb 60s). The study consisted of laboratory surface sizing experiments on different base papers, paper analysis, surface size analysis, and sizing agent analysis. The existing laboratory scale sizing method was first studied and optimized to obtain comparable results. Then, a variety of surface sizing agents were tested on different base papers.

In this section, all relevant materials, equipment, and methods used in this work are presented.

5. Materials

Eight **base paper mill samples** were used in the study: five unsized testliners (TL 1, TL 2, TL 3, TL 4, and TL 5), one testliner with diluted surface size starch (TL + S) one unsized kraftliner (KL) and one copy paper grade (C). The base papers were analyzed, and the results are presented in Chapter 9: Effect of base paper properties.

Starch 1 and **Starch 2** were part of Roquette's "Stabilys A" product line of low viscosity modified potato starches. Starch 2 had a slightly higher viscosity. The structure of the starches simulates enzymatically converted starch.
Both starches were available in powder form and cooked with a jet cooker at 134 ºC at a set level of solids content.

45 different **surface sizing agents** (SSAs) named *SSA 1-45* were tested, including development products and references of different origin. All SSAs were tested on testliner 1, SSA 30 and SSA 31 were also tested on the other base papers. Most of the SSAs were tested both with and without the addition of poly aluminum chloride (PAC),

denoted *SSA X* and *SSA X + PAC*. The surface sizing agents were analyzed, or previous analysis data was used, to compare performance with SSA properties. The results are presented in Chapter 10: Effect of SSA properties on sizing effect.

6. Methods

6.1. Laboratory surface sizing method

Part of the objective of this master's thesis was to refine an existing laboratory surface sizing method and eliminate possible variables to obtain repeatable and comparable results. The aim was to achieve a constant addition level of surface size to the base paper (35-45 kg/t) and a repeatable hydrophobization effect of sizing agent dosage. The following section will describe how the surface sizing method was tested, which parameters were controlled and the final laboratory surface sizing method.

6.1.1. Surface sizing equipment

Starch was jet-cooked with variations in cooking speed, slurry solids content and temperature. The cooked starch's solids content was measured with a CEM 5 microwave oven. The surface size was prepared by mixing cooked starch with hot water and surface sizing agent with a laboratory magnetic mixer. Temperature, agitation time and solids content were controlled. The surface size was analyzed (solids content, pH, temperature, Brookfield 100 rpm) after preparation. The surface size was applied to the base papers using a Mathis pond-type size press (Figure 9) with soft rolls (70 shore D). The laboratory size press has adjustable speed (2-16 m/min), adjustable pressure (0-100 on a scale, the actual pressure was not known) between the rolls and the rolls can be heated with hot water before pouring the surface size into the pond. After surface size was added into the pond, four base paper sheets were run through the sizing solution and dried. The surface sized paper sheets were dried either in an oven or with an infrared dryer with variations in temperature and drying time.

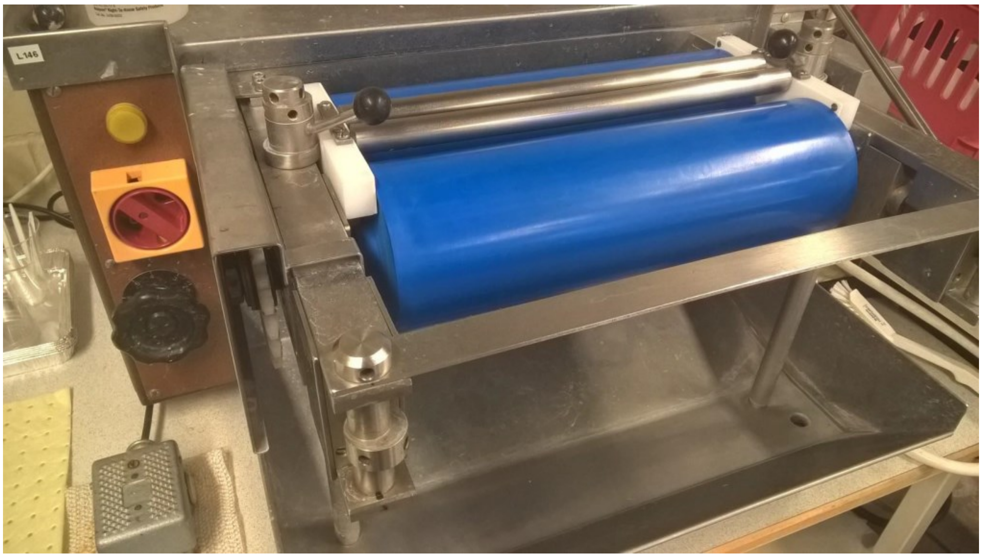

Figure 9. Laboratory Mathis pond-type size press

6.1.2. Experimental layout for testing the method

To achieve a constant sizing pickup and consistent sizing effect in the size press, the parameters that can influence the process were first defined. Then, the parameters were set to benchmark values, which enabled testing of the effect of each one with a number of experiments on the same base paper (testliner with starch, TL + S) by adjusting one parameter at the time. The benchmark and tested settings are presented in

Table . For the parameter test, a sizing solution of starch and SSA 1, an anionic, widely used reference surface sizing agent, was used.

Table 1. Benchmark settings for surface sizing parameter testing

Parameter	**Benchmark**	**Tested parameter values**
Paper moisture content	6-7%	7-8%, 6-7%, oven dried (ca 0%)
Size press speed	4 m/min	2,4, 8 m/min
Size press pressure	20	ca 0, 5, 10, 15, 20, 40
Pond starch volume	250 ml	20, 50, 75, 100, 150, 200, 250, 300 ml
Oven drying temperature	105 °C	60, 80, 105, 125, 145, 180 °C
Oven drying time	3 min	1, 3, 5 min
Surface size solids content	18%	10, 15, 16, 17, 18%
Surface size temperature	60 °C	20, 40, 60, 65, 70, 75 °C

6.1.3. Adjusting the laboratory surface sizing parameters

Paper moisture content

The effect of base paper moisture content was investigated with an exicator cabinet using saturated sodium chloride solution instead of silica to produce a higher base paper moisture content than that of the standard conditioned sheets (7-8% and 6-7%, respectively). Oven-dried base paper was used to investigate the effect of extremely low moisture content.

Size press speed

Speed was controlled by a wheel on the laboratory size press with a range of 2 m/min to 16 m/min; the tested values were 2, 4 and 8 m/min.

Size press pressure

The pressure was similarly controllable on the machine with a lever going from 0 to 100. However, the working pressure at lever position 100 was not known. The tested pressure lever positions were ca. 0 (barely holding the surface size in the pond), 5, 10, 15, 20 and 40.

Starch volume in pond

The effect of starch volume in the pond was tested by using starch volumes of 20, 50, 75, 100, 150, 200 and 300 ml.

Drying conditions

Drying method, temperature and drying time were investigated both with oven and infrared drying. The moisture content of the sized paper after drying and after conditioning was measured for some test points. For oven drying, temperatures of 60, 80, 105, 125, 145 and 180 °C were tested with different drying times resulting in completely dry (moisture content < 1%) and even burnt ($t > 105$ °C) samples. The infrared dryer was tested with drying times of 10, 15 and 20 s with the sized paper in the middle or at the bottom of the infrared dryer rack.

Surface size solids content

For base paper 1, surface size solids contents of 10, 15, 16, 17 and 18% were tested. For the other base papers, surface size solids content of 12% was used as a guide to determine optimal solids content for correct pick-up.

Surface size viscosity

Viscosity was altered by using Starch 1 as baseline and testing Starch 2, which had a slightly higher viscosity but identical chemical structure and properties. Both starches were jet-cooked and diluted to solids contents appropriate for the base papers studied, and the highly effective SSA 1 was added.

Surface size temperature

Temperatures tested were ambient (c. 20 °C), 40, 60, 65, 70 and 75 °C. Higher temperatures would have damaged the size press rolls.

6.1.4. Surface sizing method used for hydrophobicity tests

Results of the parameter testing can be found in Chapter 8: Effect of surface sizing method parameters. The surface sizing method used for hydrophobicity tests in this study is presented in Table 2.

Table 2. The surface sizing method used in further experiments

Parameter	**Value**
Paper humidity	6-7%
Size press speed	4 m/s
Size press pressure	5
Starch volume in pond	150 ml
Oven drying time (105 °C)	3 min
Surface size solids	base paper dependent
Surface size temperature	60 °C

6.2. Experimental layout for hydrophobization efficiency testing

To study differences in SSA hydrophobization efficiency, 45 different surface sizing agents were tested on testliner 1. SSA 30 and SSA 31 were also tested on the other base papers to shed light on differences in hydrophobization efficiency between the base papers. In every test, the surface size recipes were formulated for a 40 kg/t pickup with x kg/t starch, y kg/t SSA and z kg/t PAC, so that the sum of x, y, and z was 40. The dosing of SSA's tested on testliner 1 was 1, 2, and 4 kg/t SSA. Other base papers were not as receptive of SSA hydrophobization, and a testing regimen of 1, 3 and 6 kg/t was used for these base papers. When PAC was used with the sizing agent, it was added at a constant addition amount of 2 kg/t regardless of SSA dosage. Because the surface size is applied to both sides of the paper in the pond size press, dosing amounts should not be considered to reflect the actual case in metered film press surface sizing, when the SSA is applied on one side only.

6.3. Paper analysis

6.3.1. Hydrophobicity

Cobb 60 s tests were performed according to standard ISO 535 (TAPPI T 441) with an L&W Cobb Sizing Tester. A 10 cm^2 area of the paper was exposed to a 1 cm high water pillar for 45 seconds. The water was poured off and at the full testing time (60 s) paper was sandwiched between blotting sheets and rolled with a 10 kg roller. Weight increase was used to calculate water absorption in g/m^2. Two tests were made for each test point and results were averaged.

Contact angles with water of sized papers (and surface sizing agent films) were measured with Fotocomp DropPrint software. Ten drops of ion-exchanged water were dropped from a height of 5 mm on the specimen and photographed at 0,5 s. The obtained photographs were processed and calculated with the software, and contact angles were averaged.

An **ultrasonic dynamic penetration tester** (Emtec PDA.C 02 Module MST Standard) was used to study base paper and sized paper water penetration. Samples were cut and fastened on a sample holder with two-sided tape. The device immersed the sample in ion-exchanged water and immediately an ultrasound signal was passed through the sample, and the received signal was recorded. During wetting, the air was displaced with water and the received ultrasound signal changed as a result of different scattering and absorption mechanisms. Measurement data was processed to extract the following calculated parameters: intensity at 5 seconds I(5 s), time at 50% intensity t(50), time at 95% intensity t95, time at maximum intensity tMAX and absorption value A30. PDA A30 results have been shown to correlate with Cobb 60s values (Lopes et al., 2010).

6.3.2. Structure and porosity

Porosity of the samples was measured with PASCAL 140/440 mercury porosimeter at Åbo Akademi University. In mercury porosimetry, the pore structure of a sample can be determined by the pore volume displaced by mercury. A sample is put in a vacuum chamber and the chamber is filled with mercury while pressure and volume are monitored. The resulting data can be used to calculate pore volume and pore diameters of the sample. Thus, results on both the total porosity and the pore size distribution are obtained.

Gurley air permeability was measured with an L&W air permeance tester. A sample was put in the testing device where the time required for a volume of air to flow through the sample is recorded. Results are given in seconds for flow of 1 liter of air.

Porosity and smoothness were measured with a **Bendtsen** type tester. The Bendtsen tester measures air leakage both through the sample (porosity) and between the measuring head on the sample and the sample surface (smoothness). Results are given in ml/min.

Roughness/smoothness was also tested with **Parker Print-surf (PPS)** equipment. The PPS measurement is based on the resistance to airflow between the sample surface and a metal band in contact with the paper. The result is a measure of roughness in micrometer.

6.3.3. Strength properties

Short-span compression (SCT) was analyzed at KCL (Oy Keskuslaboratorio - Centrallaboratorium Ab). In SCT measurement, a sample cut in machine direction (MD) is fixed with two clamps having a short distance between them. The clamps are brought together with increasing force until the samples structural integrity collapses. The final corrugated board box compression resistance depends directly on the liner and fluting strength, which is usually measured as SCT or ring crush test (RCT) for liner and as Concora medium test (CMT) for fluting (Holik, 2013).

Z-direction strength was measured with an L&W Z-direction tester. A sample (dimensions 10 x 30 cm) was fed into the tester between two rolls of double sided tape. The tape was attached to the paper by clamping from the topside and backside, and the force required to separate the clamps with paper tearing is recorded.

6.3.4. Other paper analyses

Dynamic water retention (DWR) was used to measure starch pickup or starch affinity of the paper. Samples of the base papers were used and a 12% solids starch solution of starch 1 was kept at 60 °C before filling the DWR testing equipment cylinder. The device lets starch flow past the surface of the paper sample, and DWR was measured as weight increase of the paper sample in g/m^2.

6.4. Surface sizing agent (SSA) analysis

The charge of the SSA’s was measured with a CAS Charge analyzer. A sample was diluted to 0,1% strength, and the device measured the required amount of anionic (PES-Na) or cationic (poly-DADMAC) titrant to neutralize the sample.

Hydrophobicity was measured with contact angle measurements from films. SSA was diluted to 25% solids, and a 150 µm wet film was drawn on a glass plate. The film was dried in a 100 °C oven to mimic the surface sizing method. After drying, the film was allowed to stabilize overnight in a conditioned room (t 23 °C, RH 50%) before measuring water contact angles with Fotocomp DropPrint equipment and software.

The particle size of the SSA solutions was measured with a Malvern Zetasizer. A diluted sample is put into the machine, and light scattering is used to measure the particle size distribution.

III RESULTS AND DISCUSSION

7. Differences in SSA efficiency

In the surface sizing experiments a broad range of sizing effect, measured in Cobb 60 s of the sized paper, was witnessed on testliner 1 (see Figure 10). Some sizing agents gave a low Cobb value with a small addition amount, while other SSAs had barely any effect even at higher addition amounts.

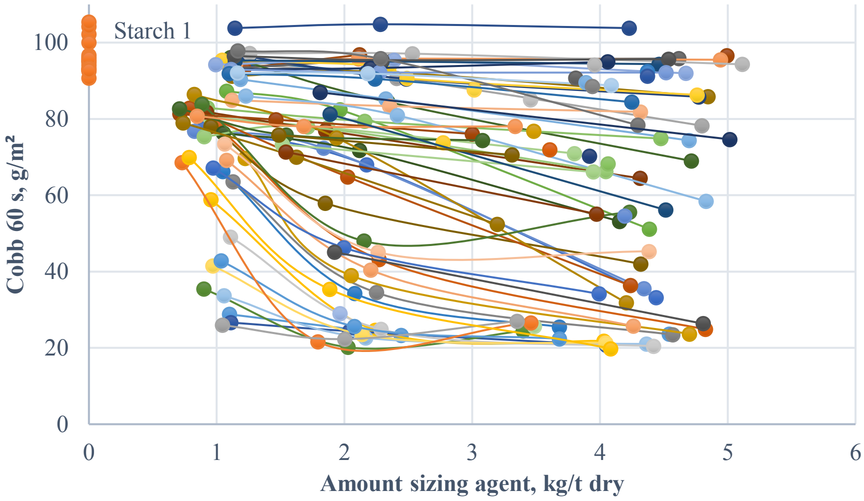

Figure 10. All surface sizing test points on testliner 1

Figure 11 and Figure 12 illustrate a significant difference in the sizing effect of SSA 31 and SSA 30 between the different base papers. Testliner 1 seems to respond very well to sizing, while testliner 4 is most difficult to hydrophobize. The differences in sizing effect between sizing agents and between different base papers are well known in the industry. A study by Karademir et al. (Karademir, Ozdemir & Imamoglu, 2007) investigated the differences in sizing effect for office paper, old corrugated, magazine paper and newspaper.

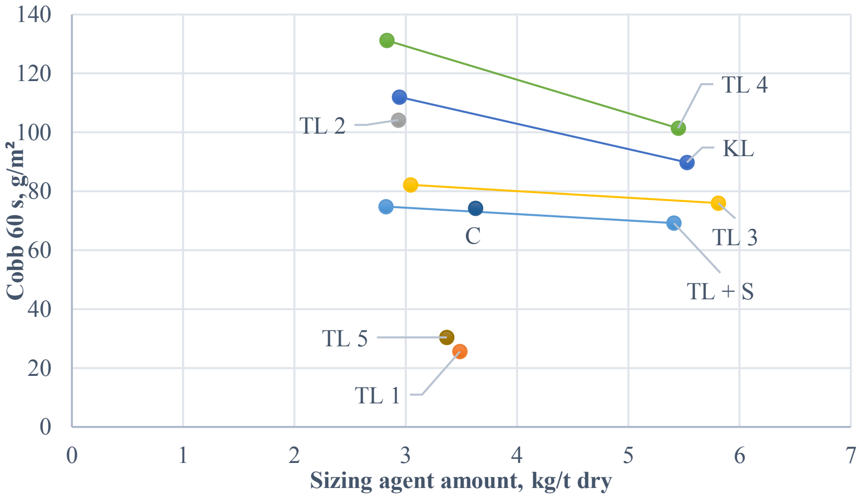

Figure 11. Sizing effect of SSA 31 on the different base papers (TL = testliner, KL = kraftliner, C = copy paper)

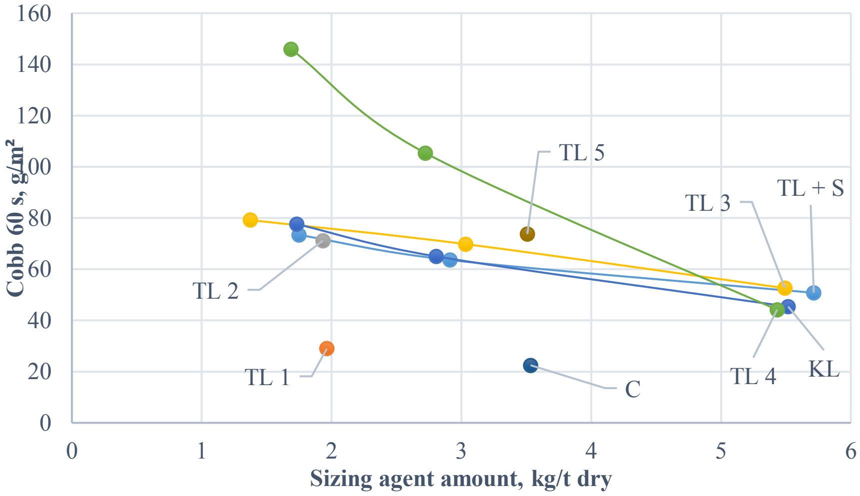

Figure 12. Sizing effect of SSA 30 on the different base papers

8. Effect of surface sizing method parameters

Before actual experiments on the sizing effect of SSAs could be made, the laboratory surface sizing method was studied. The following chapter details effects witnessed on surface size pickup and sizing effect when adjusting the surface sizing method parameters.

Paper moisture content

The moisture content of the base paper was not found to affect either the surface size pickup or the sizing effect. It was decided to keep the conditioned base paper sheets in sealed plastic bags before surface sizing so that moisture content variability would be minimized.

Previously, the sized sheets were brought to the conditioning room and left to stabilize overnight in piles after surface sizing. The conditioning was found to be ineffective because the bottom samples had not stabilized quickly enough due to lack of airflow around the samples. Clips with hangars were used to condition the surface sized sheets in bunches of approximately ten sheets/clip overnight.

Size press speed

Size press speed was not found to have a measurable effect on starch pickup even though a pickup increase with increasing paper machine speed has been reported in the literature (Maurer, 2009; Brander, James.,Thorn, Ian., 1997). However, the laboratory size press operates at extremely low speeds compared to industrial scale paper machines. Small changes in the speed probably did not cause measurable effects at the low speeds used in laboratory. Similarly, it was found in other studies that a speed increase from 40 to 100 m/min did not increase starch pickup (Shirazi et al., 2005). No effect on sizing efficiency was found.

Size press pressure

Higher size press nip pressure decreased the surface size pickup in the laboratory size press. Similar effects for pond type size presses in industrial and laboratory scale have been reported in the literature (Maurer, 2009; Shirazi et al., 2005). Figure 13 shows the effect on testliner + starch base paper sized with 18% solids surface size. It was decided to use as low pressure as possible which could still be monitored to prevent surface size solids content from becoming too high while achieving the goal of 40 kg/t starch pickup; this was determined to be “5” on the pressure lever.

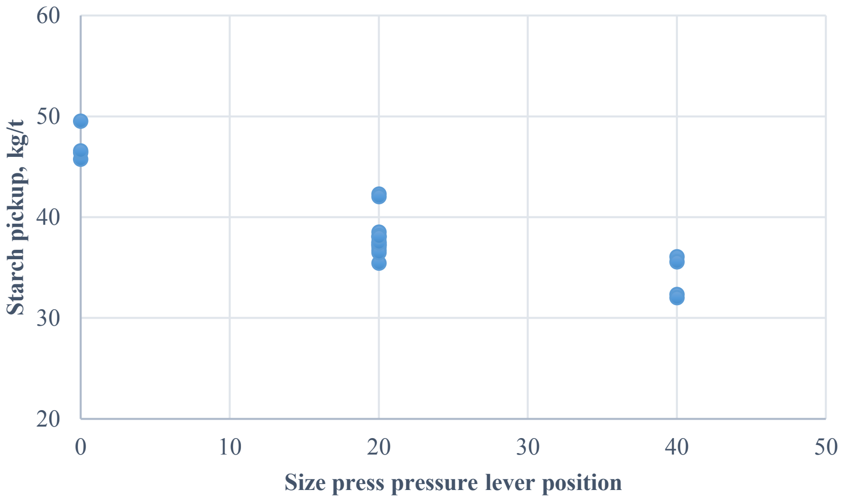

Figure 13. Size press pressure and 18% starch pickup (base paper TL + S)

Starch volume in pond

The starch volume in the pond did not influence pickup or sizing effect, except when the small volume of 20 ml left dry patches on the first sheet run through the size press. It was decided to use 150 ml as starch volume to facilitate Brookfield viscosity measurements in a 200 ml decanter.

Drying conditions

IR drying and oven drying above 105 °C burned the sized sheets, causing them to appear overly hydrophobic. The IR dryer was deemed too unpredictable and powerful to produce even, consistent drying results. Oven temperature and time did not affect pickup, except when drying continued during conditioning and pickup seemed too high. The drying method was left as it was, 3 min in a 105 °C oven.

Surface size solids content

Surface size solids content was the parameter that affected pickup the most in the laboratory size press. For base paper TL + S, an ideal pickup, with the other parameters adjusted, was obtained at solids content of 17%. For testliner 1, 9% solids content was found to give 35-45 kg/t pickup, and for testliner 3, 12% solids content was suitable. When testing further base papers, a correlation between the pickup at 12% solids content and the needed solids % for 40 kg/t pickup was found (Figure 14). This correlation could be used to determine appropriate solids % for testing of new base papers.

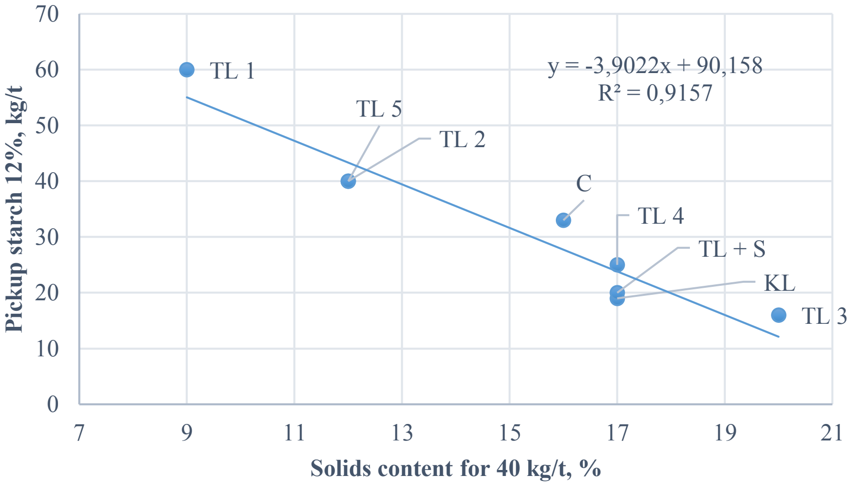

Figure 14. Correlation between size pickup at 12% solids content and solids content required for 40 kg/t pickup for different base papers.

Surface size viscosity

The viscosity of the surface size with starch 1 and starch 2 is shown in Table 3. A more substantial difference in viscosity was witnessed with higher solids content.

Table 3. Viscosity of surface size with Starch 1 and Starch 2

		Base paper 2 Solids 9%		**Base paper 3 Solids 12%**		**Base paper 1 Solids 18%**	
		Starch 1	**Starch 2**	**Starch 1**	**Starch 2**	**Starch 1**	**Starch 2**
Brookfield 100 rpm	mPas	14	16	18	22	31	47

The holdout of surface size was expected to increase with the higher viscosity starch 2, as described in the literature (Maurer, 2009; Gess, Rodriguez, 2005; Shirazi et al., 2005; Jeong et al., 2012). When comparing the pickup of surface size on the different base papers (Figure 15), the increased holdout may explain the differences observed. The higher holdout of starch 2 may prevent penetration through the highly porous testliner 1, thus decreasing pickup. For the dense testliner + starch base paper, starch holdout may be high irrespective of the starch, and thus the higher viscosity may cause more starch to stay on the paper surface through the nip passage, increasing pickup.

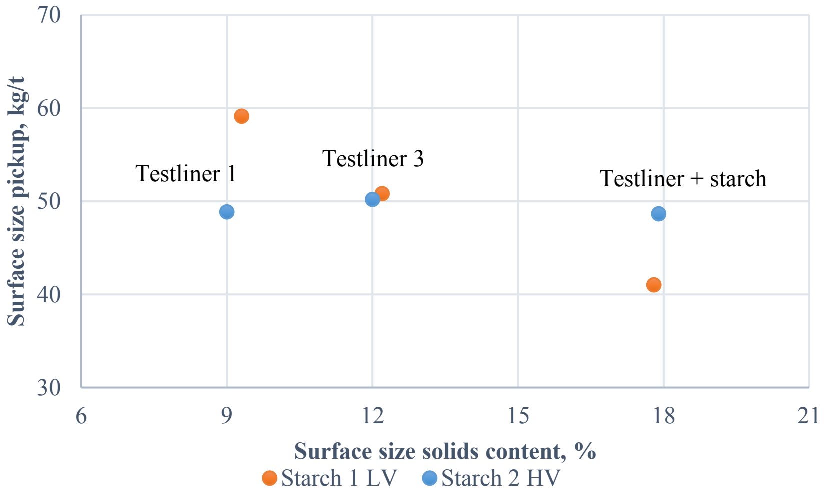

Figure 15. The effect of starch viscosity on surface size pickup (LV = low viscosity, HV = high viscosity)

The higher viscosity starch decreased the porosity of the papers, as measured with Bendtsen air permeability (Figure 16), consistent with results obtained on a pilot scale paper machine in a doctoral thesis study. (Lipponen, 2005) For base paper testliner + starch, the difference is negligible, probably because of the already low porosity of the dilute-starch-containing base paper. No significant differences in Cobb 60 s values were found.

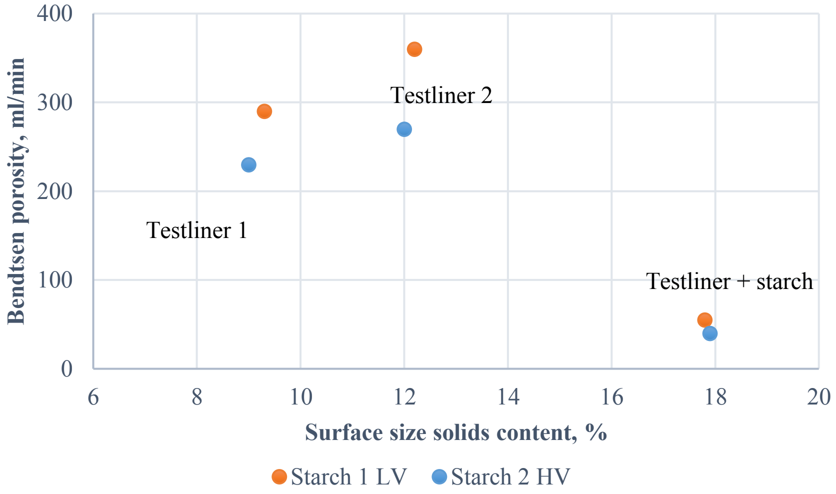

Figure 16. The effect of starch viscosity on Bendtsen porosity

Surface size temperature

Surface size temperature was not shown to affect either pickup or hydrophobicity.

Laboratory surface sizing method evaluation

When testing the effect of the sizing method parameters on the sizing effect, an extremely well-functioning anionic surface sizing agent was used (SSA 1), and no effect on Cobb results was found when adjusting method parameters. However, this surface sizing agent may have distorted the results because of its excellent sizing effect so that differences may not have been measurable.

9. Effect of base paper properties

In this chapter, the measured base paper properties are presented. Then, the effects of base paper properties on starch pickup, paper strength and sizing effect are studied.

9.1. Base paper properties

The results of the basic paper analyses are presented in Table 4. The copy paper is more porous and less rough than the liners, and the testliner with starch is least porous. Also between the testliners, differences in bulk, porosity and roughness can be seen, despite the similar raw material composition. PPS and Bendtsen roughness show that the other base papers have very rough surfaces, especially the kraftliner, except the copy paper which is smoother. Ash content is lower for the virgin fiber containing kraftliner, as expected, and higher for the filled copy paper.

Table 4. Basic base paper properties

Base paper properties		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
Grammage	g/m²	84	97	95	150	107	116	90	78
Thickness	µm	139	164	147	231	187	202	136	120
Bulk	cm³/g	1,7	1,7	1,5	1,5	1,8	1,7	1,5	1,5
Bendtsen porosity	ml/min	360	440	300	450	380	370	210	1050
Gurley	s	34	28	44	24	31	31	55	10
Cobb 60s	g/m²	109	140	96	228	156	136	86	82
Bendtsen roughness									
topside	ml/min	1100	1600	800	950	1300	2000	950	330
backside	ml/min	1450	1100	800	950	1800	2200	1200	370
PPS									
topside	µm	8	11	9	8	10	12	9	6
backside	µm	11	10	10	9	13	12	12	7
Ash content									
450C	%	15	12	17	15	14	6	13	21
925C	%	10	8	12	11	10	5	10	12

The Hg-porosimetry results (Table 5 and Figure 17) show similarly that the copy paper is most porous, while the testliner with starch is least porous. The testliners are equal in porosity, except testliner 4 which is more porous.

Table 5. Hg-porosimetry

Hg-porosimetry		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
Pore volume	mm^3/g	530	537	525	605	598	494	395	621
Porosity	%	32,0	31,8	33,9	39,3	34,2	28,4	26,1	40,4

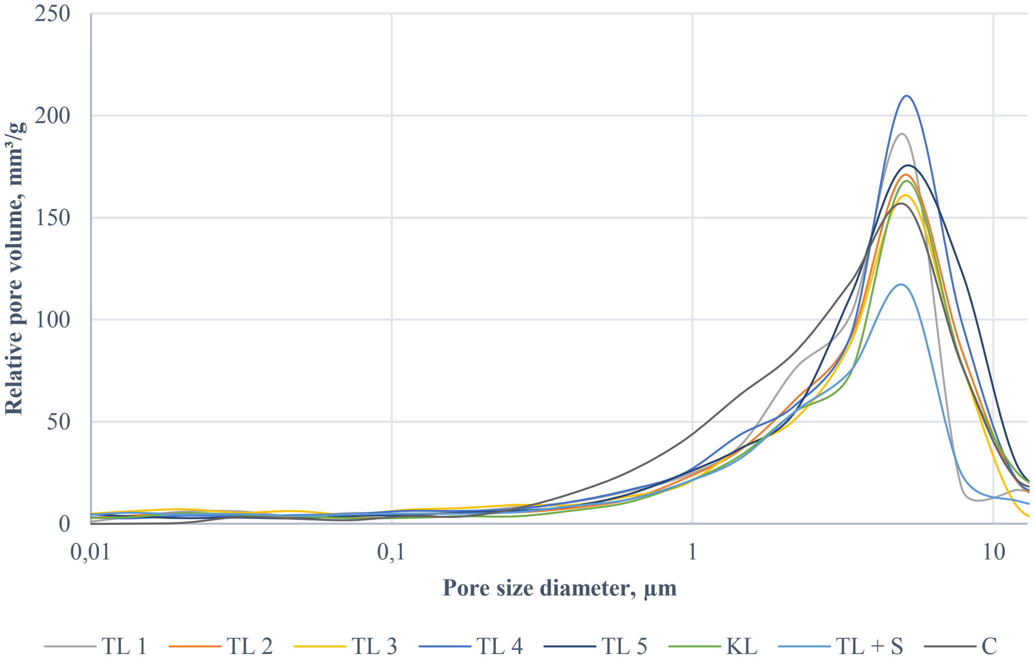

Figure 17. Hg-porosimetry pore size and volume

Dynamic water retention measurements with starch (Table 6) show that testliner 1, 2 and 5, and the copy paper, absorb the highest amounts of 12% starch. The same testliners also have the lowest t(MAX) values with the ultrasonic dynamic penetration tester, which means that their surface wetting time is fastest. The W roughness values are also low for these base papers.

Table 6. DWR and ultrasonic dynamic penetration tester results

DWR		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
DWR starch 12%	g/m²	68	82	47	62	72	52	50	69
Ultrasonic dynamic penetration tester, water									
I(5s)	%	12,86	10,29	50,48	4,63	10,71	70,83	22,76	32,32
t(50%)	s	0,59	1,19	5,04	1,57	0,58	9,80	2,77	3,50
t95	s	0,23	0,35	1,26	0,43	0,15	1,24	0,75	1,00
tMAX	s	0,13	0,16	0,52	0,21	0,08	0,45	0,32	0,47
W		0,20	0,28	2,03	0,51	0,01	0,90	0,44	1,19
A 30		21,70	24,30	26,90	26,80	24,90	24,10	26,90	25,70

9.2. Starch pickup

Starch pickup, and therefore solids content for 40 kg/t surface size, varies significantly between the base papers (Table 7). For all base papers studied, DWR with 12% starch correlated with 12% starch pickup (Figure 18), except a high starch pickup for testliner 1. DWR measurements with starch could therefore in many cases be used to predict starch pickup of the base paper.

Table 7. Starch pickup

Starch pickup		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
Pickup starch 12%	kg/t	60	40	16	25	40	19	20	33
Solids for 40 kg/t	%	9	12	20	17	12	17	17	16

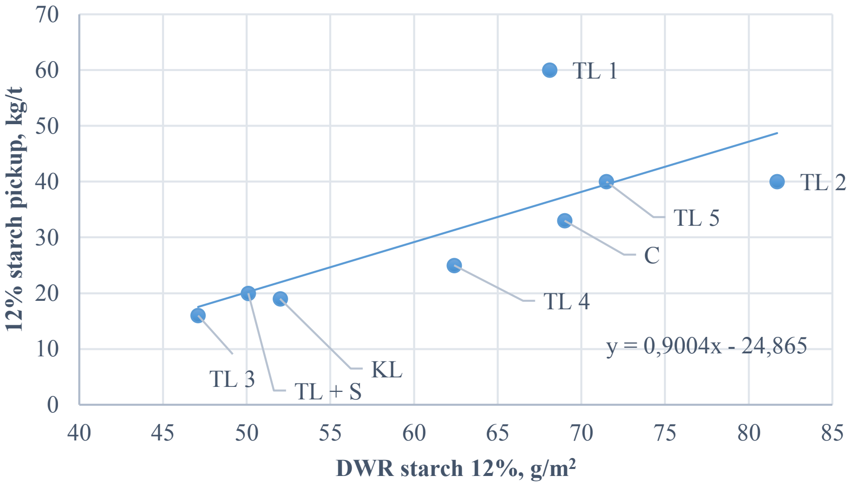

Figure 18. DWR with 12% starch correlation to 12% starch pickup

9.3. Paper strength

Figure 19 illustrates how an increased starch amount applied to testliner 1 increased the short-span compression (SCT) strength of the base paper. The results indicate that the laboratory surface sizing method produces a steady strength increase. Further, the achieved SCT strength of 1,5 kN/m with 40 kg/t is a typical value for commercial surface sized testliners of similar grammage. (Mondi group, 2018; Saica, 2018)

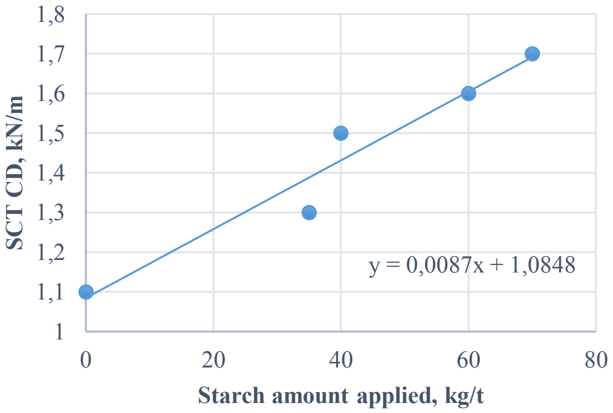

Figure 19. Testliner 1 strength increase with increased starch amount

Table 8. Z-direction strength and SCT strength

Z-direction strength		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
base paper	kPa	638	527	791	420	569	495	850	634
with starch 40 kg/t	kPa	750	580						
SCT, cd									
base paper	kN/m	1,1	1,5	1,8	1,7	1,5	2,0	2,1	1,2
with starch 40 kg/t	kN/m	1,5	2,0	2,2	2,6	1,9	2,4	2,3	1,6
increase	kN/m	0,4	0,5	0,4	0,9	0,4	0,4	0,2	0,4
increase	%	36	33	22	53	27	20	10	33

Base paper and surface sized paper strength is presented in Table 8. The kraftliner and the testliner with starch have the highest SCT strengths, and the testliner with starch also has the highest Z-direction strength. This is to be expected because of the higher strength and increased bonding potential of virgin fibers compared to recycled fibers, and because the added starch serves to glue together the base paper.

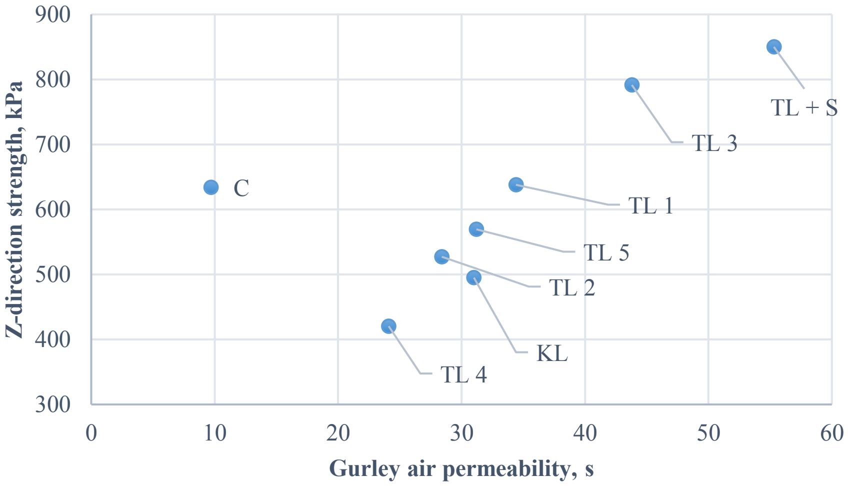

Figure 20. Gurley air permeability and Z-direction strength

For the liners, Z-direction strength correlates with porosity measured by air permeability (Figure 20). The copy paper has higher Z-direction strength with higher porosity, probably because of the different raw material and production process. SCT strength of sized paper correlates with SCT strength of base paper (Figure 21), which means that liner can be strengthened by either adding more starch or strengthening the base paper.

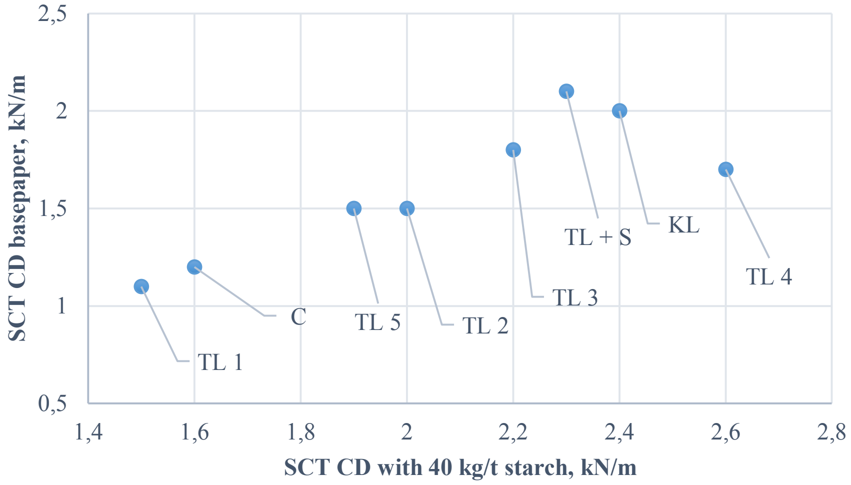

Figure 21. SCT for 40 kg/t starch sized base paper depends on base paper SCT

9.4. Sizing effect

The sizing effect, measured in Cobb 60 s, of SSA 30 and SSA 31 on different base papers is presented in Table 9. Testliner 1 and testliner 5 had the highest sizing effect with both sizing agents, while testliner 3, testliner with starch and copy paper had the lowest sizing effect.

Table 9. SSA sizing effect

Sizing effect - Cobb 60s		**TL 1**	**TL 2**	**TL 3**	**TL 4**	**TL 5**	**KL**	**TL + S**	**C**
Base paper	g/m²	109	140	96	228	156	136	86	82
SSA 30, 3 kg/t	g/m²	29	71	79	146	23	78	73	74
decrease	%	73	49	18	36	86	43	15	10
decrease	g/m²	80	69	17	82	134	58	13	8
SSA 31, 3 kg/t	g/m²	26	104	90	162	30	103	80	74
decrease	%	76	26	6	29	81	24	7	9
decrease	g/m²	83	36	6	66	126	33	6	8

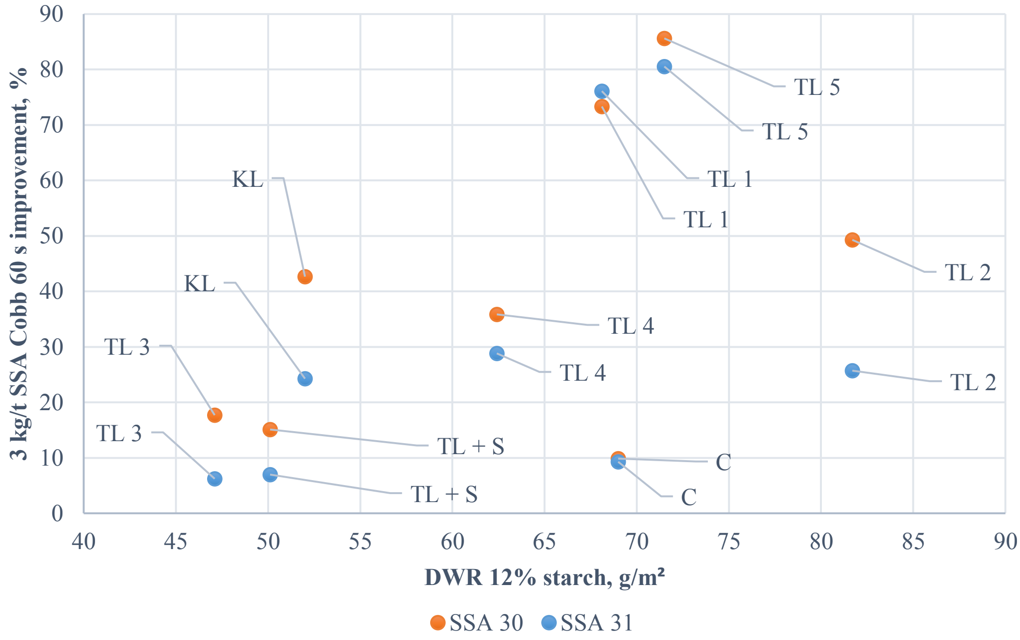

Figure 22. DWR 12% starch correlation with sizing effect

Both testliner 1 and testliner 5 have high DWR values with starch 12% (Figure 22), however, so does the copy paper and testliner 2 despite having a lower sizing effect. When comparing only the testliners, a higher DWR value seems to indicate better sizing effect.

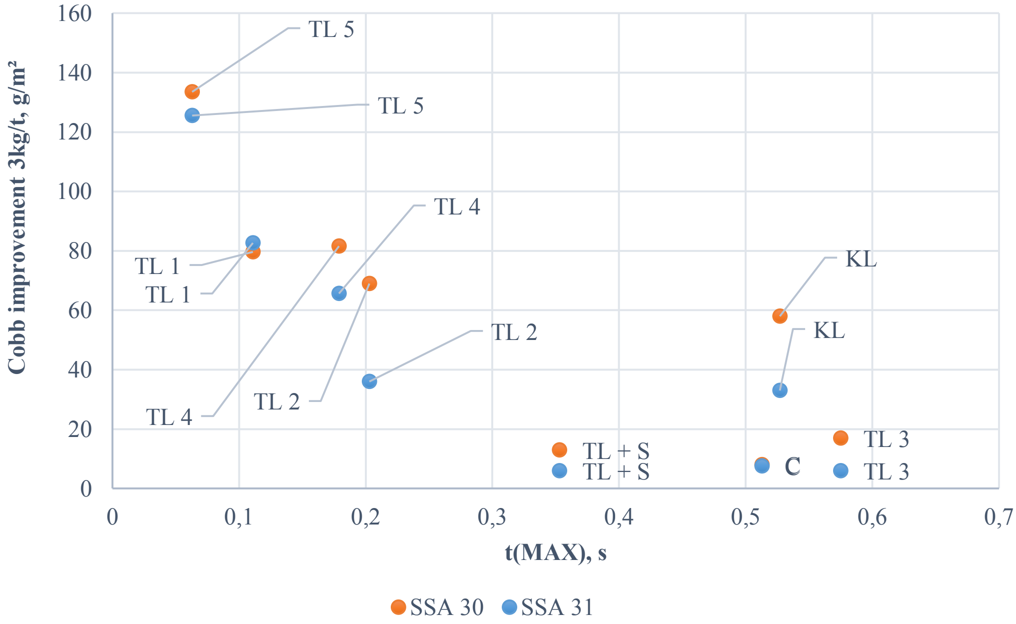

Figure 23. t(MAX) and sizing effect

Figure 23 shows that the t(MAX) parameter in ultrasonic dynamic penetration testing does correlate with the sizing effect. The t(MAX) parameter signifies the time point when the surface of the paper is wetted, and could thus indicate whether the paper surface is already hydrophobic or not. The base paper usually contains trace amounts of internal sizing agents to control surface size pickup and prevent web breaks, which could explain the differences in t(MAX). Fiber refining processes, and recycled fiber prior sizing could also cause differences in the paper surface chemistry.

Similarly, the parameter W in the ultrasonic dynamic penetration testing correlates with sizing effect (Figure 24). The W parameter is a machine-calculated value for surface roughness characterization.

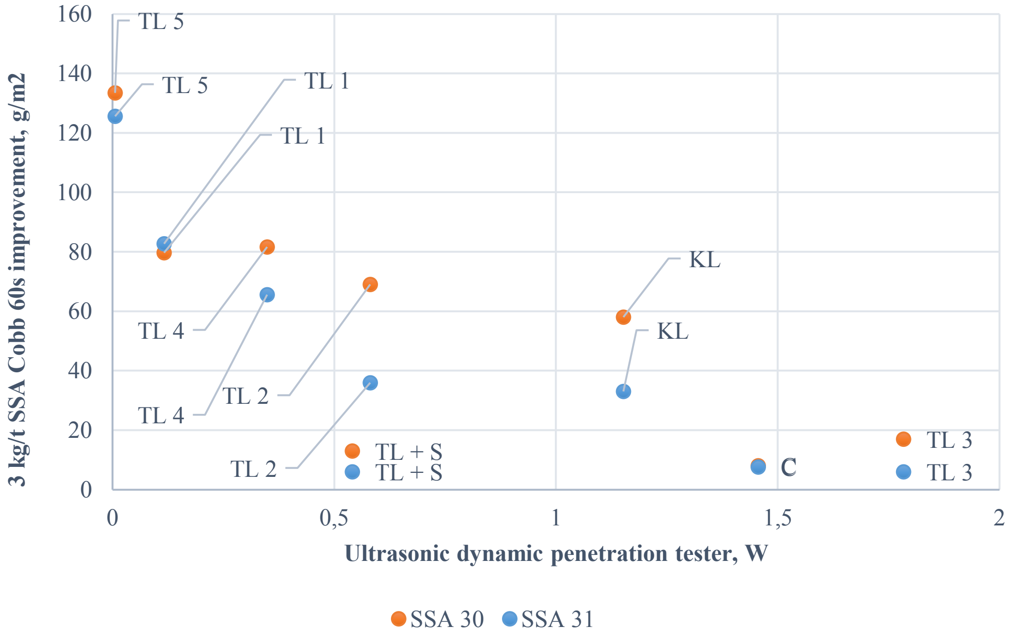

Figure 24. Parameter W and sizing effect

10. Effect of SSA properties on sizing effect

Particle size

A smaller particle size of the sizing agent was found to give better sizing effect, and PAC addition aids the sizing further (Figure 25 and Figure 26). Smaller SSA particles should logically cover more of the paper surface because the number of particles is higher for the same weight of SSA and therefore the specific surface area is higher.

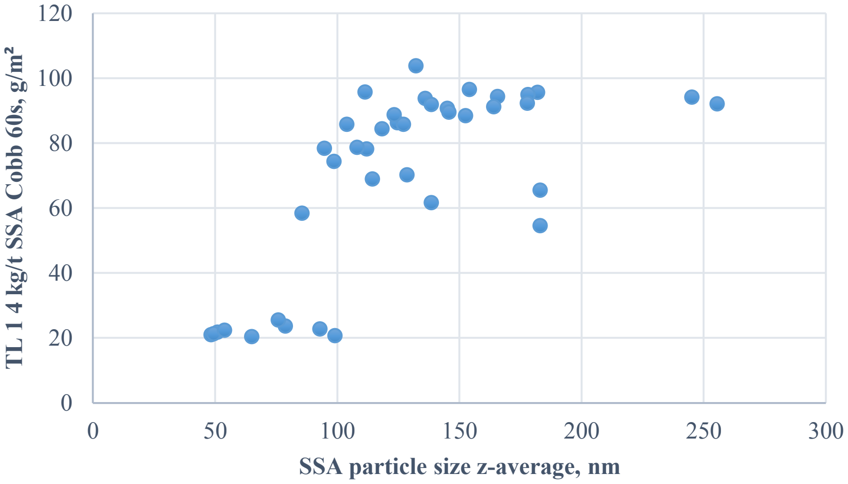

Figure 25. Sizing effect and SSA particle size, no PAC

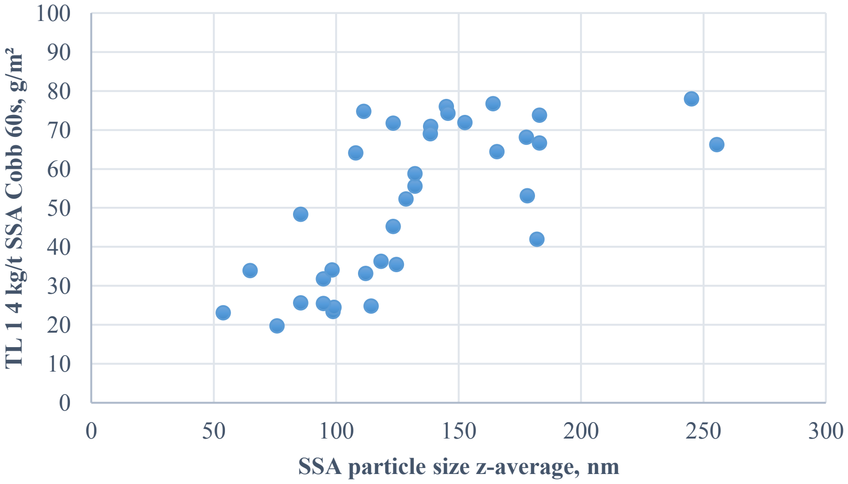

Figure 26. Sizing effect and SSA particle size, with PAC

Contact angle (hydrophobicity)

In Figure 27 and Figure 28, the sizing effect is correlated to the SSA hydrophobicity, measured by water contact angle on oven-dried films of 25% solids content SSA. Figure 27 shows sizing effect with PAC, and Figure 28 without PAC. SSA hydrophobicity seems to correlate with sizing effect without PAC, however with PAC there is no clear correlation. The use of PAC may, therefore, either increase the hydrophobicity of the final surface size solution or have some SSA particles aligned more favorably for hydrophobicity.

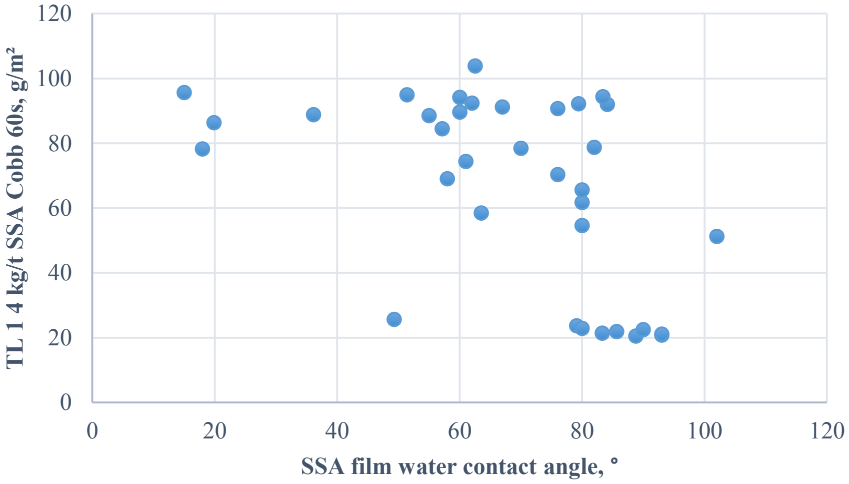

Figure 27. Sizing effect and SSA film water contact angle, no PAC

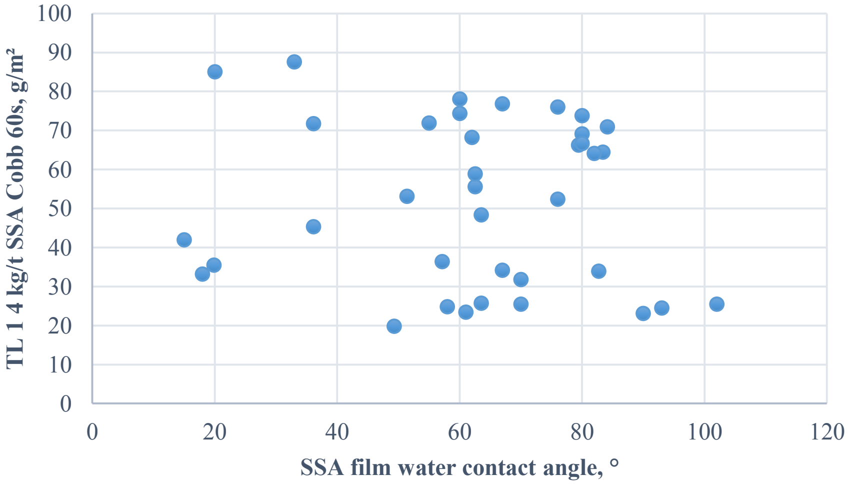

Figure 28. Sizing effect and SSA film water contact angle, with PAC

Conclusions

In this study, eight different base papers were analyzed, and 45 different surface sizing agents (SSA's) were tested. The goal was to optimize a laboratory scale method for studying surface sizing and to increase the understanding of the mechanisms that control hydrophobization of paper by surface sizing.

Differences in base paper properties were found to impact the starch pickup, paper strength, and sizing efficiency. For SSA's both the particle size and the particle hydrophobicity was found to influence the sizing effect.

A range of sizing effects with the same dosage of different SSA's was witnessed on testliner 1. Some SSAs gave a low Cobb value with a small addition amount, while others did not respond to even higher dosages. Differences were also witnessed between base papers; the same SSA worked well with some base papers while others were more difficult to make hydrophobic.

The surface sizing method was optimized for 40 kg/t starch pickup for all the base papers. Nip pressure and surface size solids content affected the starch pickup. Nip pressure was set to a minimum and solids content was adjusted for each base paper. The starch pickup for each base paper could then be estimated using DWR measurements with starch. Surface size viscosity affected the porosity of the surface sized paper, and porosity of the base paper affected the starch pickup.

SCT strength of surface sized paper depended on base paper SCT strength and the applied starch amount. A more porous base paper was weaker in Z-direction, as expected.

The sizing effect correlated with wettability of the base paper, and DWR measurements with starch. The easier the base paper was to wet and the more starch it absorbed in DWR measurements, the stronger was the sizing effect.

Sizing effect was further affected by the SSA particle size, SSA hydrophobicity, and PAC usage. Smaller SSA particles gave a stronger sizing effect, which is logical given the increased surface coverage due to the larger specific surface area. A more hydrophobic SSA also generally gave a higher sizing effect, but with the use of PAC, the hydrophobicity of the SSA lost significance.

The results indicate that base paper properties can be optimized for starch pickup and surface sizing effect. The costs of applying excess SSA and excess starch to the paper surface could thus be decreased. Further studies are recommended on adjusting the base paper properties to improve sizing effect and on SSA particle interaction with the paper surface, especially in combination with PAC or other promoters. Printability and gluability of surface sized testliner should also be considered in further studies.

Swedish summary - Svensk sammanfattning

Vattenavstötande ytlimning av testliner

I detta diplomarbete behandlas hydrofobisk ytlimning av testliner. Ämnet är relevant eftersom den växande internationella näthandeln höjer efterfrågan på billiga, hållbara förpackningsmaterial, såsom korrugerade förpackningar av wellpapp. Förpackningsmaterialens andel i pappersindustrin ökar därtill, medan andelen papper som används för kommunikation minskar. Dessutom återvinns allt mer papper och kartong, vilket leder till en förökad användning av testliner tillverkad av returfiber jämfört med nyfiberbaserad kraftliner (CEPI, 2016; Holik, 2013; ERPC, 2016).

Ytlimningsprocessen, dvs. applikationen av stärkelse och ytlimningsmedel till pappersytan, är en gammal process. Trots detta är ytlimning av testliner utmanande på grund av det stora antalet variabler som påverkar hydrofoberingen. Tidigare hydrofoberades liners uteslutande genom mäldlimning, dvs. limningsmedel lades till i våtändan på pappersmaskinen. Våtändan blir dock lätt komplicerad och kan orsaka produktionsstopp, speciellt i testlinertillverkning då returfibrerna kan innehålla en oändlig mängd olika kemikalier. Nyligen har ytlimning blivit allt vanligare på grund av strävan efter förenklad våtända, besparingar i mängden ytlimningsmedel då medlet appliceras endast på ytan och bättre möjligheter att finjustera pappersytans egenskaper (Bajpai, 2015; Zeng, 2013).

Hydrofoberingsmekanismen i ytlimning är inte väl förstådd och laboratoriestudier korrelerar sällan med verkliga test på pappersmaskiner. Det finns inte heller något ytlimningsmedel som skulle fungera lika bra på alla testliners. Med en högre förståelse för ytlimningsprocessen kunde ytlimningsmedel appliceras mer sparsamt och ytlimningsmedel kunde utvecklas effektivare. En pålitlig laboratoriemetod skulle underlätta utvecklingen av ytlimningsmedel och förbättra möjligheterna att förutsäga ytlimningsmedlens effektivitet i praktiken.

Målet för detta diplomarbete var att närma sig en förståelse för hydrofobiseringsmekanismen i ytlimning av testliner. Först undersöktes och optimerades en laboratoriemetod för ytlimning och sedan testades 45 olika ytlimningsmedel på åtta olika baspapper. Baspappren och ytlimningsmedlen analyserades och resultaten undersöktes för korrelation med stärkelseupptagning och ytlimningseffekt.

Baspappren som användes i arbetet var fem olimmade testliners, en testliner med utspädd ytlimningsstärkelse, en olimmad kraftliner och ett kopieringspapper. Två modifierade lågviskositetsstärkelser från Roquettes ”Stabilys A” produktsortiment användes, den ena med något högre viskositet. Stärkelsernas struktur simulerar enzymatiskt konverterad stärkelse. Båda stärkelserna var i pulverform och kokades med jetkokare i 134ºC till en bestämd torrhalt. Ytlimningsmedlen inkluderade både kommersiella referensprodukter och utvecklingsprodukter. Två av ytlimningsmedlen testades på alla baspapper och alla ytlimningsmedel testades på testliner 1, de flesta både med och utan polyaluminiumklorid (PAC).

Laboratoriemetoden testades och optimerades först för att uppnå en konstant stärkelseupptagning på 35-45 kg/t för alla olika baspapper och en konstant ytlimningseffekt. Variablerna som ändrades var limpressens tryck, limpressens hastighet, ytlimmets torrhalt, papprets fukthalt, stärkelsevolymen i dammen, torktiden, torktemperaturen och ytlimmets temperatur. Testerna utfördes så att alla variabler hölls i utgångsläge, utom den som testades.

Variabeltesterna visade att ytlimmets torrhalt och limpressens tryck påverkade stärkelseupptagningen. Ett högre limpresstryck gav lägre stärkelseupptagning och högre torrhalt ökade stärkelseupptagningen. Eftersom testlinern med utspädd stärkelse hade väldigt låg stärkelseupptagning och ytlimmets torrhalt påverkade upptagningen mest, bestämdes det att ett konstant lågt limpresstryck skulle hållas för alla baspapper och att stärkelseupptagningen skulle ställas in med hjälp av torrhalten.

För att uppnå 40 kg/t stärkelseupptagning användes torrhalter från 9 % till 17 % beroende på baspapper. Det kunde också konstateras att stärkelseupptagningen av 12 % ytlim kan användas för att förutspå rätt torrhalt för 40 kg/t upptagning. Ingen av variablerna påverkade ytlimningseffekten. Ytlimningsmedlet som användes i metodtesterna var dock väldigt effektivt och det är möjligt att hydrofobiciteten var för hög för att skillnader i variablerna kunde upptäckas.

För att undersöka skillnader i ytlimningseffekten mellan baspappren och ytlimningsmedlen ytlimmades de olika baspappren med olika ytlimningsmedel. Ytlimsreceptet utgick från 40 kg/t ytlimsupptagning med x kg/t stärkelse, y kg/t ytlimningsmedel och z kg/t PAC så att summan av x, y och z blev 40. Ytlimningsmedlen doserades med 1, 2 och 4 kg/t på testliner 1, för de övriga baspappren användes 1, 3 och 6 kg/t på grund av sämre ytlimningseffekt. Då PAC användes, var doseringen 2 kg/t oberoende av ytlimningsmedlets dosering. Ytlimmet applicerades på båda sidorna av pappret i laboratorie-filmpressen, och därmed kan doseringsmängderna inte direkt jämföras med ensidiga filmpressar i industrin.

Baspappersanalyserna utgjordes av vattenabsorption (Cobb 60s och dynamisk penetrationstestare med ultraljud), kontaktvinklar för vatten, porositet (kvicksilverporosimetri, Gurley luftpermeabilitet och Bendtsen luftpermeabilitet), släthet (Bendtsen och Parker Print-surf (PPS)), styrka (kompressionsstyrka och z-styrka) och stärkelseupptagning med en dynamisk vattenretentionsmätare. Ytlimningsmedlens laddning, hydrofobicitet genom kontaktvinklar på film och partikelstorlek mättes. Ytlimmets pH, viskositet, torrhalt och temperatur analyserades vid ytlimningarna.

Vid ytlimningarna av testliner 1 med alla ytlimningsmedel uppstod markanta skillnader i limningseffekt. Vissa ytlimningsmedel gav ett lågt Cobb värde med en liten tillsatsmängd, medan andra ytlimningsmedel hade knappt någon effekt trots större tillsatsmängder. Mellan baspappren fanns också stora skillnader, testliner 1 verkade vara lätt att hydrofobera, medan testliner 4 hade minst limningseffekt.

Stärkelseupptagningen varierade avsevärt mellan baspappren. För testlinersen korrelerade totala porvolymen med stärkelseupptagningen. Skillnaderna i porvolym mellan testlinersen kan bero på olika fiberraffineringsmetoder och grader av fiberraffinering och skillnader i retention av fyllmedel och finmaterial. Dynamiska mätningar av vattenretention med 12 % stärkelse korrelerade med upptagningen av 12 % stärkelse för alla andra baspapper, utom testliner 1. DWR mätningar kunde alltså användas för att förutsäga stärkelseupptagning.

Liner baspapprens Z-styrka korrelerade väl med luftpermeabiliteten, så att ett mer poröst papper var svagare. Kopieringspappret hade högre Z-styrka trots hög luftpermeabilitet, men råmaterialet och produktionsprocessen skiljer sig också från liners. Kraftlinern och testlinern med stärkelse var, som förväntat, starkast i Z-riktning, eftersom nyfibrer är starkare än returfibrer och har bättre bindningspotential mellan fibrerna och stärkelsen limmar ihop testlinern för högre styrka. Mätt med kvicksilverporosimetri korrelerade porositeten med kompressionsstyrkan för alla baspapper. Kompressionsstyrkan för ytlimmat papper var beroende av baspapprets styrka och den applicerade stärkelsemängden, så att kompressionsstyrkan ökade logiskt med större mängder stärkelse. För testliner 1 mättes en kompressionsstyrka på 1,5 kN/m med 40 kg/t stärkelse, vilket är ett typiskt värde för kommersiella liners av samma ytvikt.

Limningseffekten, mätt i Cobb 60s, varierade mellan baspappren. Högre stärkelseupptagning i de dynamiska vattenretentionsmätningarna med stärkelse, verkade tyda på bättre limningseffekt för baspappren, med undantag för kopieringspappret och testliner 2. Den dynamiska penetrationstestaren med ultraljud gav ett vätningsvärde t(MAX) för baspappren och detta värde korrelerade bra med limningseffekten. t(MAX) anger tiden då papprets yta är i fullständig kontakt med vattnet och kunde alltså rapportera den hydrofobiska pappersytans egenskaper. Mindre hydrofobiska ytor, eller baspapper med lägre t(MAX) värde, hade högre limningseffekt. Skillnaderna i ythydrofobicitet beror antagligen på små mängder mäldlimningsmedel i baspappren eller andra fiberraffineringsprocesser och råmaterial.

Av ytlimningsmedlens egenskaper gav en mindre partikelstorlek bättre ytlimningseffekt och tillsatsen av PAC gav generellt bättre ytlimningseffekt. Mindre partiklar täcker mer av pappersytan på grund av att partikelmängden blir större för samma tillsatsmängd och ytarean blir högre. Högre hydrofobicitet på ytlimningsmedlet, mätt med kontaktvinkelmätningar på film på glasplatta, gav också bättre limningseffekt utan PAC. Med PAC fanns det ingen tydlig korrelation. PAC höjer därmed antingen hydrofobiciteten för ytlimmet eller justerar partiklarnas position för bättre hydrofobicitet.

Dessa resultat antyder att genom pappersanalys kan baspappret optimeras för stärkelseupptagning och limningseffekt. Kostnaderna för att applicera ett överskott av stärkelse och ytlimningsmedel kunde därmed minskas. Ytterligare studier rekommenderas av justering av pappersegenskaper för ytlimningseffekt och av ytlimningspartiklarnas interaktion med pappersytan, speciellt i kombination med PAC eller andra främjande tillsatsmedel. Tryckbarhet och limbarhet av ytlimmad testliner borde också betraktas i fortsatta studier.

References

Andersson, L., Ridgway, C.J. & Gane, P.A.C. 2013, "Defining the mechanism of sizepress starch penetration in filled unsized fibrous products - a traditional technology revisited", vol. Nordic Pulp & Paper Research Journal Vol 28, no. 4, pp. 547-558.

Bajpai, P. 2015, "Chapter 3 - Pulp and Paper Chemicals∗ " in *Pulp and Paper Industry*, ed. P. Bajpai, Elsevier, Amsterdam, pp. 25-273.

Brander, James.,Thorn, Ian., 1997, *Surface application of paper chemicals,* Blackie Academic & Professional, London; New York.

CEPI 2016, *CEPI Key Statistics 2015*, Confederation of European Paper Industries.

ERPC 2016, *ERPC Monitoring Report 2015*, European Recovered Paper Council.

Forsström, U. 2003, *Interactions between base paper and coating color in metered size press coating*, Keskuslaboratorio.

Gane, P.A.C. 2001, "Surface treatment: Sizepress tradition, current development and a pigmented chemical future", vol. Twelfth Fundamental Research Symposium.

Gess, J.M. & Rodriguez, J.M. 2005, *The sizing of paper,* 3. ed edn, TAPPI Press, Atlanta, GA.

Hagiopol, C. & Johnson, J.W. 2012, *Chemistry of modern papermaking,* CRC, Boca Raton, FL.

Höke, U., Höke, U. & Schabel, S. 2010, *Papermaking science and technology. Book 7, Recycled fibre and deinking,* 2nd ed., totally updated version edn, Paper Engineers' Association : Paperi ja puu, Helsinki.

Holik, H. 2013, *Handbook of paper and board,* 2nd, rev. and enl. ed edn, Wiley-VCH, Weinheim.

Jeong, Y.B., Lee, H.L., Youn, H.J., Jeong, K.H. & Ryu, H. 2012, "Influence of the Viscosity of Surface Sizing Starch Solutions on Surface Sizing Effect of Linerboard", *Journal of Korea Technical Association of The Pulp and Paper Industry,* vol. 44, no. 5, pp. 54.

Jonhed, A. 2006, *Properties of modified starches and their use in the surface treatment of paper*, Karlstad University, Faculty of Technology and Science, Chemical Engineering.

Karademir, A., Ozdemir, F. & Imamoglu, S. 2007, "Effects of Alum-Rosin Sizing on the Properties of Some Wastepaper Grades", vol. Biotechnology, no. 6, pp. 148-152.

Khantayanuwong, S. 2002, "Effects of beating and recycling on strength of pulp fibers and paper", vol. Kasetsart Journal of Nat. Sci, no. 46, pp. 193-199.

Lee, H.L., Shin, J.Y., Koh, C., Ryo, H., Lee, D. & Sohn, C. 2002, "Surface sizing with cationic starch: its effect on paper quality and papermaking process", *TAPPI JOURNAL,* vol. 1, no. 1, pp. 34-40.

Lehtinen, E., Klass, C.P., Suomen Paperi-insinöörien Yhdistys & Technical association of the pulp and paper industry 2000, *Papermaking science and technology. / 11, Pigment coating and surface sizing of paper,* Fapet Oy : Published in cooperation with the Finnish Paper Engineers' Association and TAPPI, Helsinki.

Lipponen, J. 2005, *Surface Sizing With Starch Solutions at High Solids Contents, Dissertation for the degree of Doctor of Science in Technology*, Helsinki University of Technology, Laboratory of Paper Technology.

Lopes, P., Preciso, C., Sousa, A.M.d. & Ferreira, P. 2010, "Sizing evaluation of uncoated fine papers", .

Maurer, H.W. 2009, "Chapter 18 - Starch in the Paper Industry" in *Starch (Third Edition)*, eds. J. BeMiller, , & R. Whistler, Academic Press, San Diego, pp. 657-713.

Mondi group 2018, 2018-last update, *ProVantage Testliner* [Homepage of Mondi Group], [Online]. Available: https://www.mondigroup.com/en/products-and-solutions/categories/containerboard/provantage-testliner-3/ [2018, 8].

Nazhad, M.M., Li, K., Sutjipto, E.R. & Pongpattanasuegsa, S. 2008, "Effect of recycling on paper properties", vol. Tappsa Journal.

Pandian, V.E., van Calcar, D. & Wolff, B.W. 1994, *Use of zirconium salts to improve the surface sizing efficiency in paper making*, Google Patents.

Ryu, J. & Lee, H.L. 2007, "Improvement of plybond strength of two-ply sheets by spraying of starch blends", *TAPPI JOURNAL,* vol. 6, no. 5, pp. 3-8.

Saica 2018, 2/2018-last update, *Product information* [Homepage of Saica], [Online]. Available: http://www.saica.com/wp-content/uploads/2018/02/ds_ENG.pdf [2018, 8].

Shirazi, M., Esmail, N., Garnier, G. & van, d.V. 2005, "Starch Penetration into Paper in a Size Press", *Journal of Dispersion Science and Technology,* vol. 25, no. 4, pp. 457-468.

Sievänen, H. 2010, *Suitability of foam coating on application of thin liquid films*, Lappeenranta University of Technology, Faculty of Technology, Chemical Technology.

Sirviö, J. & Nurminen, I. 2004, *Paper Properties - Systematic Changes in Paper Properties Caused by Fines*, National Business Publications Ltd, Westmount, P.Q.

Valmet 2017, 2017-last update, *OptiSizer Spray - spray sizing for best controllability*. Available: http://www.valmet.com/board-and-paper/board-and-paper-machines/sizing/spray-application/ [2017, 4/3].

Vanier, N.L., El Halal, S.L.M., Dias, A.R.G. & da Rosa Zavareze, E. 2017, "Molecular structure, functionality and applications of oxidized starches: A review", *Food Chemistry,* vol. 221, pp. 1546-1559.

Wygant, R., Kendrick, J. & Walter, J. 2008, "Metered Size Press Pigmentation for Fiber Reduction", *TAPPI/PIMA PaperCon '08 Conference, May 4-7 2008*.

Wygant, R., Lucidi, G. & Kendrick, J. 2009, "Pond Size Press Pigmentation with Platy Kaolin", *TAPPI PaperCon'09 Conference*.

Zeng, H. 2013, *Polymer Adhesion, Friction, and Lubrication (1),* John Wiley & Sons, Incorporated, Somerset, US.