Parameters influencing hydrophobization of paper by surface sizing

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Frida Iselau*, Kerstin Malmborg-Nyström, Krister Holmberg and Romain Bordes

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Abstract: Paper surface hydrophobization, also referred to as "surface sizing", is often necessary for printing and packaging purposes. Typically, hydrophobic polymeric nanoparticles, in combination with starch are applied on the paper surface at the dry-end of the paper machine. In the surface sizing process, the nature of the nanoparticles, starch type, starch concentration and ratio between starch and nanoparticles, paper quality, ionic strength, and application as well as drying temperature are parameters that influence the result. The aim of this work was to systematically evaluate these parameters in order to create knowledge to be used for optimization of the process. Laboratory scale surface sizing trials were performed and the results from the trials showed that cationic particles gave superior performance compared to anionic particles. Both the starch type and the concentration of the oxidized starch had an impact on the performance. The effect of the ionic strength was found to depend on the particle charge: for cationic particles, the addition of salt was detrimental while for the anionic particles it was beneficial. An increase of the application or the drying temperature was found to enhance the performance up to a temperature around the glass transition temperature of the polymer.

Keywords: ionic strength; nanoparticles; paper; starch; surface sizing; temperature.

Introduction

Packaging is a growing market for the paper industry. A packaging material should be water resistant in order to withstand various storage conditions such as moisture and liquid exposure without losing its strength or shape. Due to the intrinsic hydrophilic character of the cellulosic fibres, packaging paper grades are hydrophobized to reduce penetration and wetting by water. In the paper manufacturing industry this treatment is frequently referred to as sizing. If the hydrophobizing agent is added to the pulp it is referred to as internal sizing, and if it is applied on the paper surface it is called surface sizing (Gess 2005).

The recent development in paper hydrophobization has focused on surface sizing due to its efficient retention which facilitates the dosing of the hydrophobic compound even when the fibre composition is very heterogeneous, as for recycled fibres (Klass 1991, Anderson 1997).

Surface sizing is typically achieved by applying a combination of hydrophobic nanoparticles and starch at the dry-end of the paper machine (Klass 1991, Ranson 2004, Moutinho et al. 2009, Xu and Hu 2012). The hydrophobic nanoparticles normally consist of a hydrophobic core and a stabilizer. The hydrophobic core is typically a styrene-acrylate co-polymer and the stabilizer is starch or a synthetic polymer (Exner 2002, Andersson and Järnström 2006, Xu and Hu 2012). The nature of the stabilizer defines the particle charge and cationic, anionic or amphoteric particle systems are used today. In the surface sizing process the particle suspension is first mixed with a starch solution and the mixture is then applied on the paper surface in the paper making process (Carceller and Juppo 2004).

In the surface sizing process, starch is mainly used in order to increase the surface strength of the paper. A starch film is formed and this contributes to the paper stiffness (Gray and Rende 2005). Depending on the initial porosity of the paper surface, the formed starch film can also reduce the porosity and thus contribute to a reduction of the water absorption rate (Klass 1991).

The surface sizing takes place at the dry-end of the paper machine. Some factors are already known to influence the surface sizing, for instance the type of particles used and the particle/starch ratio are known to be important variables (Iselau et al. 2015, Iselau et al. 2017). However, there are other parameters that could influence the surface hydrophobization. Paper quality and porosity could give rise to differences in surface topography, the type of

*Corresponding author: Frida Iselau, Chalmers University of Technology, Department of Chemistry and Chemical Engineering, SE-412 96 Göteborg, Sweden, e-mail: Frida.iselau@chalmers.se
Kerstin Malmborg-Nyström, Kemira Kemi AB, SE-251 09 Helsingborg, Sweden, e-mail: Kerstin.Malmborg-Nystrom@kemira.com
Krister Holmberg, Romain Bordes, Chalmers University of Technology, Department of Chemistry and Chemical Engineering, SE-412 96 Göteborg, Sweden, e-mails: krister.holmberg@chalmers.se, Bordes@chalmers.se

starch and the starch concentration used for surface sizing can vary. The temperature of the surface sizing formulation will influence the viscosity, which, in turn, is decisive of the degree of penetration into the porous material. A sufficiently high surface sizing temperature will also increase the flexibility of the polymer chains, which may influence the retention of the particles after application. A high drying temperature means faster water transport through the paper matrix and this may influence the migration of the particles. The drying temperature may also influence the film forming. The type and concentration of electrolytes in the water used for dilution of the particle suspension to the desired concentration may also play a role. In short, there are many parameters that can influence the surface hydrophobization.

In previous papers, we have identified the aggregation behaviour of the hydrophobic particles in presence of starch as a key factor in the surface sizing process. Aggregates formed by particles and starch were found to be beneficial for the water uptake reduction (Iselau et al. 2015, Iselau et al. 2016b, Iselau et al. 2017).

A study of the aggregation mechanism of the formed SP+/starch complexes demonstrated the impact of the starch composition. Regular potato starch that is normally used as size press starch, consists of 80 wt. % amylopectin and 20 wt. % amylose (Swinkels 1985). We have previously reported that it is mainly the amylopectin fraction of the potato starch that participates in the aggregation with SP+ (Iselau, Phan Xuan et al. 2016a). We also found in another study that the starch composition did have an impact both on the aggregate size and on the kinetics of the relaxation of the formed aggregates (Iselau et al. 2016a). It was therefore of interest to investigate the colloidal behavior and surface sizing performance of SP+ in the presence of another starch type; a waxy potato starch that consists only of amylopectin.

The aim of this paper is to evaluate the importance of the parameters described above for the process.

Materials and methods

Materials

Surface sizing particles labelled SP+, SPA+ and SP- were synthesized as described in a previous paper (Iselau et al. 2015). In short, SP+, SPA+ and SP- have the same hydrophobic core consisting of a co-polymer of styrene, n-butyl acrylate and tert-butyl acrylate but differ in the type of stabilizer. SP+ has a synthetic, cationic stabilizer, SPA+

Table 1: Particle properties.

Particle type	Diameter nm	ζ potential mV
SP+	29	+56
SPA+	58	+15
SP-	66	-29

and SP- particles are stabilized with an oxidized, degraded starch. In the case for SPA+, this is also cationized. The size and the surface charge of the three types of particles are summarized in Table 1. NaCl, $CaCl_2$ and Na_2SO_4 were all from SigmaAldrich, and used as purchased.

Starch powders, oxidized regular potato starch and oxidized waxy potato starch, were both obtained from Avebe, and were used as received.

Starch consists of repeating units of glucose that can form two types of polymer chains: amylose and amylopectin. Amylopectin is a highly branched, high molecular weight polymer while amylose is shorter and mostly linear. Regular starch has a composition of 20 wt. % amylose and 80 wt. % amylopectin while waxy starch consists of 100 wt. % amylopectin. Molecular weights of the starches, as well as their colloidal charge and solution viscosity, are summarized in Table 2 (Iselau et al. 2016a).

As test paper, a liner grade and a fine paper grade were used in this study. The liner was a 100 % recycled, unbleached, not internally sized commercial paper grade with a basis weight of 140 g/m^2, ash content of 11 wt. % and a Cobb60 value of 140 g/m^2. This means that the liner grade contains residues of lignin and rosins that render the paper slightly hydrophobic, which is needed in the size press to avoid disintegration. The fine paper grade consisted of 100 % virgin fibers from birch with a calcium carbonate filler content of 16–18 wt. %, and had a basis weight of 80 g/m^2. It was produced on a pilot machine and was internally sized with alkylketene dimer in order to withstand the forces in the size press without disintegrating. The Cobb60 value for the fine paper was 80 g/m^2.

Methods

Turbidity study: Turbidity measurements were performed on an Agilent Cary 60 UV/Vis instrument, using disposable acrylic cuvettes and the baseline was recorded in Milli-Q water. As a measure of the turbidity, the value of the absorbance at 400 nm was used. The particle suspension, 0.1 wt. % solids content, was filtered using a 0.2 µm hydrophilic syringe filter (Sartorius) before a 2 mL sample

Table 2: Starch properties.

Starch type	Colloidal charge µeq/g	M_n[*] kD	M_w[**], kD	M_w/M_n	Viscosity[***] mPas
Regular starch	-180	202	870	4.3	8
Waxy starch	-130	1380	3090	2.2	15

[*]Number average molecular weight
[**]Weight average molecular weight
[***]8 wt. % starch solutions

was transferred to the cuvette. The 3 wt. % waxy starch solution was also filtered using a 0.2 µm hydrophilic syringe filter before it was added to the particle suspension. After the starch addition, the cuvette was shaken vigorously before being put into the UV/Vis instrument to record absorbance value.

Starch cooking for turbidity measurements: 3.5 g of starch powder was suspended in 100 ml Milli-Q water under vigorous stirring. The suspension was allowed to boil heavily for 10 minutes, yielding a clear, slightly pale yellow starch solution. The solution was cooled and diluted to a final concentration of 3 wt. %, calculated on dry weight of the starch.

Size press trials: In a size press trial, the hydrophobic nanoparticles in combination with starch are applied on a test paper surface. Oxidized starch solution used for the surface sizing tests was prepared in a jet batch cooker, where high temperature, high pressure and high shear forces from the steam gave a fully hydrated starch in solution (Kearney 2005). The starch solution was diluted to the required concentration and was maintained at approximately 60 °C during storage to prevent retrogradation (Klass 1991). The hot starch solution was added to the suspension of hydrophobic particles to give a final concentration of 0.03–0.5 wt. % particles. In order to compensate for the difference in pickup, the dosage of SP+ and SP- was adjusted according to the wet pickup. The mixture was then applied on test papers in a size press laboratory equipment from Mathis AG. The size press rubber rolls had a diameter of 110 mm and a rubber hardness of 70–80 shore A. The roll speed was 1.8 m/min and the roll pressure was 2 kg/cm². The surface sized paper sheets were dried with a contact dryer at 80 °C for 100 seconds, if not stated otherwise. The surface sized paper sheets were then stored in a climate room at 23 °C and 50 % relative humidity overnight. Hydrophobic resistance was evaluated after 24 h by the Cobb 60 test method (Cobb and Lowe 1934) according to TAPPI standard method 441. The result from the Cobb test is water uptake by the paper presented as g/m². A paper sheet with a water uptake of 30 g/m² or below is commonly regarded as having a sufficiently hydrophobized surface. For the size press trials where the ionic strength was increased,

salt was added to the particle-starch mixture as aliquots of a stem solution and corrections were made for the dilution. In the size press trials with salt, the mixture was used in the size press after a two hours waiting time in order to allow the system to equilibrate (Iselau et al. 2017). After the surface sizing application the test paper sheets were dried in order to remove excess water. Drying was therefore done to obtain a specific residual moisture content of the paper, which is typically around 6 wt % (Brungardt 1997). A drum drier was used and the dryer's temperature and rotation speed could be adjusted in order to achieve the desired moisture content. This meant that in the case of lower drying temperatures, the rotation speed in the dryer was decreased. In the series of trials with different drying temperatures, both the drying temperature and the rotation speed were varied in order to achieve comparable moisture contents.

Differential Scanning Calorimetry, DSC: A DSC Star System instrument (Mettler Toledo) was used to determine the glass transition temperature. Particle suspensions were casted on a glass slide and allowed to dry at room temperature. A sample, 5–7 mg, was transferred to an aluminum pan and sealed hermetically. The DSC measurements were done with repeating cycles of heating-cooling. The test cycle was repeated twice and consisted of a temperature ramp of 10 °C/min from 20 °C to 120 °C, where the temperature at the inflection point in the second cycle was defined as the glass transition temperature.

Tensile strength: Tensile strength was measured for the surface sized paper sheets where different amounts of starch had been applied in the size press. Paper stripes with the dimension 100 × 15 mm were cut out for each dosage: five paper stripes in the machine direction and five in the cross direction. The paper stripes were tested in a tensile tester from Lorentzen & Wettre. The clamp distance was 70 mm and the test speed was 100 mm/min.

Paper surface roughness determination: Paper surface roughness was measured using a Bendtsen equipment according to standard ISO 8791-2:2013. With this method, pressurized air flows along the paper surface to determine surface roughness.
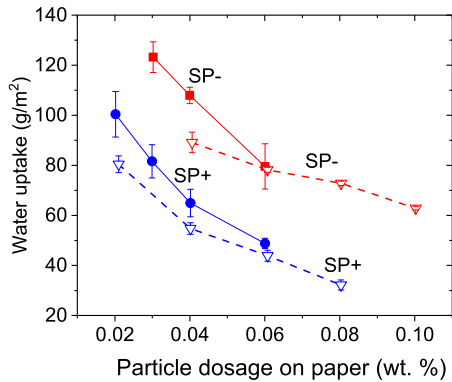
Figure 1: Water uptake versus particle dosage for SP+ and SP- in combination with 8 wt. % starch when applied on either liner (solid lines) or fine paper (dotted lines).

Results

Three different types of surface sizing particles, labelled SP+, SPA+ and SP- were used in the studies. In the surface sizing procedure the particles are mixed with starch before being applied on the paper surface using a puddle press.

Influence of paper type and surface roughness

Surface roughness, determined by the Bendtsen air flow equipment, showed a clear difference for the two paper grades, the measured air flow was six times lower for the fine paper than for the liner.

Two size press trials were performed with the particle types SP+ and SP- in combination with 8 wt. % starch on the liner grade and the fine paper grade. Results from the size press trials, presented as water uptake versus particle dosage, are shown in Figure 1. From these trials it can be concluded that SP+ has a superior performance compared to SP-, both on the liner and on the fine paper. The better efficacy of SP+ compared to SP- has been discussed in previous papers (Iselau et al. 2015, Iselau et al. 2017) and was attributed to the ability of SP+ to form aggregates with the oxidized starch.

For SP-, the impact of dosage is less pronounced for the fine paper than for the liner, as seen in Figure 1 by the smaller slope. This means that higher amounts of SP- are needed when applied on the fine paper compared to when applied on the liner in order to reduce the water uptake to the same extent. However, for SP+, the shape of the curve is the same irrespective of if fine paper or liner grade is used.

A more open paper structure would be expected to require a larger dosage of the hydrophobic nanoparticles. However, our results show that the paper roughness measured by air flow did not have a large impact on the surface sizing performance, especially for SP+, as seen from the similar curves for SP+ on fine paper and liner.

Aggregation depends on the starch composition and influences the surface sizing performance

The aggregation behavior of SP+ in combination with regular or waxy starch was evaluated by the means of turbidity, Zeta potential and radius of hydration measurements.

Waxy starch showed the same colloidal behavior as the regular starch, but more pronounced. The maximum aggregate size for SP+ in combination with the waxy starch was 156 nm compared to 112 nm when the regular starch was used. A comparison of the colloidal behavior of waxy and regular starch is shown in Figure A1 in Appendix.

In order to evaluate if the enhanced aggregation achieved by SP+ in combination with the waxy starch will have an impact on the surface sizing performance, a size press trial was performed using waxy starch applied on the liner grade. Two starch concentrations were employed; the normally used starch concentration, which is around 8 wt % and a lower starch concentration, 0.3 wt %, corresponding to the starch concentration that gave rise to the maximum in aggregation. The anionic particle type, SP-, had previously been found to not interact with the starch (Iselau et al. 2015) and the surface sizing performance of SP- was not affected by the starch concentration when regular starch was used. (Iselau et al. 2017) SP- was therefore used as a reference in this size press trial. Water uptake values plotted versus SP- dosage are shown in Figure 2. From this figure it can be seen that the water uptake was not affected for SP-, regardless of starch concentration. This is as expected since there are no interactions between the particles and the starch. For the two starch concentrations, 0.3 and 8 wt. %, the solution viscosity is very different. It is known that the starch viscosity governs the penetration depth of the starch solution into the paper matrix. (Remmer and Eklund 1992, Olkkonen and Lipponen 2007) A lower viscosity liquid will penetrate deeper, which will result in less efficient surface sizing. (Bung 2004) This was not seen in the size press trial for SP-, implying that the SP- penetration was not affected by the presence of starch.

For the cationic particles there was a significant difference between the two starch concentrations, as seen in
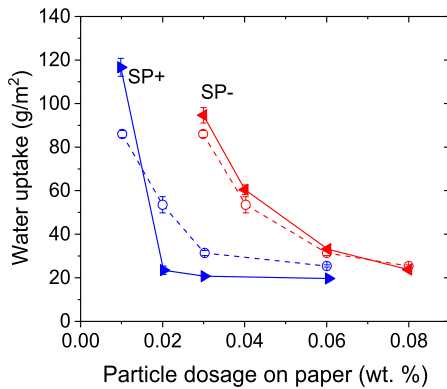
Figure 2: Water uptake plotted versus particle dosage for SP- and SP+ with waxy starch used as size press starch, on the liner grade. Solid lines represent 0.3 wt % starch and dotted lines represent 8 wt % starch in the formulation.

Figure 2. A low starch concentration, corresponding to the maximum in aggregation, gave better hydrophobization for particle concentrations above 0.01 wt. %. The size press trials were performed right after the starch was added to the particle suspension; thus, the SP+/starch complexes were in a state of non-equilibrated flocculation.

Comparing the water uptake values for the SP+ dosage of 0.02 %, there was a smaller gain in water reduction between the high and the low starch concentration for the waxy starch, 30 g/m^2, compared to the gain in water reduction for regular starch that in a previous study had been found to be 60 g/m^2. This difference can be understood in view of the turbidity results for the formed SP+/starch aggregates when regular or waxy starch was employed. The turbidity value at higher starch to particle charge ratios, corresponding to higher starch concentrations, levels out on a plateau value of around 0.5 when the waxy starch was used and of around 0.2 for the regular starch (values obtained from Figure A1 in Appendix). It is likely that SP+ and waxy starch are more aggregated also at higher ratios than SP+ and regular starch.

The starch concentration influences the surface sizing performance

Size press trials were performed on the liner grade using either SP+ or SP- in combination with different starch concentrations: 0, 2, 4 and 8 wt. %. These starch concentrations are in accordance with the concentrations used in other related studies. (Brungardt 1997, Lipponen et al. 2004) The amount of liquid absorbed by the test paper during the surface sizing depends on the viscosity of the liquid which in turn depends on the starch concentration.
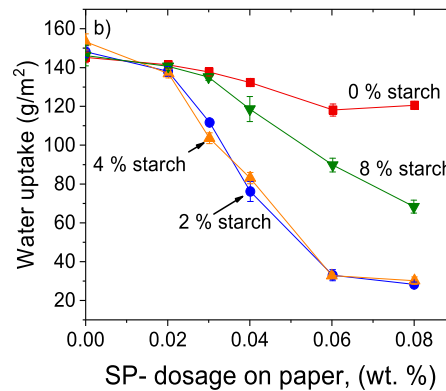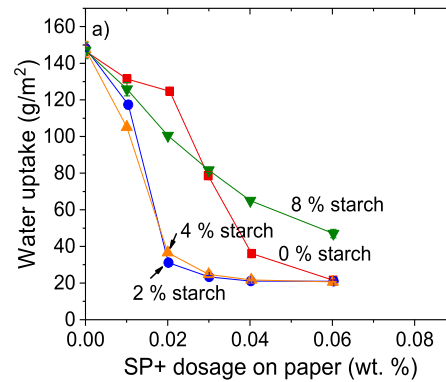

Figure 3: Water uptake plotted versus dosage of a) SP+ and b) SP-, in combination with 0, 2, 4 and 8 wt. % starch on the liner.

(Lipponen et al. 2004, Shirazi et al. 2004) The comparison for SP+ and SP- at 0.3 and 8 wt. % was discussed above, and the improved performance for SP+ at 0.3 wt. % compared to at 8 wt. % was attributed to the formation of aggregates. At starch concentrations of 2, 4 and 8 wt. %, however, the SP+/starch aggregation monitored by turbidity has reached a plateau, see Figure A1 in Appendix (Iselau et al. 2015) and the formed aggregates are thus not significantly affected by the difference in starch concentration. For SP- the starch concentration did not have an impact on the colloidal behavior, which means that the performance of SP- should be independent of the starch concentration.

The results from the size press trials for SP+ and SP- combined with the different starch concentrations are shown in Figure 3. For all starch concentrations, SP+ has a superior performance compared to SP-. This was expected since the aggregation of SP+ with starch has in previous studies been found to be beneficial and in the starch concentrations range used in this study SP+/starch complexes are present. When no starch was used in the size press trial, the cationic particles will, as a result of electrostatic
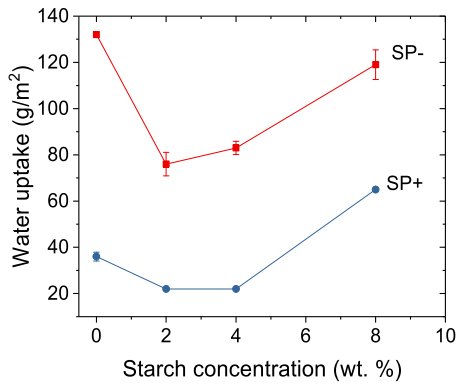
Figure 4: Plot of water uptake versus starch concentration for SP+ and SP- at the dosage of 0.04 %. Note; this figure is a merger of two trials (SP+ and SP- were tested separately) and the interpretation should therefore only be on trends, not on absolute values.

attraction, be retained on the paper surface and thus still give better performance compared to SP- that carries the same charge as the fibers in the test paper.

An interesting and somewhat surprising result was the reduction in water uptake for both SP+ and SP- at intermediate starch concentrations: 2 and 4 wt. % starch. The water uptake curves for both SP+ and SP- had a much steeper slope compared to when 8 wt. % starch was used, as displayed in Figure 3. The impact of the starch concentration thus seemed to be a general effect. A tentative explanation could be that application of starch on the paper surface has an optimum somewhere. Too low an amount of starch on the paper surface is not sufficient to decrease the porosity and thereby decrease the rate of water uptake and too high an amount on the surface will increase the hydrophilicity of the paper, thereby counteracting the desired hydrophobization effect achieved with the hydrophobic nanoparticles SP+ and SP-. In Figure 4 this counteracting effect is displayed as a minimum in the plot of the water uptake versus starch concentration, for the SP+/SP- dosage of 0.04 %.

Starch is used in surface sizing mainly to increase the surface strength. Tensile strength for paper surfaces with different amounts of starch applied on the surface was measured in both machine direction (MD) and cross direction (CD) of the paper. A paper sheet is generally much stronger in MD compared to CD due to alignment of the fibers in the machine direction during the formation of the paper. As expected, there was a linear increase in strength with increasing starch concentration.

The strength increase was similar in both MD and CD. A plot of tensile strength as a function of starch concentration is shown in Figure A2 in Appendix.
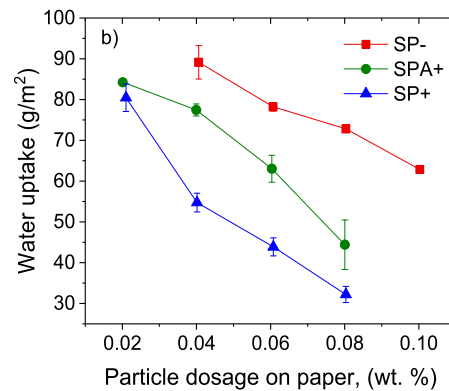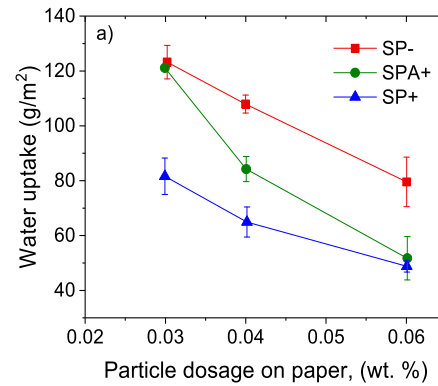

Figure 5: Plots of water uptake versus particle dosage for SP+, SP- and SPA+. a) Applied on a liner grade, b) applied on a fine paper grade.

The nature of the stabilizer influences the surface sizing performance

SP+ in combination with the oxidized starch gave a superior surface sizing effect compared to SP- on both fine paper and liner. Since both the charge and the structure of the stabilizer differ between SP+ and SP-, it remains unclear what parameter is decisive of the effect.

A size press trial was performed where a new type of particle, labelled SPA+, was used. SPA+ was titrated with the oxidized starch in the same way as previously reported for SP+ (Iselau et al. 2016b) and the interactions were monitored by turbidity. SPA+ showed a partly reversible aggregation behavior, similar to what had previously been seen for SP+, with a maximum turbidity correlating with the charge neutralization point (data not shown here).

In Figure 5, the water uptake for SP+, SP- and SPA+ on both liner (6a) and fine paper (6b) are shown and it can be seen that for both paper types the hydrophobization efficiency declines as SP+ > SPA+ > SP-. Thus, it seems that a positive charge is important and the stronger the charge, the better.
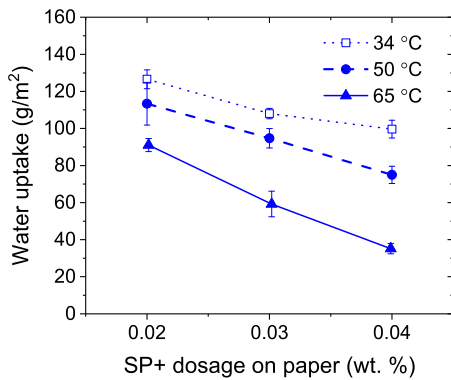
Figure 6: Plot of water uptake on a liner grade versus particle dosage for SP+ at different application temperatures.

Figure 7: A merged plot of water uptake values at different dosages for SP+ at different drying temperatures, from three different trials.

The surface sizing performance depends on the temperature

Glass transition temperature; The glass transition temperature, Tg, was determined using DSC. SP+ and SP-, which have the same hydrophobic core, exhibit similar glass transition temperatures, 66.9 °C and 65.7 °C, respectively. Therefore, only SP+ was employed in the further studies of the role of the temperature.

SP+ at different application temperatures: An elevated application temperature, commonly 60 °C, is always employed in paper mills in order to avoid retrogradation of the starch. (Bung 2004, Lipponen et al. 2004) In order to evaluate the impact of the application temperature, size press trials were performed at 34 °C, 50 °C and 65 °C. In this trial the liner grade was used. Wet pickup was determined for all three temperatures to 16.9, 18.2 and 20.4 wt. %, respectively. The wet pickup was used to adjust the particle dosage in the particles/starch mixture in order to apply the same amount of particles on the paper sheet even if the pickup varied due to changes in temperature. If the temperature dependence on the surface sizing performance was only due to the amount penetrated into the paper sheet, the wet pickup correction would lead to a similar surface sizing performance irrespective of sizing temperature. This was not the case, however.

Water uptake versus particle dosage for different sizing temperatures is plotted in Figure 6. Even if the wet pickup was used to adjust the particle dosage, a temperature dependence on the surface sizing performance remained. Two trends were observed when the sizing temperature was increased. (1): An overall increase in performance seen as a decrease in water uptake for the same dosage. (2): A larger increase in performance between the 50 °C and 65 °C curves. The highest temperature, 65 °C, was close to the Tg for SP+. The large improvement in water
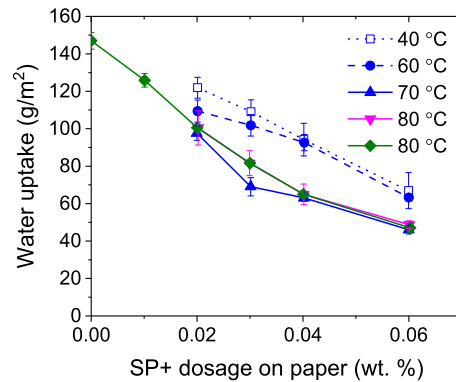
uptake reduction when the Tg was approached indicates that film formation is beneficial for the performance. The same effect of temperature was obtained on fine paper (see Figure A3 in Appendix).

Surface sizing performance of SP+ at different drying temperatures: After application of the surface sizing formulation, an additional drying is needed in order to remove excess water. In a paper mill the energy demand is high and in order to decrease the energy consumption the drying temperature is held as low as possible. A size press trial with SP+ was performed on the liner grade, and the drying temperature was varied while the other parameters were held constant.

Figure 7 shows that the water uptake was similar, for the same particle dosage, at low and intermediate drying temperature. Data obtained from another trial at 80 °C were also merged. Since these values were obtained at two different occasions, the plot should be seen as a trend display only. At high drying temperature, above Tg for SP+, the water uptake was considerably less, however.

Use of a higher drying temperature, 80 °C, which is normally employed in surface sizing, did not further improve the performance, indicating that Tg is an important parameter. In order to be efficiently retained on/in the paper the temperature has to exceed the glass transition temperature of the particles but further temperature increase does not improve the hydrophobization. A similar effect was seen when SP+ was applied on fine paper and then dried at different temperatures (Figure A3 in Appendix).

Increased ionic strength can have opposite effects depending on particle type

The influence of ionic strength on sizing performance was assessed in a series of trials where salts were added to
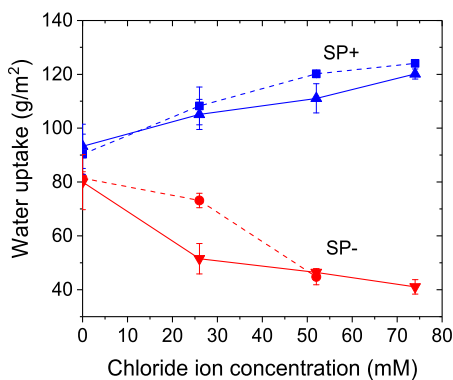
Figure 8: Plot of water uptake versus chloride ion concentration for SP+ and SP- on a liner grade using 0.3 wt. % starch. Dashed lines: addition of NaCl, solid lines: addition of CaCl$_2$.

the starch/particle suspension. Both SP+ and SP- were employed and the test paper was the liner grade. The starch concentration was set at 0.3 wt. % because the efficiency of SP+ is at maximum at this starch concentration. The results are shown in Figure 8. Addition of NaCl or CaCl$_2$ was detrimental to the effect of the cationic particles, with the water uptake increasing with increasing salt concentration. The opposite was found for the anionic particles, for which the water uptake decreased. Thus, the hydrophobization effect of SP- was enhanced by addition of salt. The detrimental effect of salt on SP+ was also observed in a previous study where the negative impact on the performance was rationalized in terms of floc formation (Iselau et al. 2017). A tentative explanation of the positive effect of salt on the performance of SP- could be that there is a screening effect of the anionic charge of the particles that gives rise to better retention of the particles on the paper surface. Turbidity measurements on SP- in combination with starch and with varying amounts of NaCl/CaCl$_2$ showed no sign of interaction, see Figure A4 in Appendix.

No changes in the water uptake values for paper surfaces treated with only starch could be found when the ionic strength was varied (data not shown). This can be explained by the paper sized with only starch being fully saturated with water in the Cobb60 test, preventing further water uptake. However, the results from the size press trials with SP+ and SP- showed that the increase in water uptake by the addition of salt was not due to the salt *per se* since opposite effects were seen for SP+ and SP-. Instead, it must be due to specific interactions of the salt with the particles.

Conclusions

SP+ in combination with starch gave a superior surface sizing effect compared to SP- on both fine paper and liner. The cationic product, SP+, was also less sensitive to base paper type, liner or fine paper, than SP-, which required larger amounts when a fine paper grade was employed.

The amylopectin content in the starch was found to influence the surface sizing. With waxy starch, which contains only amylopectin, the aggregation was more pronounced and occurred at a higher starch to particles charge ratio than with regular starch, which contains 20 wt. % amylose and 80 wt. % amylopectin. The relationship between starch concentration and surface sizing performance is complex because there are two effects that pull in different directions: film formation, which is beneficial for the sizing effect, and increasing hydrophilicity, which works against hydrophobization.

An increase of both the application temperature and the drying temperature was found to increase the surface sizing efficiency up to the glass transition temperature of the polymer. Beyond the T_g there was not much further effect.

Salts are present in the paper mill, originating either from the raw water source or from additives in the papermaking process. An increased concentration of NaCl or CaCl$_2$ was found to be detrimental to the surface sizing performance for the cationic particles while it was beneficial for the performance when the anionic particles were used. Even if cationic particles generally give better surface sizing, the overall conditions will therefore govern which particle type gives the best surface sizing result.

Some parameters are fairly easy to adjust in order to optimize the performance while other require larger changes or change of product/starch type. In any case, the understanding gained from this work will hopefully render optimization of the surface sizing process more knowledge-driven.

Conflict of interest statement: The authors do not have any conflicts of interest to declare.
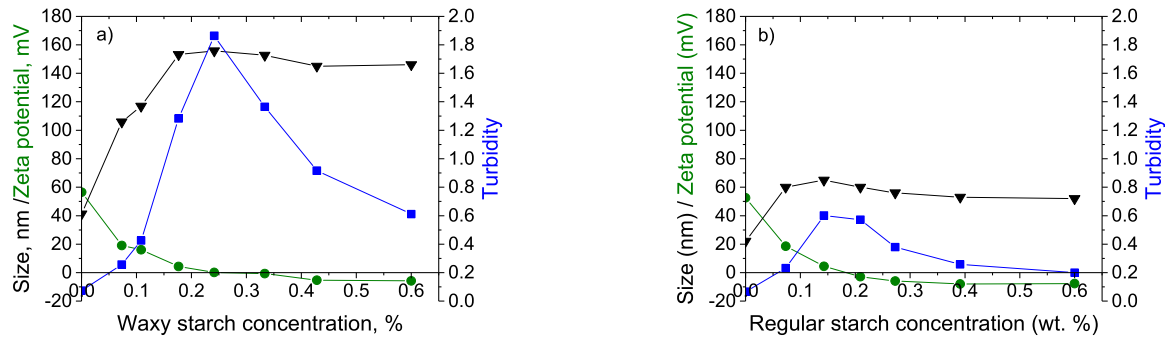
Appendix

Figure A1: Plots of size (triangles), Zeta potential (circles) and turbidity (squares) for SP+ in combination with a) waxy starch or b) regular starch.
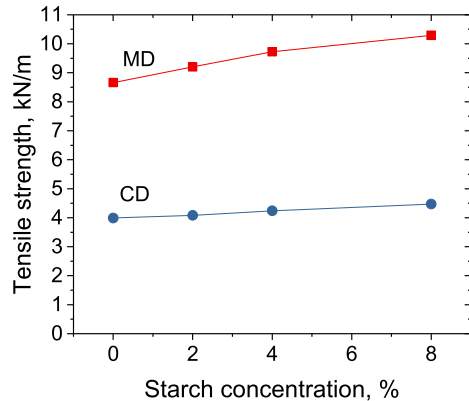

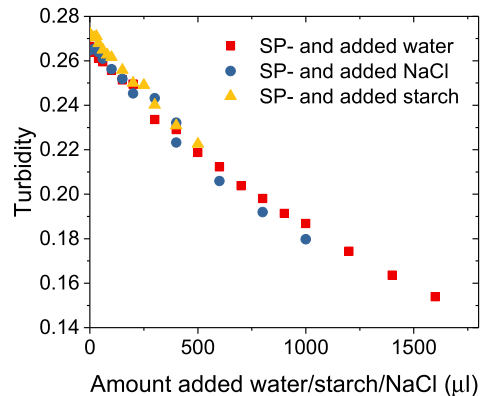**Figure A2:** Plot of tensile strength versus amount starch added to the paper.

Figure A4: Plot of turbidity versus amount added of water/3 wt. % starch/0.3 M NaCl to a SP- 0.1 wt. % suspension. The same behaviour is indicative that no interaction takes place.
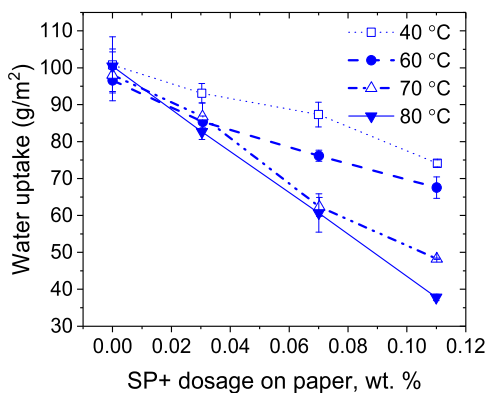

Figure A3: Water uptake versus dosage for SP+ on fine paper at different drying temperatures.

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