Potential of Coating Comprising Hydroxypropylated Starch for Dye-Based Inkjet Printing

Katriina Mielonen[1], Sami-Seppo Ovaska[1], Kaj Backfolk[1];

[1] *Lappeenranta University of Technology, School of Energy Systems, Group of Packaging Technology, P.O. Box 20, 53851 Lappeenranta, Finland.*

Abstract

The potential of hydroxypropylated starch –based composite coatings as inkjet receptive coatings was studied using water based inks with dye colorants. The variable in the development program was the proportion of various functional nanopigments such as kaolin and synthetic layered silicate. Also the effect of styrene-butadiene latex co-binder addition was investigated. From the viewpoint of print quality, the coated substrates showed excellent print density values, but low water fastness results, which was ascribed to dissolution of the coating-ink interface.

Introduction

Environmental concerns over the use of non-renewable oil-based polymers in the coatings of fiber-based substrates have increased interest in using renewable resources. Starch, an abundant and biodegradable raw material widely used in the paper industry for several purposes, is generally recognized as having a potential for use as binder in coatings of printing papers but its efficiency alone is often only moderate [1], which has limited its usage in high-quality printing papers. The use of starch in coated graphical grades for inkjet printing is relatively unexplored although traditional mineral coatings comprising starch binders are often not suitable due to poor ink adhesion and poor (slow) ink absorption capacity.

Anionic dye-based inks in particular need a cationic fixative to improve print quality, which thus means that most of the traditional anionic coating binders are less suitable for colorant fixation. Usage of nanostructured pigments with cationic and nonionic starches in the coatings of printing papers has been studied earlier [1]. General requirement for dye-based inks is that the coating has high and rapid solvent uptake, for example via a large number of fine capillaries. The presence of latex binder, however, has been reported to decrease the number of capillaries in the case of pigment-based coatings. In addition to the pigment characteristics and the microporosity, the role of binder chemistry and binder dosage levels have been investigated and debated in several papers. For example, Vikman and Vuorinen (2004) [2] showed the role of weakly cationic modified styrene-acrylate latex-starch binders in pigment coatings on inkjet print quality and ink adhesion. Additionally, having a cationic component in the coating layer is essential in order to obtain good water fastness. [3]

Synthetic silicates such as Laponite are used in several applications as stabilizers, thickeners or film-formers [4]. Laponite forms a colloidal dispersion of crystals when dissolved in water. The face of these crystals has negative charge, whereas positive charges are located in the edge area. The charge of the edge increases with pH, but becomes neutralized at pH levels > 11, so maintaining the pH below this limiting value is necessary [5]. The size of Laponite crystals is very small (approx. 25 nm) compared to natural clays such as bentonite [6]. These properties make Laponite also an interesting pigment for the production of high-performance printing papers comprising a composite coating [7].

The purpose of this work was to investigate and develop a sustainable biopolymer coating recipe for water based dye inks, which provides high print density, rapid ink setting behavior and low ink set-off tendency. Two commercial pigments, a high aspect ratio kaolin clay and a nanopigment, were used together with a water-soluble biopolymer at various concentrations.

Methodology

A4 SBS paperboard sheets (Stora Enso Oyj, Imatra) with a grammage of 350 g/m^2 were used as substrates. The sheets were either single or double coated in a bent-blade coating mode with a pilot coater (DT Laboratory Coater, DT Paper Sciences, Finland). The targeted coat weight was 4 g/m^2/layer. Coated sheets were dried with an infrared dryer with a heating power of 6 kW. The drying time was approx. 12 seconds depending on the proportion of pigment in the coating dispersion

Dispersed synthetic silicate (Laponite RDS, Rockwood Additives Ltd, UK) or kaolin (Barrisurf HX, Imerys Minerals Ltd, UK) was used in combination with cooked potato-based, low-viscous hydroxypropylated starch (Solcoat P55, Solam GmbH, Germany) with and without the addition of styrene-butadiene latex (Styron HPW-184, Styron Europe GmbH) with a glass transition temperature of -9°C. The mean particle size of the latex was measured with a Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd.) to 160 nm.

The nominal compositions of the coatings, given as relative amounts of the dry mass, are given in Table 1. The dispersions contained 0-40 pph of pigment (silicate or kaolin) and were prepared with and without a 10 pph addition of latex. The latex addition was calculated on the basis of the total dry matter content of the other components. The dispersions were prepared by first mixing the latex and the pigment together. The resulting blend was then poured into starch solution using continuous mixing. The dry solids content of the dispersions was adjusted to 16.5 wt% with tap water. The viscosities of the dispersions were measured with a Brookfield DV-II+ viscometer using spindle #5 at 100 rpm.

Table 1: Composition of coating dispersions. Pigments used in coating were synthetic silicate or kaolin.

Test point	Starch [pph]	Pigm. [pph]	Latex [pph]	pH Lapon.	pH kaol.	pH
1	100	0	0			5.9
2	100	0	10			7.3
3	95	5	0	7.3	6.1	
4	95	5	10	7.7	6.8	
5	90	10	0	8.1	6.2	
6	90	10	10	8.3	6.9	
7	85	15	0	8.6	6.1	
8	85	15	10	8.6	6.7	
9	80	20	0	8.9	6.1	
10	80	20	10	8.8	7.0	
11	70	30	0	9.2	6.2	
12	70	30	10	9.1	7.1	
13	60	40	0	9.3	6.3	
14	60	40	10	9.1	7.2	

Ink-substrate interaction was investigated with contact angle measurements. Dynamic and static contact angle measurements were performed on the surface treated samples (Attension Theta optical tensiometer, Biolin Scientific) for distilled water (γ=72.8 mN/m), for 99 % diiodomethane CH_2I_2 (DIM, Alfa Aesar, γ=50.8 mN/m), for 99.8 % ethylene glycol 1,2-ethanediol (EG, VWR Prolabo, γ=48.0 mN/m) and for dye-based ink (Memjet M101 black ink). A 420 Hz camera (Basler A602F-2 with Navitar optics) was used to capture images of the drop placed on the sample surface. The droplet volume was 3.0 µl for the water, EG and dye-based ink and 1.0 µl for the DIM. Contact angle was recorded immediately after the drop was released from needle and when surface spreading and absorption started. The change of the contact angle was measured from initial contact to 10 seconds or complete wetting.

The surface free energies (SFE, γ) were calculated using the acid base approach, which allows closer inspection of solid (s) surfaces (Eq 1). The Acid-Base calculation is based on summing the three SFE components, Lifshitz van der Waals (LW), electron-acceptor (+), and electron-donor (-) components, and thus requires a three-equation system, which can be written as [8]:

$$(1+cos\theta_i)\gamma_{li} = 2\left(\sqrt{\gamma_{li}^{LW}\gamma_s^{LW}} + \sqrt{\gamma_{li}^{+}\gamma_s^{-}} + \sqrt{\gamma_{li}^{-}\gamma_s^{+}}\right) \quad (1)$$

The coated papers were printed printing on Memjet, Lomond Evojet Office desktop printer that uses water-based inks with dye colorants. The printed samples were characterized with respect print evenness and ink drying behaviour but especially to print density. The print density was measured with an X-rite SpectroEye spectrophotometer in the 100% tone value areas for the CMYK-colors. The water fastness was tested using a beaker with deionized water (water equilibrated for at least 5 minutes). The printed sheet was placed in the beaker for 1 minute and then removed and dried and the optical densities of the black printed area and the original white area adjacent to the printed area were measured. The ratio of the optical density of the water-soaked inked area to the optical density of the unsoaked inked area gives the percentage water fastness. [9]

Results

Interactions between coating components

Figure 1 shows the viscosities determined for the coating dispersions with kaolin pigment and Laponite proportions of 0-40 pph. The used synthetic silicate forms a thixotropic gel, which increases the viscosity of the coating dispersion rapidly with the increasing addition level. This is in line with an earlier study [6], in which the viscosity of the Laponite based slurries were studied at different solid contents. With lower Laponite proportions (< 30 pph), the addition of latex increased the viscosity slightly, whereas in the case of 30 and 40 pph Laponite concentrations the viscosity of the dispersion decreased, which obviously can be ascribed to changes in the colloidal stability and interparticle interactions in the dispersion. All the studied coating dispersions were blade-coated without runnability problems, but the addition of pigment to the nonionic starch suspension had different effects on the interactions which was seen both as a change in viscosity and subsequently also the blade coating process, which required adjustments in the coater setup.

The viscosity of dispersions with kaolin pigment was very similar with different pigment levels. The presence of latex increased viscosity slightly with pigment contents of 0-30 pph. As for the blade coating process, reasonable flow profile of platy pigment-containing dispersions is definitely a favorable property, although obtaining the targeted coat weight was more challenging with dispersions with high content of kaolin pigment compared to Laponite-based dispersions.

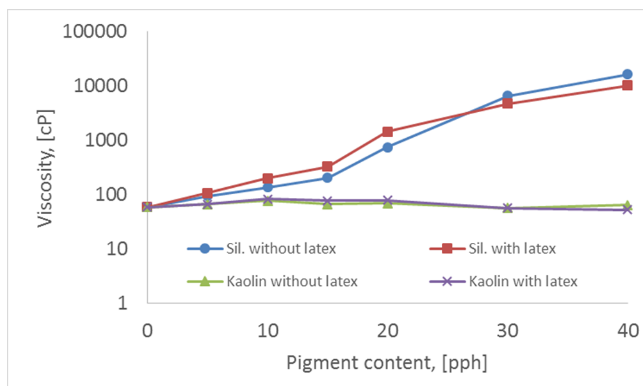


Figure 1. Viscosity (cP) of the coating dispersions. The standard deviation of the viscosity values was in the range of 0-5%.Note logarithmic scale on y-axis.

Contact angle of water, EG, DIM and black ink

Contact angles of liquids and black ink were determined on all the double-coated samples (coat weight 8 g/m^2) but result only for the latex-free substrates are presented. Contact angle for the water stayed at the same level (approximately 40°) during the measurement for the most of the samples, and no changes of the droplet volume were observed. Small decrease of the contact angles were seen (from 20° to 6° in 5 seconds) when the paper was coated with 100pph kaolin pigment without latex addition. No changes in the droplet volume occurred suggesting that there were no absorption of the droplet. Contact angle results obtained for the water-based black ink were quite similar with results obtained with water and EG and no effect of pigment proportion was noticed. Contact angle decreased after 0.5s on the surfaces containing

Laponite (Figure 2a). After that, contact angle stayed at the same level suggesting that no spreading occurred. Droplet volume did not change during measurements indicating that substantially no absorption occurred which might be associated with the barrier coating behavior of the starch coating. Contact angle of the ink was remarkably higher when coating consisted of plain silicate (100 pph) compared to the kaolin pigment (100 pph) suggestion that spreading in the latter case is more obvious.

With EG, on the other hand, all the samples behaved similar, i.e. contact angle decreased from 60° to 15° in 5 seconds and practically no effect on pigment proportion for the contact angle results were noticed (Figure 3). Contact angle results measured with DIM were also quite similar between the samples. Contact angles stayed at the same level (40-50) during the entire measurement and droplet volume stayed stabile suggesting that no absorption or surface spreading occurred.

When latex was used in the coatings, contact angles were higher with all the model liquids (water, EG and DIM) as well as with black ink but droplet behavior during the measurements were still similar compared to latex-free samples.

The effect of starch in the coating can be seen in both Laponite and kaolin pigment containing samples, but the effect of pigment in these coatings is slight. Sample containing 100pph starch had a water contact angle of 51° after 1 s, and the value remained unchanged for the 5 s test period. Similar behavior was also observed with other probe liquids, EG and DIM. This result indicates that the properties of starch dominated the liquid – substrate interactions as well in the case of composite-type coatings.

Table 2 shows the surface energies of the coatings determined according to Eq 1. Using latex together with pigments resulted in a slightly lower total surface free energy. However, no clear trends were seen in the latex-free test data, though SFE value is remarkably higher when kaolin pigment amount is high (40 pph) in the coating layer.

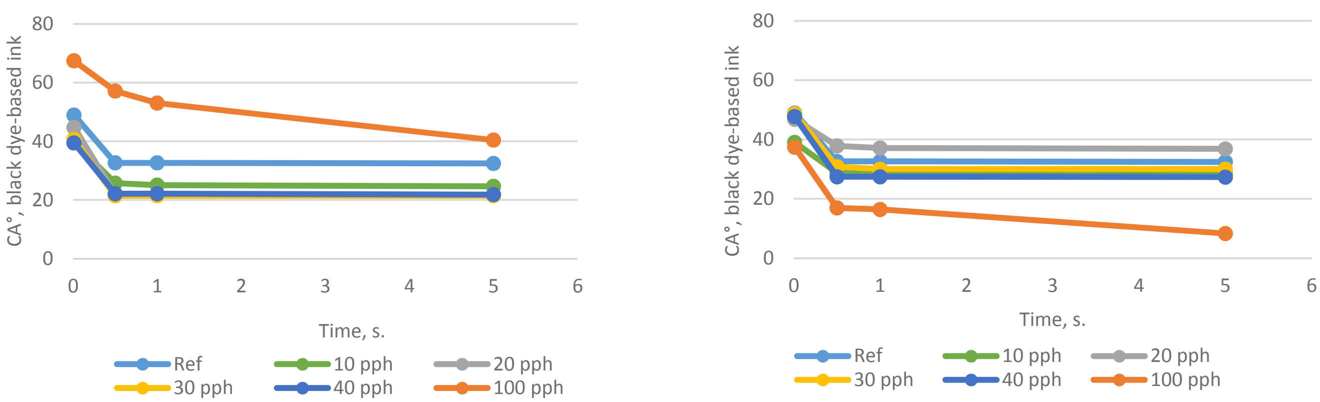


Figure 2a and 2b. Contact angle results measured with black ink for the (left) Laponite and (right) kaolin pigment containing, latex-free substrates.

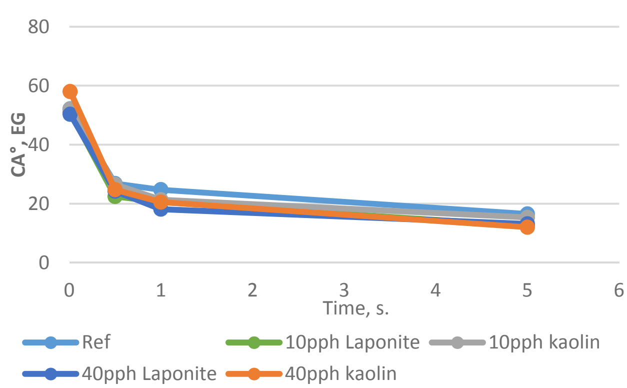


Figure 3. Contact angle results measured with EG for the Laponite and kaolin pigment containing, latex-free substrates.

Table 2. Acid/base surface free energy values. On uncoated reference paper SFE value is 37.5 mJ/m².

Pigment proportion	SFE, mJ/m²			
	Laponite		Kaolin pigment	
	Latex 0 pph	Latex 10 pph	Latex 0 pph	Latex 10 pph
0	48.4	42.8	48.4	42.8
10	46.9	43.7	48.0	-
20	45.3	40.5	46.9	42.0
30	47.4	36.2	46.3	37.8
40	46.8	34.2	54.2	40.9

Print quality

Substrate-ink interaction and print quality was evaluated by means of print density and visual inspection of the double-coated (coat weight 8 g/m^2) and printed samples. Print density values for the black ink on the coated papers were measured from the 100% tone area. Results shows that for the reference sample, i.e. 100 pph starch based coating, a print density value approximately 1.8 is obtained while a slight increase is seen when adding 10 pph latex to the formulation. Both these values are significantly higher than obtained for the reference sample (uncoated paperboard), which gave a print density of about 1.3

When the kaolin mineral pigment was used in the coating, the print density values were approximately 0.5 units lower, see Figure 4b. There was no remarkable effect of latex addition in this case either, thus confirming the above statement. The role of film forming binders such as the latex and HPS used in this case, can obviously be used in selected formulations and with certain inks. The results from Ridgway et al. (2011), for instance, suggested that absorbed or free cationic polymer will be located on the high surface area walls of the fine pores or will migrate to the fine pore regions during the drying process and leading the absorption efficiency due to lost pore volume and lost capillarity.

However, when Laponite was used in the coating, a significant improvement in print density was gained (ca 20%) already at fairly low pigment concentrations. At further addition of the Laponite to the coating layer, the density values remained at the same density level (approximately 2.5 unit), see Figure 4a. There was no significant effect of latex as a co-binder in the coating layer, which hence imply that the ink absorption and solvent removal is not dominated by capillary suction.

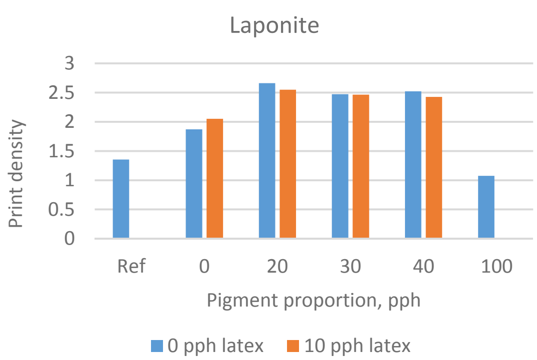
The low ink drop absorption behavior presented above is in fact supporting the high print density values, density values are in line with contact angle results determined with dye-based ink. Contact angle is lower when the coating is made with 100 pph kaolin instead of 100 pph silicate indicating greater tendency to lateral spreading which in turn confirm that density values are lower.

Water fastness

Water fastness was determined for only part of the samples, see table 3. The water fastness value obtained for the reference samples, i.e. sample coated with solely starch gave poor water fastness results, which can be attributed to solubility behavior of the ink-coating layer and substantially no curing or cross-linking within the coating. For the coating comprising clay pigment, slightly higher water fastness were achieved although the improvement is not significant. However, the coating with starch and Laponite showed a clear increase in water fastness and especially for the coating comprising 100 pph Laponite, i.e. 79.6%. Despite the low value for coating comprising 40 pph Laponite, these results indicate that starch-Laponite coating forms a coating with temporarily water fastness behavior. The results from CA measurements with water, showed actually that the 100 pph silicate sample had a much higher water repellency property, which hence would confirm improved water resistance of the coating structure at short immersion times.

Table 3. Water fastness results. Water fastness of the uncoated reference sample was 64.3%.

Pigment proportion	Water fastness, %			
	Laponite		Kaolin pigment	
	Latex 0 pph	Latex 10 pph	Latex 0 pph	Latex 10 pph
0	16.4	13.2	16.4	13.2
10	48.1	-	16.7	-
40	16.3	20.6	20.8	9.6
100	79.6	-	41.7	-



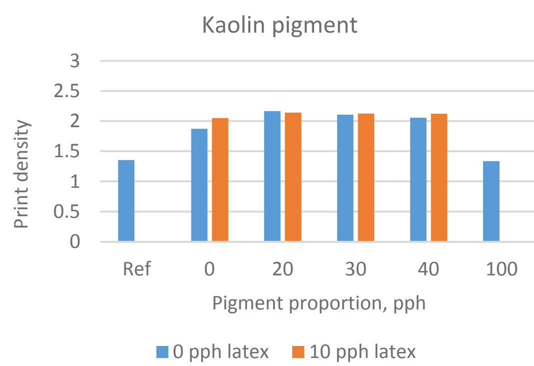


Figure 4a and 4b. Print density results for the sample (left) including modified Laponite and results for samples (righ) including high aspect ratio mineral.

Summary

A novel hydroxypropylated starch–based composite coatings were developed and their efficiency as a substrate for dye-based inkjet printing was evaluated. It was found that the printability of the substrates evaluated by means of optical density were excellent and improved with increasing addition of synthetic silicate content. The results showed that even a small amount of Laponite among hydroxypropylated starch led to substantial improvement in print quality, suggesting that the combination of low-cost starch and Laponite additive is an economically feasible approach for producing substrates for water based inkjet inks. Latex addition had a very little impact on the results showed in this paper, suggesting that the co-binder is not a critical component in hydroxypropylated starch–based coatings. Interestingly, also using kaolin pigment instead of Laponite provided a significant improvement in print density, but only the presence of Laponite resulted in superior printability. The results thus suggest that excellent print quality can be obtained by using hydroxylpropylated starch–based coatings in dye-based inkjet printing, and by re-engineering coating formulation it is possible to develop a low cost substrates for modern inkjet printing technologies.

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Author Biography

M. Sc. Katriina Mielonen is a post-graduate student and a member of the Group of Packaging Technology in Lappeenranta University of Technology, School of Energy Systems. The focus of her research is on inkjet printing and environmental aspects of printing. Earlier she has worked with e.g. fiber-based health care- and nursing products and been a project manager in a research project related to biorefineries.