Tuning liquid absorption and ink spreading by polyelectrolyte multilayering on substrates with different levels of internal sizing

Katriina Mielonen, Sami-Seppo Ovaska, Kaj Backfolk*

Lappeenranta University of Technology, Packaging technology P.O. Box 20, 53851 Lappeenranta, Finland.

Abstract

The effect of base paper hydrophobicity and polyelectrolyte multilayer surface treatment on the subsequent liquid absorption and ink–substrate interaction was studied. It was found that the internal sizing degree affects the inkjet print quality, but that it is dependent on deposited polyelectrolyte layer chemistry and composition. A rather different ink absorption and spreading behavior was seen with dyes than with pigment-based inks.

Introduction

Cationic polymers have often been used as additives in the surface treatment of papers to improve print quality in inkjet printing [1, 2]. Anionic dye-based inks in particular need cationic fixative agents for efficient fixation via electrostatic interaction [3]. The cationic surface treatment of substrates made with surface sizing or priming improves not only the print quality but also the water fastness of the prints [4, 5]. Resin-based coatings usually contain cross-linking agents to further promote ink adhesion and water fastness and also to adjust solvent absorption.

Surface treatment compositions with a cationic polyelectrolyte, such as polyethylene imine (PEI), and polyvinyl alcohol (PVOH) [6, 7], polyvinyl amine (PVAm) [8, 9] or polydiallyldimethylammonium chloride (PolyDADMAC) [4, 9] as binder have been tested in the surface size with various results. In addition to the preferred use of cationic or nonionic polymers, studies have shown that anionic hydrophilic CMC also enhances inkjet print quality, i.e. a high dye gamut and optical density are favored by a relatively low porosity and pore size of the coating [10].

The effect of internal sizing on inkjet print quality has been reported for example by Pal et al. (2007) showing that alkyl ketene dimer (AKD) has a negative effect on optical properties. An increasing absorbency was observed for some samples when the amount of AKD was increased, even though the overall effect of surface sizing was to reduce the absorbency of the paper [11]. Lundberg et al., on the other hand, studied the effect of alkyl succinic anhydride (ASA) on inkjet print quality and found that internal sizing reduced the rate of absorption of water-based dye and claimed that the rate of evaporation affected the result. In the uncoated papers, the internal sizing reduced the apparent surface energy, the droplet spreading and the rate of ink absorption. The coated inkjet papers exhibited relatively low surface roughness and small pore sizes and gave rise to rapid inkjet ink absorption and a cylindrical distribution of the colorant of the ink in the coating layer [12].

To our knowledge, the effect of a thin multilayer surface treatment of a polyelectrolyte coating on paper substrates with various levels of internal sizing has not been studied. Previous work on the surface treatment with polyelectrolytes [13] shows, however, that bilayering comprising similar polymers but with opposite charges apparently leads to cross-linking and hence gives a different swelling behavior in liquids. The effect of on the interaction with inkjet inks multilayering of polyelectrolytes has not been investigated.

Materials and methods

The base paper used in this study was a wood-free 80 g/m^2 fine paper prepared on a pilot paper machine at a speed of 100 m/min. The paper contained different levels of ASA, see Table I, and the retention chemicals were cationic polyacrylamide and bentonite. The target filler content (PCC) was 25%.

A4 sheets were cut from the base paper and then surface treated using a spray coater (Spalas Coating System, Nanotrons).

The ink-receptive coatings were prepared by a multilayer surface treatment where (A) denotes anionic sodium carboxymethylcellulose (CMC, Finnfix 30, CP Kelco) and (C) denotes a cationic polydiallyldimethylammonium chloride (PolyDADMAC, Catiofast BP, BASF GmbH). Three-layer-treatments were prepared according to the wet-on-wet principle, i.e. AAA, CCC, CAC and ACA. The target coat weight for one layer was 1 g/m^2. The total coat weights of the three layers are shown in Table I. After the surface treatment, the papers were dried at 23°C and 50% RH.

Table I. Coat weights of the multilayer treated samples.

ASA amount, kg/t	0	0.5	1	1.5
Coat weight, g/m^2				
AAA	4.7	5.1	6.1	5.3
CCC	4.5	4.5	4.7	4.6
ACA	3.0	3.5	3.3	3.0
CAC	3.3	3.9	3.4	3.0

The Bendtsen roughness (ISO 8791-2), Parker Print Surf (PPS) roughness (ISO 8791-4), grammage (ISO 536) and coat weight determined at 23 °C and 50% RH are shown in Table II. The untreated paper was very rough and there are no remarkable differences between the roughness values.

Table II. PPS and Bendtsen roughness values.

ASA amount, kg/t	0	0.5	1	1.5
PPS, µm				
Uncoated base paper	9.5	9.8	9.3	9.6
AAA	10.9	10.9	9.5	9.4
CCC	9.6	10.0	10.3	9.8
ACA	10.2	10.4	9.7	9.5
CAC	10.2	10.7	9.9	9.6
Bendtsen, ml/m				
Uncoated base paper	912	842	884	798
AAA	1132	1053	924	887
CCC	1037	1010	1049	1052
ACA	1019	1097	1008	900
CAC	1047	976	985	879

Contact angle measurements

Contact angles were determined with an Attension Theta optical tensiometer (Biolin Scientific) using distilled water, and 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 0.8 µl.

Printing and print quality

The untreated and multilayer-treated papers were printed with three different inkjet desktop printers: printer 1 (HP Officejet Pro 8000 Enterprise) uses water-based inks with a pigment colorant (Pigment ink 1), printer 2 (Memjet, Lomond Evojet Office) uses water-based inks containing dye colorants (Dye ink 1), and printer 3 (Brother MFC-J5910DW) uses water-based inks with a pigment colorant in the black ink (Pigment ink 2) and a dye colorant in the CMY inks (Dye ink 2).

The printed samples were characterized with respect to print density, mottling, bleeding and wicking. The print density was measured with an X-rite SpectroEye spectrophotometer in the 100% tone value areas for the CMYK-colors. Mottling, bleeding and wicking were determined by an Intelli IAS program with an Epson Expression 1680 scanner.

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. [14]

Results

Role of thin polyelectrolyte layers in pigmented ink-substrate interaction.

Figure 1 shows the contact angle of water on different internally sized papers. The internal sizing clearly gives a hydrophobic surface at an ASA dosage of 1.0 kg/t and higher.

Figure 2 shows the contact angle of water on substrates with an internal sizing level of 0.5 kg/t and different multilayer surface treatments. It reveals that the multilayer surface treatment on a rather hydrophilic substrate (0.5 kg/t ASA) can effect both the initial contact angle (short contact times) and the absorption behavior (1-5 sec.). The anionic-cationic multilayering apparently creates an interfacial cross-linking reaction and thus a thin coating which reduces the rate of liquid absorption. A cationic multilayer treatment (CCC) increased the hydrophobicity of the paper, while an anionic treatment (AAA) increased the rate of absorption into the paper. The complex multilayers (CAC, ACA) with a hydrophilic character gave a paper a low absorption rate.

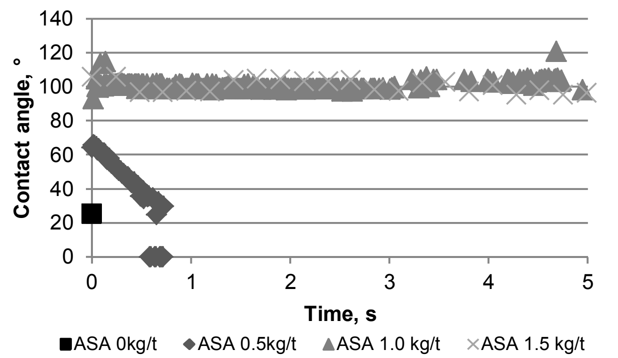

Figure 1. Contact angle of water on uncoated paper.

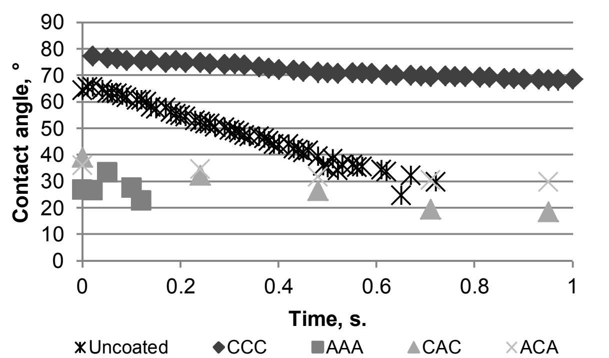

Figure 2. Contact angle of water on multilayer-treated substrates with 0.5 kg/t ASA.

Effect of degree of internal sizing on print quality (uncoated substrates)

Print density values for the black, cyan, magenta and yellow inks were measured on the 100% tone area (results not shown here), and there were some differences in the density values between different inks of the same color. The highest density level (1.6) for black ink was achieved with pigment ink 2 on the substrate with 0.5 kg/t of ASA. An increase in the amount of ASA led to increase in print density for black but only for pigment ink 2.

For the cyan ink areas, there were remarkable differences between the inks (not shown here). The density of the dye ink 2 was much lower (0.5 units) than that obtained with pigment ink 1 or dye ink 1. It was also found that with increasing amount of ASA, the density values of all the cyan inks decreased slightly, suggesting that a higher substrate hydrophilicity promotes solvent absorption leaving the colorant on the surface.

Print mottle was determined in the black ink areas (100%) on the different substrates (results not shown here). For the pigment ink 1, the mottling increased by approximately 0.1 units when the level of ASA was increased. For pigment ink 2 and dye ink 1 the print mottle was independent of the amount of ASA.

Effect of polyelectrolyte multilayer surface treatment on print quality

The print density of the black pigment ink 1 (100%) on substrates having different multilayer treated surfaces is shown in Figure 3. It can be seen that the cationic surface (CCC) gave the highest density, particularly at higher levels of internal sizing. The surface treated with the anionic polyelectrolyte, AAA, gave the lowest black density values, with little or no effect of the internal sizing level. The densities of the black pigment ink 2 and dye ink 1 were not affected by the amount of ASA. The density increased from 1.65 to 1.8. of dye ink 1 on the CCC layer (results not shown here).

It was further observed (Figure 3), that polyelectrolyte multilayering alternately with cationic and anionic polyelectrolytes (CAC and ACA) gave a higher density of pigment ink 1 then the totally anionic sample (AAA) but a lower density than that obtained on the cationic surface (CCC).

Figure 4 shows the mottling values for the black pigment ink 1 (100% areas) on the multilayer-surface-treated papers. It appears that there is less mottling on the surfaces containing cationic polyelectrolytes (CCC or CAC), although the uncoated reference was almost at the same level. On the anionic surface (AAA), however, the mottling increased significantly when the amount of ASA was increased from 1.0 kg/t to 1.5 kg/t. suggesting that sizing causes an uneven absorption and levelling of the inks.

The print mottle of the cyan pigment ink 1 was similar to that of the black pigment ink 1 (results not shown here), the greatest mottling of the pigment cyan ink 1 being on the AAA surface. For the other surface-treated samples, there were no differences between different ASA levels.

The mottling values with black pigment ink 2 and black dye ink 1 were lowest on the uncoated reference and the multilayer surface treatment had no effect on ink spreading or print evenness with these inks.

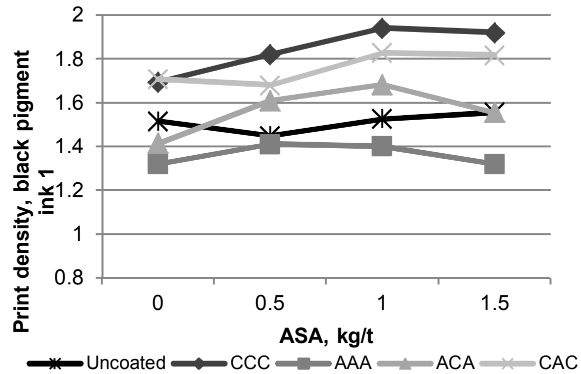

Figure 3. *Print densities for the 100% black tone areas.*

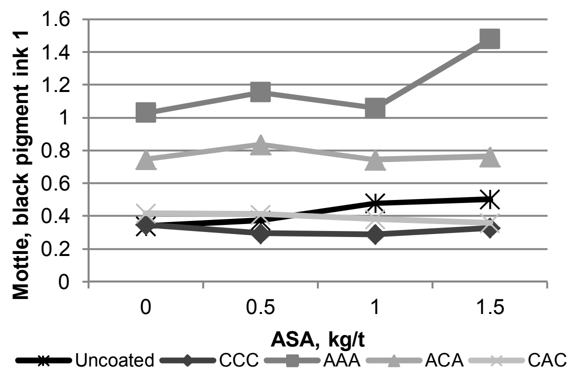

Figure 4. *Mottling values for the black 100% tone pigment ink 1 (100%).*

Figure 5 shows the results from wicking tests determined for pigment ink 1 on the multilayer surface treated substrates. The wicking behavior decrease significantly for the AAA sample when the amount of ASA increases. Moreover, low wicking values is particularly seen for cationic samples (CCC, CAC) at high level of internal sizing. The bleeding behavior determined for the samples (not shown here) showed only minor differences between multilayer-surface-treated surfaces and a trend that raggedness decreased with increased level of internal sizing.

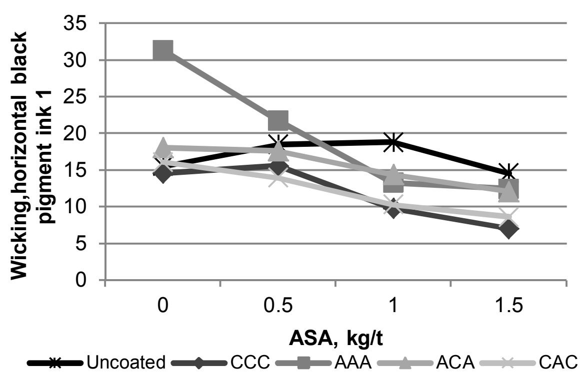

Figure 5. *Wicking values for the black pigment ink 1 lines printed on multilayer treated paper surface.*

Effect of thin polyelectrolyte layers on water fastness

Water fastness of the different inks was determined on the substrates having different levels of internal sizing and different multilayer surface treatments. The water fastness of the pigment ink 1 was almost 100% on the multilayer-surface-treated samples regardless of the level of internal sizing. For the sample with the anionic coating, AAA, the water fastness value decreased from 72% to 10% when the amount of internal sizing was increased.

Results for pigment ink 2 are shown in Figure 6. On the AAA surface, the water fastness decreased significantly with an increasing amount of ASA in the base paper, but for the samples have a cationic polymers CCC surface the water fastness value was 100% even with no internal sizing. When the ASA amount was increased, the water fastness value increased from 100 % to 130 % in the CCC surface indicating that the cationic surface together with ASA creates a surface where ink pigment particles become more visible when immersed in water. For the samples containing CAC or ACA, no significant effect of the level of internal sizing was seen.

Figure 7 shows the result for the dye ink 1. In this case, the water fastness was better for the ACA sample than for the CAC surface treatment. It is known that the substrate does not influence the absorption of liquid after deposition of the first few layers, after which the charge balance between the polyelectrolytes dominates the polyelectrolyte multilayer formation [15]. It is possible, in our case, that the ACA surface promotes fast ink absorption and captures the colorant within the structure.

It was also observed that the water fastness for dye ink 1 on the CAC-treated surface was higher than that on the CCC surface, which further suggests that the water fastness is strongly dependent on the ink composition. The influence of the amount of ASA was most evident for the base paper and the multilayer-surface-treated paper with AAA. The water fastness value decreased from 33% to 17% when the ASA amount was increased from 0 to 1.5 kg/t.

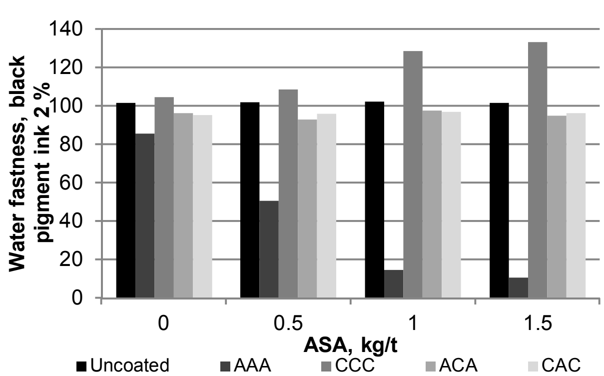

Figure 6. *Water fastness values for pigment ink 2.*

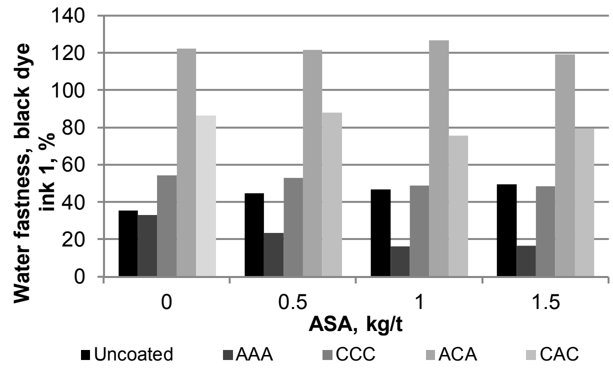

Figure 7. *Water fastness values for dye ink 1.*

Conclusions

The results showed that the spreading and absorption behavior of inkjet inks on substrates can be adjusted by polyelectrolyte multilayer treatment on the surfaces on papers with different levels of internal sizing of the base paper. The multilayer treatment increased the contact angle of water, especially for CCC and ACA surface-treated samples.

Multilayer treatment with CCC and CAC increased the print quality, i.e. a higher density level was achieved than on the uncoated base paper. The print density was increased by up to 25 % especially for the pigmented inks by appropriate adjustment of the cationic and anionic polyelectrolyte layering.

A substantial difference in the water fastness of the print was seen, suggesting that multilayer treatment can capture colorants and lead to durable prints despite the low coat weights.

Finally, the multilayer surface treatment of substrates with different hydrophobicities further reveals significant differences between the inks, suggesting that the method can be used to study ink-substrate interactions.

References

[1] Hamada, H., Bousfield. D. W., Effect of cationic additives on ink penetration. Journal of Pulp and Paper Science 35.3-4 (2009): 118-122.

[2] Storbeck, W., Dietrich D., Schneider, R., Fixation of Pigmented Black Ink on Matte Coated Inkjet Substrates. NIP25 & Digital Fabrication Conference. Vol. 2005. No. 1. Society for Imaging Science and Technology, Louisville, Kentucky USA. 2005

[3] Donigian, D., W., Wernett, P., C., McFadden, M., G., McKay, J., J. Inkjet dye fixation and coating pigments. Tappi Journal 82.8 (1999) 175-182.

[4] Ryu, R. Y., Gilbert, R. D., Khan, S. A., Influence of cationic additives on the rheological, optical, and printing properties of inkjet coatings. Tappi journal 82.11 (1999): 128-134.

[5] Vikman, K., Vuorinen, T., Water fastness of ink jet prints on modified conventional coatings. Journal of Imaging Science and Technology 48.2 (2004): 138-147.

[6] Khoultchaev, K., Graczyk T. Influence of PolymerPolymer Interactions on Properties of Ink Jet Coatings. Journal of imaging science and technology 45.1 (2001): 16-23.

[7] Lee, H. K., Joyce, M. K., Fleming, P. D. Influence of pigment particle size and pigment ratio on printability of glossy ink jet

 ©2014 Society for Imaging Science and Technology

paper coatings. Journal of imaging science and technology, 49(1), (2005). 54-60.

[8] Hossain Z. Luckham, R. Smith, A., Lebert,J. Davies,L. Pelton, R. Filipe, C. Brennan J. Development of a bioactive paper sensor for detection of neurotoxins using piezoelectric inkjet printing of sol−gel-derived bioinks. Analytical chemistry 81.13 (2009): 5474-5483.

[9] Shaw-Klein, L. Effects of mordant type and placement on inkjet receiver performance. IS&T's NIP14: International Conference on Digital Printing Technologies. Toronto, Canada. IS&T, USA, (1998): pp. 129-132.

[10] Nilsson, H., Fogden A. Inkjet print quality on model paper coatings. Appita Journal: Journal of the Technical Association of the Australian and New Zealand Pulp and Paper Industry 61.2 (2008): 120.

[11] Pal, L., Agate, S., & Fleming, P. D. Effects of paper manufacturing factors on inkjet print quality and lightfastness. In NIP & Digital Fabrication Conference, Vol. 2007, No. 2, pp. 749-754). Society for Imaging Science and Technology. (2007).

[12] Lundberg, A., Örtegren, J., Alfthan, E., & Ström, G. Microscale droplet absorption into paper for inkjet printing. Nordic Pulp Paper Res. J 26.1 (2011): 142-150.

[13] Lefebvre, J., Gray, D. G., AFM of adsorbed polyelectrolytes on cellulose I surfaces spin-coated on silicon wafers. Cellulose 12.2 (2005): 127-134.

[14] Rahman, L. Factors affecting the performance of inkjet papers. Proceedings from Spring Technical Conference & Trade Fair, Chicago, IL, USA (2003).

[15] Hoogeveen, N. G., Cohen Stuart, M. A., Fleer, G. J., & Böhmer, M. R. Formation and stability of multilayers of polyelectrolytes. Langmuir, 12(15), 3675-3681 (1996).

Biography

Katriina Mielonen, M. Sc., is a post-graduate student and a member of the Packaging Technology research group of the Lappeenranta University of Technology, Faculty of Technology, Department of Mechanical Engineering. The focus of her research is on inkjet printing, surface treatment and printing in packaging technology. Earlier she has worked with fiber-based health care and nursing products and has been project manager of a research project related to biorefineries.