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Inkjet ink spreading on polyelectrolyte multilayers deposited on pigment coated paper

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ABSTRACT

Mechanisms of inkjet ink spreading and absorption on a coated paper have been studied using a polyelectrolyte multilayering technique. By applying alternating sequences of cationic and anionic polyelectrolyte layers on a mineral coated paper, the role of the interfacial chemistry was evaluated. The polyelectrolyte multilayer was created to imitate a thin resin-like liquid-absorptive layer and to clarify the role of the charge of the protruding polyelectrolyte layer on ink spreading and colorant fixation. The formation of a thin polyelectrolyte layer and coating coverage was confirmed by X-ray photoelectron spectroscopy (XPS). A submolecular mechanical imaging of the polyelectrolyte complexes with an atomic force microscope (AFM) revealed differences in modulus and different nanosize agglomerates were identified which were ascribed to polyion complexes. The polyelectrolyte coatings significantly affect the solid–liquid interaction and particularly the ink spreading revealed as intercolor bleeding and wicking. The interfacial interaction between the ink and the applied polyelectrolyte layers showed differences between dye- and pigment-based colorants, which could be emphasized by the polyelectrolyte chemistry.

1. Introduction

Water-based inkjet inks usually have a very low viscosity, low surface tension, an anionic character, and they are therefore not usually suitable for standard commodity grade coated glossy offset paper. The dense surface and the anionic character of the coated paper provide few sites for specific interactions with inkjet colorants, but by incorporating microporous or nanostructured coatings or cationic additives, it is possible to retain the colorants on the surface and to fix dye-based colorants with cationic mordants [1,2]. Water-based ink jet inks with pigment-based colorants, on the other hand, can be coagulated with salts through precipitation mechanisms [3–6], although the lack of a polymeric binder may cause problems with regard to print durability. The preferential route to ensure fast ink carrier absorption by incorporating microporosity might give problems with e.g. print gloss. Resin-based coatings for inkjet-based dye inks provide glossy prints, but pose challenges with their slow drying. However, by making double or multilayer coatings with porous pigments, the absorption rate and liquid absorption capacity can be improved and adjusted, thus solving the problem of slow drying speeds, although the gloss and ink adhesion may be a problem. Thus, the substrates for high quality inkjet inks usually contain thick layers of either porous pigments or resin-based coatings, possessing both advantages and disadvantages. The role of interfacial chemistry of paper with thin coating layers (1–5 μm) on the inkjet ink interaction in high-speed inkjet printing is still a relatively unexplored area.

Surface treatment such as surface sizing, surface pigmentation, coating or priming is an important way of improving paper print quality. Surface sizes based on starch and additives [7] have been studied as well as the use of nanopigment-based formulations [8], styrene maleic anhydride SMA [9,10], polyvinyl alcohol PVOH [11,12], high-porosity pigments with a large specific surface [13–15], polydiallyldimethylammonium chloride (PDADMAC) [16], modified starch [17], and precipitated calcium carbonate (PCC) [18,19]. Nilsson and Fogden [20] used carboxymethylcellulose (CMC) as a binder in pigment coating to study the effect on inkjet print quality using both dye-based and pigment inks and showed that hydrophilic binders favor e.g. optical density. Lamminmäki et al. [21], on the other hand, used PDADMAC to produce cationicity when studying the effect of surface charge on the ink penetration and the resulting print quality, and they showed that reduced bleeding and improved water fastness could be achieved when

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cationic additives were used in pigment coating on a paper substrate. The application of a cationic additive specifically to the coating layer surface retarded the ink penetration into the paper structure, by reducing coating layer permeability and by bonding the anionic colorant at the top layer via electrostatic charge interaction [21]. Rahman [22] used cationic polymers together with silica particles to improve the paper surface properties and found e.g. improved water fastness which was attributed to a specific interaction between the colorants and a receptive layer of the paper, an observation similar to that obtained with PDADMAC and PCC by Sreekumar et al. [23,24].

Different micrometer size silica-particles thus provide a combination of high porosity micropores and high surface area, which give rapid ink drying and dye fixation. The pigment-based inks form a pigment-rich layer on the silica coating surface, whereas dye-based inks penetrate into the pores of the silica pigments [25]. Lamminmäki et al. [26] studied porous olivine-silicate based mineral pigments as coating pigments for matt inkjet papers. The coatings containing the experimentally produced silica gave print density, print-through, print gloss and bleeding results very similar to those obtained with the commercial silica grade.

Vikman and Vuorinen [27] showed the role of cationic PVA-PDADMAC binders and weakly cationic modified styrene-acrylate latex-starch binders in pigment coatings on print quality and particularly on water fastness. The interfacial adhesion between ink and coating will be more critical when the image is in physical contact in the presence of water or condensed moisture [28–30], and this emphasizes the role of the interactions. Yu et al. [31] used a porous χ-Al_2O_3, one of the transition phases of alumina, which has a high porosity, high specific surface area, and positive surface charges, as a pigment in the coating. A high dye-fixing ability was obtained, which was obviously due to the cationic character of the pigment and its porosity.

It is known that the water fastness of pigment-based inks is better that that of dye based inks because of their crystalline structure [32], although their dry adhesion is lower [33]. The cationic nature of the coating or pigmented surface of an inkjet paper leads to charge neutralization between the surface and the anionic dyes. This gives the print water fastness properties and it may also enhance optical density and print quality, making it particularly suitable for color printing [34].

Different pigment coating formulations, coating additives, and surface sizing based on anionic and cationic chemicals have been observed to affect the printability and the properties of the printed paper. However, to our knowledge, the role of micrometer-thin anionic–cationic layered polyelectrolyte coatings on inkjet printability of uncoated or coated papers has not been studied. Lefebvre and Gray [35] studied the properties of multilayers consisting of anionic CMC and cationic PDADMAC prepared by immersing the samples to give a nanocrystalline cellulose surface and showed that these polymers can undergo complex formation and thus reveal a localized gel-like behavior, i.e. when the salt concentration is increased to 10 mM. The 5 bilayer sample swelled more than the 3- and 1-multilayer samples. This suggests that such polyelectrolyte ion complexation could offer a route to new types of coating to control the dissolution of the coating as well as a more efficient fixation of the colorant in the water-swollen 3D structure of the polyelectrolyte multilayer. The binder should not only act as a fixative for the colorant but might also be designed to control the liquid phase absorption and chromatographic separation of colorants, which in turn affect the drying rate and print quality. [36].

The purpose of the present work is to clarify whether the physico-chemical character of the mineral coating layer could be adjusted by applying a micrometer-thin polyelectrolyte multilayer. The deposited layers were characterized by contact angle, atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) in order to determine the macroscopic and microscopic features in the surface. The polyelectrolyte multilayers were studied and utilized to reveal new insight into the mechanism of ink absorption and spreading. The commercial paper was surface treated in a size press with intermediate drying using cationic and anionic polyelectrolytes, before being characterized and printed. The samples were printed on various desktop printers equipped with water-based dye and nanopigment colorants.

2. Materials and methods

A one-side, glossy pigment-coated flexible packaging paper for rotogravure, flexographic or offset paper (LumiFlex 90 g/m^2, Stora Enso Oyj) was surface treated using a size press applicator operating at a speed of 100 m/min. The surface-treated web was dried on-line with contact (cylinder) drying before the next polymer layer was applied. The chemicals applied to the paper surface were anionic sodium carboxymethylcellulose (NaCMC, Finnfix 30, CP Kelco) and cationic polydiallyldimethylammonium chloride (PDADMAC, Catiofast BP, BASF GmbH). The NaCMC had a molar mass of approximately 80 000 g/mol and a D.S. of ca 0.8 according to the supplier. The NaCMC was dissolved in tap water to a solids content of 2.9 wt%. The PDADMAC had a molar mass of 200,000–300,000 g/mol and a charge density of 6.0 meq/g according to the supplier. The solution was diluted in tap water to a solids content of 14.7 wt%. The Brookfield viscosity (100 rpm, spindle number 5) of the PDADMAC was 48 cP and of the NaCMC 136 cP, the pH of the PDADMAC solution was 6.7 and of the NaCMC solution 6.8.

2.1. Physical testing

Physical properties of the papers were determined at 23 ± 1 °C and 50 ± 2% relative humidity. Bendtsen roughness was measured with Lorentzen & Wettre Bendtsen tester (ISO 8791-2) and Parker Print Surf (PPS) roughness with Messmer instrument LTD tester (ISO 8791-4), grammage (ISO 536) and polyelectrolyte multilayer coat weight were determined for the samples. The moisture content was determined according to ISO 287.

2.2. Atomic force microscope (AFM) and scanning electron microscope (SEM) imaging

The nano-scale topography and mechanical properties of the multilayer-treated papers were measured using an atomic force microscope (Bruker Multimode 8 Scanning Probe Microscope). All images were captured in the PeakForce QNM mode at a spring constant of $k = 5$ N/m using probes with a tip radius <8 nm. All AFM tests were carried out under ambient conditions (25 ± 3 °C, 40 ± 10% RH). The resolution of the images was typically 512 × 512 pixels and the scanning rate was 0.3 Hz. Roughness values were calculated as root mean square (RMS) values for areas of 2 × 2 μm^2. Changes in structure of the surface visible to the naked eye were confirmed in an optical microscope and further surface morphology measurements were carried out with nano-scale resolution.

Microscope images of the samples were captured using a high resolution scanning electron microscope (HR-SEM) microscope with a 7.0 kV accelerating voltage and a 11.9 mm working distance. Digital microscope images were taken from the Leica DFC450 microscope with an Olympus SZX9-camera.

2.3. X-ray photoelectron spectroscopy (XPS)

The chemical compositions of the surfaces by the polyelectrolyte multilayering method were evaluated by X-ray Photoelectron Spectroscopy, XPS, using a state-of-the-art electron spectrometer