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Investigating chromatographic interactions in porous pigment coatings between inkjettable polyelectrolytes and model colorant solutions

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Abstract

Printed, self-contained sensor designs based on capillary transport and microfluidic principles form a major part of current research in printed functionality. Previous work into such designs has mainly focused on cellulosic papers as base substrates. In this study, novel findings are presented employing alternative custom-designed functional pigment coated substrates, locally functionalised by inkjet printed polyelectrolytes, to separate or transport anionic or cationic molecules by surface chemistry tailoring. Both anionised and cationised coatings are tested and found to transport similarly charged model colorants successfully, while separating those of opposite charge, with the extent of separation depending on colorant concentration. Furthermore, surface chemistry reversal by cationic (polyethyleneimine, polyDADMAC) and anionic (carboxymethyl cellulose) polyelectrolyte inks is demonstrated as a complementary method for analyte separation or concentration. However, the deposition of the polyelectrolyte ink itself was found to affect the cationised coating by solubilising and re-depositing coating components, while the printed polyethyleneimine was found to be partially dissolved and transported by water elution, suggesting limited adsorption under tested conditions.

Keywords: polyelectrolyte, inkjet printing, functional printing, functional coating, chromatographic separation

Abbreviations

CMC	Carboxymethyl cellulose
FCC	Functionalised calcium carbonate
FTIR	Fourier transform infra-red (spectroscopy)
MFC	Microfibrillated cellulose
NaPA	Sodium polyacrylate
PEI	Polyethyleneimine
PolyDADMAC	Poly-diallyl dimethyl ammonium chloride
PVOH	Polyvinyl alcohol

1. Introduction

During the past decade, academic researchers have been developing designs for simple, portable and self-contained assays especially for medical and environmental applications by combining porous materials and microfluidic concepts. Examples of such demonstrated concepts include colorimetric detection of Influenza A from lysed samples [1], fluorescence-based detection of HIV infection from blood plasma [2] and glucose level measurement from tear samples [3].

Self-contained devices, without external pumping, can be designed from porous and permeable substrates transporting liquid by capillary action. So far, the most commonly tested substrates have been cellulosic chromatography and filter papers, resulting in development of paper-based microfluidics or paperfluidics. However, similar principles can be applied to other planar, porous and permeable materials, the study of which the present authors call, more generally, sorption fluidics, covering the fields of liquid wicking and chemical species ab- and adsorption.

By employing porous approximately spherical pigment particles, microscale permeable strongly wicking structures with adjustable surface chemistries can be produced. So far, studies with such coatings in the field of species sorption have been few, and commercial paper pigment coating formulations comprising standard non-porous particles and latex and/or starch binders do not provide sufficient capillary transport of liquids, especially aqueous solutions. Therefore, the authors have been working on highly absorbing custom-designed speciality pigment coatings, with previous published studies covering coating design [4], hydrophobic patterning [5, 6] and application of coatings as enzyme test platforms [7]. In parallel, other researchers have demonstrated a non-absorbing TiO_2 nanoparticle coating for surface-spreading microfluidic applications by forming a hydrophobic coating which can be selectively patterned to become hydrophilic by surface UV-treatment [8]. Such patterned coating can be further combined with a hydrophobic film, providing capillary transport in the narrow gap, track-limited by the coating and the film, but accelerated by the combination of the hydrophobic film cover material and the hydrophilised substrate [9].

In the present study, the authors expand their previous work on model analyte separation on coatings [10], based on charge interactions between pore surfaces and sample molecules in dilute solution transported by capillary action inside thin pigment coating, with the coating component surface charges locally modified by inkjet printed polyelectrolytes. While it is known that external electrical fields can be employed for molecular charge-based separation in porous media, as demonstrated on both 2D [11] and 3D [12, 13] channel designs on filter paper, this requires external instrumentation. In contrast, pore surface chemistry modification provides an integrated, equipment-free separation mechanism for charged molecules. The previous demonstration of this principle [10], however, highlighted two shortcomings that are addressed in this work. Firstly, while separation of anionic model colorants by printed polyelectrolytes could be demonstrated, separation of cationic colorants by printed anionic polyelectrolyte could not be effectively studied due to the anionic nature of the coating itself arresting the colorants. Secondly, the two tested polyelectrolyte inks were limited by either unreliable jetability or limited solubility.

Previous test coatings consisted of functionalised calcium carbonate (FCC) pigment, containing mainly zwitterionic hydroxylapatite at the pigment particle surface, and micro-fibrillated cellulose (MFC) as binder, having an anionic nature due to surface carboxylic groups. Polyelectrolytes tested in the previous work included anionic industrial sodium polyacrylate (NaPA), with limited solubility in the water-ethanol solvent mixture employed as ink carrier liquid, and cationic poly-diallyl dimethyl ammonium chloride (polyDADMAC), with unstable jetting possibly due to high molecular weight. The viscoelastic effects of long polymer chains are generally considered to limit jetting of dissolved high molecular weight polymers, though due to their charged and self-repelling nature polyelectrolytes may be expected to have less coiled and more rod-like character in solution.

To study both anionic and cationic model colorants in more detail, coating formulations have newly been designed to provide two different surface chemistries. An anionised coating was formulated by inclusion of anionic polyelectrolyte additive directly in the coating slurry, while a cationised coating was obtained by employing polyvinyl alcohol (PVOH) as binder combined with a cationic polyelectrolyte additive. When coming into contact with a zwitterionic FCC surface, featuring both anionic and cationic surface sites, polyelectrolyte additives are expected to adsorb primarily on oppositely charged regions, thus resulting in charge reversal. When a solution of charged molecules travels through the surface-modified coating pores,

analytes of opposite charge are expected to separate from the solution while similarly charged analytes are freely transported. Subsequent inkjet deposition of polyelectrolyte onto these coatings, having prior uniform charge, enables modification of the local charge.

The inkjet-deposited polyelectrolytes in this study include polyethyleneimine (PEI), carboxymethyl cellulose (CMC) and low molecular weight poly-diallyl dimethyl ammonium chloride (polyDADMAC). Various versions of these polymers have been employed in earlier inkjet-related studies, with CMC employed as a rheological modifier for horseradish peroxide inks at concentrations of up to 1 w/w% [14], and as a dispersant in conductive graphene ink [15]. Inkjet-deposited PEI patterns have been applied for directing growth of chicken cortical neurons on plastic films [16], as well as to change surface chemistry of cross-linked albumin films to allow for local adhesion of proteins and cells [17]. PolyDADMAC-containing ink has been employed as a component of a polyelectrolyte multilayer structure for antibiotic-releasing wound dressings [18], while polyDADMAC combined with PVOH has been inkjet deposited to pattern charged mosaic membranes [19].

In separation studies, hydroxylapatite particles coated with polyethyleneimine have been investigated with proteins in liquid column chromatography, with the amount of PEI on surface found to have an effect on the retention times [20]. When such particles were eluted with various liquids, the PEI-coating was found to remain stable in sodium phosphate buffer solutions (pH 5 and 8) and acetonitrile, while 0.1 M NaOH elution partially removed the PEI coating [21].

In this work, the authors intent also is to study whether the inkjet-deposited polyelectrolytes can now be made to remain fixed on the pre charge-formulated coatings upon re-wetting during elution, instead of re-dissolving and transporting with eluting liquid. This is of practical interest for application design, since any such transported polyelectrolyte may affect reactions or detection downstream.

2. Materials and methods

2.1 Pigment coatings

Prepared coating slurries were

- i. anionised: 100 parts FCC pigment, 10 parts micro-fibrillated cellulose Arbocel MF-40-7 (J. Rettenmaier & Söhne GmbH + Co KG, Rosenberg, Germany) binder and 1 part anionic sodium polyacrylate of 8 kDa M_w (Sigma-Aldrich, St. Louis, USA, product code 416029, supplied in aqueous solution with nominal 45 w/w% and measured 41.0 ± 0.3 w/w% solid content), the whole prepared to form a slurry by dilution with de-ionised water to 15.15 w/w% solids content, and
- ii. cationised: 100 parts FCC pigment, 10 parts polyvinyl alcohol BF05 (Omya International AG, Oftringen, Switzerland) binder and 1 part cationic polyDADMAC (poly-diallyl dimethyl ammonium chloride) of < 100 kDa M_w (Sigma-Aldrich, St. Louis, USA, product code 522376, supplied in aqueous solution with nominal 35 w/w% and measured 35.8 ± 0.4 w/w% solid content and nominal pH 5-8), the whole prepared to form a slurry by dilution with de-ionised water to 15.99 w/w% solids content,

where *parts* refers to dry weight content. The experimental FCC pigment (Omya International AG, Oftringen, Switzerland) consists of 85 w/w% hydroxylapatite and 15 w/w% calcium carbonate, while featuring a high specific surface area of $110 \text{ m}^2 \text{ g}^{-1}$ due to the fine porous surface structure illustrated in Fig. 1. In terms of nominal pigment surface coverage, the formulations contain 0.91 mg m^{-2} of binder and 0.09 mg m^{-2} of polyelectrolyte additive.

Figure 1. FCC pigment surfaces imaged by scanning electron microscopy.

Slurries were applied with a wire-wound rod drawdown K202 Control Coater (RK PrintCoat Instruments Ltd., Herts, UK) on pigmented SuperYupo (Yupo Corporation, Tokyo, Japan) polypropylene sheets, of nominal 80 μm thickness and 62 g m^{-2} basis weight, with a rod applying 60 μm wet layer, and aluminium foil, with rods applying 60, 400 and 500 μm wet layers. Unless otherwise specified, experiments described in this work were with coated polypropylene sheets. Coating samples were dried overnight at room temperature, with excess slurry dried in Petri dishes.

2.2 Coating analysis

Specific pore volumes and pore size distributions were measured with an Autopore IV porosimeter (Micromeritics, Norcross, USA) from the aluminium foil coated samples applied with the 60 μm rod, a single sample being tested per coating. Specific surface areas were measured with TriStar 3000 and TriStar II 3020 instruments (Micromeritics, Norcross, USA) from 400 μm rod-coated aluminium foil samples and from slurry dried in Petri dishes, one sample in each case measured per instrument. Coating thickness was measured with an SE250D micrometer (Lorentzen & Wettre, Kista, Sweden) from ten samples.

2.3 Ink preparation

The hydrophobising ink consisted of 10 w/w% alkyl ketene dimer (AKD) Basoplast 88 (BASF, Ludwigshafen, Germany) hydrophobising agent and 0.1 w/w% yellow dye wood stain colorant 157

(Kremer Pigmente GmbH & Co. KG, Aichstetten, Germany, product number 94010) dissolved in p-xylene solvent, and will be referred to as AKD ink.

Polyelectrolyte inks contained

- i. commercial 8.5 kDa M_w polyDADMAC (Polysciences, Inc., Warrington, USA, product code 24828-100) supplied as an aqueous solution with 28 w/w% nominal and 27.4 ± 0.4 w/w% measured solid content and nominal pH 2.0, or
- ii. commercial 2 kDa M_w branched polyethyleneimine (PEI) (Sigma-Aldrich, St. Louis, USA, product code 408700) supplied as an aqueous solution with 50 w/w% nominal and 55.2 ± 2.6 w/w% measured solid content, or
- iii. experimental sodium-neutralised 16.5 kDa M_w carboxymethyl cellulose (CMC), supplied as an aqueous solution with 25.7 ± 1.2 w/w% measured solids content,

with the respective inks referred to as polyDADMAC, PEI and CMC inks. The formulations consisted of polyelectrolyte (1 w/w% for polyDADMAC and PEI, 0.8 w/w% for CMC), ethanol (25 w/w%) and de-ionised water. Reference solvent-only ink, referred to as WE ink, comprised 75 w/w% de-ionised water and 25 w/w% ethanol.

For reducing surface tension, volatile organic solvent is preferable to surfactants especially on devices involving hydrophobic barriers, since the surfactants remain on the substrate and on re-wetting can re-dissolve, adsorb on hydrophobic barriers and cause permanent leaks [5]. However, such surfactant behaviour can be utilised to advantage as a valve-opening mechanism [22]. Organic solvent may, in turn, reduce the solubility of polyelectrolytes compared to pure water. Thus, to test solubility at a higher concentration, additional solutions consisting of polyelectrolyte (5 w/w% for polyDADMAC and PEI, 4 w/w% for CMC), 25 w/w% ethanol and de-ionised water were also prepared.

2.4 Ink analysis and printing

Surface tension was measured with a CAM200 instrument (KSV Instruments, Helsinki, Finland) employing LH-L790200 low retention pipette tips (Sartorius Biohit Liquid Handling Oy, Helsinki, Finland) at 21 °C. Ten nominally 6 μ l pendant drops were each measured ten times at 1 s intervals.

Polyelectrolyte and WE ink viscosities were measured with an MCR 302 rheometer (Anton Paar, Graz, Austria) employing DG 26.7 double-gap geometry held in a Peltier temperature-controlled C-PTD200 cup holder set at 30 °C and covered with a CV-CYL/Q disc limiting evaporation. Measurement consisted of a 60 s pre-shear at 100 s^{-1} , followed by shear ramps from 1 up to 20 s^{-1} at 1 s^{-1} shear rate intervals, and from 20 up to 2000 s^{-1} at 20 s^{-1} shear rate intervals, with 10 s measurement time per interval. Three filtered samples were measured (four for the CMC ink).

AKD ink viscosity was measured with the same rheometer, employing a cone and plate geometry CP50-1 and P-PTD200 Peltier-plate set at 30 °C covered with an H-PTD200/GL hood. Measurement consisted of a shear ramp from 20 rising to 500 s^{-1} at 20 s^{-1} shear rate intervals, with 10 s measurement time per interval. Three filtered samples were measured.

Inks were printed with a DMP-2831 inkjet printer (Fujifilm Dimatix, Santa Clara, USA) with DMC-11610 cartridges, having 16 nozzles, each providing 10 pl nominal drop volume. The printhead and mounting platen temperature was set at 30 °C. The inks were filtered through 0.45 μ m GHP Acrodisc GF syringe filters (Pall Corporation, Port Washington, USA) during cartridge filling.

After printing with AKD ink, substrates were heat-treated in a 105 °C oven for 10 min to promote AKD reaction with the coating. Polyelectrolyte inks were then printed, with the patterns adjusted to compensate for the lateral 0.77 ± 0.03 % shrinkage of the polypropylene sheets during heating (determined separately from uncoated samples).

Ink jetting reliability was tested by printing a 280 x 200 mm² chessboard pattern of 5 x 5 mm² squares. After 30 min, printing was interrupted, the printhead inspected and the number of non-jetting nozzles recorded. This test was repeated 10 times, with the non-jetting nozzles recovered into jetting between repeat rounds if possible.

Inkjet-deposited average drop mass was measured by jetting 20 million (AKD ink) or 50 million (polyelectrolyte inks) drops into each of 5 pre-weighed aluminium dishes, drying at 105 °C for 30 min and re-weighing to determine deposited dry solids.

2.5 Scanning and image analysis

When required, samples were scanned with an Epson Expression 1680 flatbed scanner (Seiko Epson Corporation, Nagano, Japan) at 1 200 dpi resolution, and the scans evaluated by image analysis conducted with ImageJ software version 1.51 (National Institutes of Health, Bethesda, USA).

2.6 Printed test patterns

Three patterns were employed to characterise (I) hydrophobisation by AKD ink, (II) chromatographic species-retardation (expressed as retardation factor R_F , the ratio between distances travelled by the colorant and water fronts), and (III) transport of printed polyelectrolytes, with examples shown in Fig. 2.

Figure 2. Schematic examples of printed samples including (a) pattern I rings deposited at drop spacing values of 15 (top), 20 (middle) and 25 μ m (bottom) with ferriin solution applied in the centre, (b) similar patterns with ferriin solution applied at the centre and around, (c) pattern II and (d) pattern III on anionised coating, and (e) a schematic of pattern II channels eluted with colorant solution. Yellow indicates hydrophobic barriers, red ferriin solution, and black-outlined rectangles nominal printed polyelectrolyte areas, with the number of ink layers shown at the foot of each channel (e.g. “x1”).

Pattern I, described in earlier work [5], consisted of rings (nominal inner diameter 5 mm, outer diameter 9 mm) printed at various drop spacing settings (10, 15, 20, 25, 30 and 50 μ m) with AKD ink. Hydrophobisation was tested by applying 10 μ l drops of 1 w/w % ferriin solution into the ring interiors, and after drying evaluating possible barrier leakage visually. Pattern spreading was analysed by applying 1.7 w/w% ferriin solution additionally around the rings, with dry samples scanned and ring area measured by image analysis.

Patterns II and III combined hydrophobising and polyelectrolyte inks. Pattern II, for quantifying the R_F , consisted of 10 nominally $3.9 \times 50.0 \text{ mm}^2$ channels, separated by nominally 1.0 mm wide hydrophobic barriers, forming an overall area of $50 \times 52 \text{ mm}^2$. The 10 channels divide as: 1 unprinted control (x0), 3 containing CMC regions of 1, 2 and 3 ink layers, another 3 containing printed polyDADMAC regions (also of 1, 2 and 3 ink layers), and a final 3 containing printed PEI regions (also of 1, 2 and 3 ink layers). The printed polyelectrolyte regions measured nominally $3.9 \times 46 \text{ mm}^2$, starting 4 mm from the beginning of the channel.

Pattern III, for characterising polyelectrolyte transport, consisted of 4 nominally $6.75 \times 50.0 \text{ mm}^2$ channels, separated by nominally 1.0 mm wide hydrophobic barriers, forming an overall area of $32 \times 52 \text{ mm}^2$, the first channel being the unprinted control (x0) while the other channels had printed nominally $6.75 \times 7.0 \text{ mm}^2$ polyelectrolyte areas located 10 mm from the beginning of the channel, deposited with 1, 2 and 3 layers of same polyelectrolyte ink.

2.7 Model colorant solutions

Analytes were simulated by three model colorants, anionic tartrazine (Kremer Pigmente GmbH & Co. KG, Aichstetten, Germany, product number 94175), cationic safranin O (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany, product code B21674) and slightly cationic ferroin (Merck KGaA, Darmstadt, Germany, product code 1.09193.0100), prepared with de-ionised water into nominally 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 w/w% solutions.

2.8 Charge density measurements

Polyelectrolyte and colorant charge densities were measured with a PCD 03 particle charge detector (Mütek Analytic GmbH, Herrsching, Germany) by titrating against cationic polyDADMAC or anionic polyethylene sodium sulphate solution. At least three measurements were conducted per sample.

2.9 Wicking and retardation tests

Water wicking was measured on coated sheets, cut into $5 \times 50 \text{ mm}^2$ strips and attached with double-sided tape to glass slides, by placing each sample vertically in a closed plastic jar such that its end was immersed in de-ionised water filled to approximately 4 mm at the bottom. After 5 min the sample was removed from the jar and the distance travelled by the water front measured. Tests were conducted in a room held at $21 \pm 1 \text{ }^\circ\text{C}$. Three parallel samples were tested, with initial test carried out shortly after the coatings were prepared and repeated approximately 20 months later.

Retardation of colorant transport was measured similarly by placing a pattern II sample vertically in a closed plastic jar containing approximately 4 mm of colorant solution, illustrated schematically in Fig. 2(e). After water had travelled the full length of all channels, the sample was removed from the jar, allowed to dry and scanned, with images analysed to determine R_F for the channels. Tests were conducted at concentrations from 0.01 to 0.5 w/w% for tartrazine and safranin O, and from 0.1 to 0.5 w/w% for ferroin, with three samples per concentration. Additionally, for 10 samples per coating the times required to fill individual channels were recorded with precision of 15 s. The colorant tests were conducted at $20 \pm 1 \text{ }^\circ\text{C}$.

2.10 Polyelectrolyte transport tests

Potential water elution transport of printed polyelectrolytes was investigated with Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and ninhydrin indicator colour. Tests were conducted

with pattern III samples eluted upright in closed plastic jars, as described previously, having approximately 4 mm of distilled or de-ionised water in the bottom, until channels had filled full-length, and then dried overnight at room temperature.

FTIR analysis was conducted with a Spectrum One (PerkinElmer, Waltham, USA) spectrometer and Raman analysis with a confocal Raman microscope system Alpha 300 RA (WITec, Ulm, Germany) adopting a 532 nm excitation laser. Coating components and polyelectrolytes, dried at room temperature (Raman) or oven-dried (FTIR), respectively, were measured individually, followed by the coatings and polyelectrolyte regions from non-eluted samples, and finally spots approximately 5 mm from the top of the eluted channels. With FTIR a single spot was measured once, while with Raman 3 different spots were measured 3 times.

Ninhydrin solution (2 w/w% in methanol and sodium acetate buffer) was applied with a Preval Sprayer (Nakoma Products, Coal City, United States) on vertically-held samples, scanned after drying. Ninhydrin is light yellow, turning dark on reaction with primary or secondary amine groups. PEI contains both of these groups, while other studied materials contain neither.

2.11 Cationised coating solubility testing

Cationised coating, scraped off aluminium foil and ground into fine powder, was prepared into three 1.9 w/w% solids content suspensions by mixing with 25 w/w% aqueous ethanol solution. After 16 h in a tube rotator, the samples were twice centrifuged for 10 min to separate pigment and supernatant. Total dissolved supernatant dry solids content was determined by oven-drying at 105 °C in pre-weighed aluminium dishes. Dissolved polyDADMAC content was determined by charge density measurement.

3. Results and Discussion

3.1 Coating properties

Measured coating properties are listed in Table 1. Thickness and basis weight have been measured from samples coated on polypropylene sheets with 60 µm wet coated thickness, while specific pore volumes have been measured from similar layers coated on aluminium foil. Specific surface area has been measured from coated foil (400 µm wet coated thickness) and bulk dried sample. However, in the case of cationised coating, no representative values could be measured for the bulk sample due to non-uniform distribution of PVOH, following concentration on the top of the thick sample during the slow drying. The specific surface areas of the coatings are lower than those of the native pigment (110 m² g⁻¹), which can be attributed to partial pore filling and/or blocking by the binders and polyelectrolyte additives.

Table 1. Measured coating properties. Values given with 95 % confidence intervals where available.

Coating	Anionised	Cationised
Dry thickness (60 μm wet layer) / μm	34 ± 4	38 ± 5
Dry basis weight (60 μm wet layer) / g m^{-2}	9.5 ± 1.0	10.3 ± 2.0
Specific surface area (foil) / $\text{m}^2 \text{g}^{-1}$	95.0 ± 1.7	83.1 ± 2.0
Specific surface area (bulk) / $\text{m}^2 \text{g}^{-1}$	92.8 ± 1.2	NA
Intra-particle specific pore volume / $\text{cm}^3 \text{g}^{-1}$	0.03	0.03
Inter-particle specific pore volume / $\text{cm}^3 \text{g}^{-1}$	0.37	0.41
Total specific pore volume / $\text{cm}^3 \text{g}^{-1}$	0.40	0.44
d^* / μm	0.75	0.75
d^{**} / μm	9.90	9.90
Porosity (calculated)	0.11 ± 0.02	0.12 ± 0.03
Specific interfacial pore area (calculated) / $\text{m}^2 \text{cm}^{-3}$	240 ± 10	190 ± 10
Wicking distance (in 5 min, original) / mm	42 ± 1	19 ± 1
Wicking distance (in 5 min, after 20 months) / mm	34 ± 3	21 ± 1

In Table 1, specific pore volume is expressed as intra-particle volume (present in the fine pores within pigment particles), inter-particle volume (pores between pigment particles) and total sum of the two. Cut-off pore diameter d^* indicates transition from inter-particle to intra-particle pores, while d^{**} indicates upper pore diameter limit for inter-particle volume. Porosity values have been calculated from dry thickness, dry basis weight and total specific pore volume. Specific interfacial pore area has been calculated as a ratio of specific surface area and total specific pore volume.

In the given time, water wicks significantly farther in the anionised coating compared to the cationised coating. This difference is due to the different binders employed, as could be expected based on earlier work [5], with PVOH likely affecting coating pore connectivity and swelling rapidly by absorbing water into the interpolymer network [23]. However, the transport speed for the anionised coating is affected by aging, as a second measurement done 20 months after the original resulted in reduced fixed time wicking distance compared to the original test. Mechanisms that may have affected the coating, stored in office conditions inside a plastic pocket with limited air circulation and no light exposure, are uncertain but could be related potentially to the aging of the sodium polyacrylate additive in the coating. Various natural aging effects, including changes in solubility and swelling, have been shown to take place in films of commercial acrylic polymer dispersion [24].

Producing an alternative cationised coating by mixing FCC, MFC and polyDADMAC together would not have been feasible, since the cationic polyDADMAC and anionic MFC flocculate when exposed to each other, and similar behaviour would likely take place when mixing another cationic polyelectrolyte with this MFC product. However, as shown later in this work, polyDADMAC can be introduced on the dry coating by printing. The polyvinyl alcohol binder in the cationised coating is non-ionic, and thus unlikely to flocculate in the presence of polyelectrolyte additives.

3.2 Ink properties and jetting

Measured ink properties and selected experimentally determined jetting settings are listed in Table 2, while the designed custom jetting waveforms are described in Table 3. Additionally, for all inks, the meniscus vacuum was set at 4.0 inches H_2O (101.6 mmH_2O or ~ 10 mbar), and cleaning cycles were set to be run at the beginning (“spit spit”), as well as every 600 s or bands during printing (“spit spit”), with none at the end.

The reported viscosity is the mean for measurements from 100 to 1 900 s⁻¹ (20-500 s⁻¹ for AKD ink), over which range the samples showed effectively Newtonian behaviour. At lower shear rates, the measurement reliability for such low viscosity samples is affected by asymmetric loading artefacts [25], while at higher shear rates measurements are likely influenced by secondary flows. These measured polyelectrolyte ink steady shear viscosities are slightly higher than that of the solvent-wise almost identical WE control ink, revealing the effect of the dissolved polymer content.

Table 2. Ink characteristics and jetting settings, with 95 % confidence intervals where appropriate.

Ink	AKD	CMC	PEI	PDADMAC	WE
Density / kg m ⁻³	872 ± 38	965 ± 25	959 ± 7	962 ± 42	NA
Surface tension (at 21 °C) / mN m ⁻¹	29.0 ± 0.7	38.5 ± 1.5	38.6 ± 0.8	38.4 ± 1.4	NA
Viscosity (at 30 °C) / mPa s	0.80 ± 0.03	2.31 ± 0.08	1.85 ± 0.03	2.12 ± 0.10	1.73 ± 0.02
Jetting frequency / kHz	3	6	3	5	6
Jetting voltage / V	17	18	20	20	18
Jetting speed / m s ⁻¹	4.4 ± 0.8	4.8 ± 0.8	6.3 ± 0.8	6.3 ± 1.4	NA
Average drop mass / ng	8.1 ± 0.2	10.3 ± 1.0	6.1 ± 0.5	12.2 ± 0.4	NA
Nozzle jetting loss / %	0	2.5	4.0	0	NA

Nozzle jetting loss in Table 2 indicates the average fraction of nozzles (16 per cartridge) that were observed to be non-jetting at the end of a 30 min test period. In the case of CMC ink, all such nozzles could be easily recovered with the built-in cleaning operations. However, in the case of PEI ink, nozzles that had become non-jetting could not always be recovered. This is somewhat surprising, since the PEI product in question is liquid at room temperature, and thus there should be no risk of nozzle clogging due to drying.

Table 3. Custom waveforms for the inks: level indicates relative displacement of the piezoelectric element within the printhead, slew indicates transition rate between wave segments, and duration indicates total time length of segment.

Ink	Segment	Level / %	Slew	Duration / μs
AKD	Jetting 1	100	0.30	12.096
	Jetting 2	0	0.05	24.192
	Non-jetting 1	13	0.30	12.096
	Non-jetting 2	0	0.05	24.192
CMC and WE	Jetting 1	100	0.35	7.680
	Jetting 2	0	0.10	9.856
	Non-jetting 1	20	0.50	9.024
	Non-jetting 2	0	0.50	8.512
PEI	Jetting 1	100	0.30	7.040
	Jetting 2	0	0.50	4.800
	Non-jetting 1	20	0.30	7.040
	Non-jetting 2	0	0.50	4.800
PDADMAC	Jetting 1	100	0.30	8.000
	Jetting 2	0	0.30	16.000
	Non-jetting 1	13	0.30	8.000
	Non-jetting 2	0	0.30	16.000

The inks jetted in this study contain at most 1 w/w% polyelectrolyte. However, potential for formulations with higher concentrations was tested by solutions containing 5 w/w% polyelectrolyte (4 w/w% in case of CMC) and 25 w/w% ethanol. When these samples were visually observed, CMC was found to be not fully dissolved, while polyDADMAC appeared to be fully dissolved and PEI fully miscible. In future, the authors intend to study the jetting of this polyDADMAC product with higher dry solids content inks.

3.3 Ink and substrate interactions

According to tests conducted with pattern I, i.e. rings printed with hydrophobic ink, the amount of AKD ink required to form reliable hydrophobic barriers on anionised coating was a single layer at 15 μm drop spacing (corresponding to deposited AKD amount of $3.6 \pm 0.7 \text{ g m}^{-2}$) or less, while on the cationised coating a single layer at 25 μm drop spacing (corresponding to deposited AKD amount of $1.3 \pm 0.3 \text{ g m}^{-2}$) or less sufficed. For printing patterns II and III, the highest tested drop spacing value that resulted in reliable hydrophobic barriers was adapted.

Measured areas for the hydrophobic rings at various drop spacing values are presented in Table 4, together with certain ratios calculated based on the printed areas and drop mass, number of drops applied per ring and coating properties. These assume that the observed edge of the hydrophobic pattern on the surface matches the border inside the substrate, as well as the edge of AKD spreading.

Table 4. Ratios between applied AKD and coating in the printed area, with 95 % confidence intervals where available. Volume ratio has been calculated for liquid ink, mass ratio for deposited dry AKD.

Coating	Drop spacing / μm	Nominal ink consumption [†] on printed area / $\text{cm}^3 \text{m}^{-2}$	Hydrophobised region area ^{††} / mm^2	AKD ink to hydrophobised region coating pore volume ratio / v/v	Dry AKD to hydrophobised region coating weight ratio / w/w	Dry AKD per hydrophobised region coating pore surface area / mg m^{-2}
Anionised	10	93 ± 5	64 ± 4	24.1 ± 3.2	0.85 ± 0.11	8.9 ± 1.2
	15	41 ± 3	43 ± 4	10.8 ± 1.6	0.38 ± 0.06	4.0 ± 0.6
Cationised	10	93 ± 5	74 ± 2	17.4 ± 3.6	0.67 ± 0.14	8.1 ± 1.7
	15	41 ± 3	54 ± 3	7.2 ± 1.5	0.28 ± 0.06	3.4 ± 0.7
	20	23 ± 2	45 ± 2	5.0 ± 1.1	0.19 ± 0.04	2.3 ± 0.5
	25	15 ± 1	42 ± 2	3.5 ± 0.8	0.13 ± 0.03	1.6 ± 0.4

[†]Nominal ink consumption for various drop spacing values refers to a nominal pattern area in an ideal case, i.e. no pattern spreading on the substrate, and is included for informational purposes only.

^{††}Hydrophobised region area is the top area of the ring that was not wetted by ferroin solution placed around and inside the printed ring, as seen in Fig. 2(b), thus taking into account the pattern spreading within the coatings. The hydrophobised coating weight was calculated by multiplying the hydrophobised pattern area with the coating basis weight to provide the weight of the native coating in this region, and from this weight the corresponding native pore volume and pore surface area were calculated by multiplying the weight of the coating with specific pore volume and specific surface area, respectively.

During the printing, which takes several minutes per test pattern, depending on the drop spacing setting, previously deposited ink evaporates and part of the fresh ink deposited at the printing edge of the pattern flows to the previously printed area as replacement, resulting in deposited volumes that are much higher than would have been needed to saturate the pore matrix with a non-volatile ink. Thus, the ratios of the AKD ink to coating are specific to a given pattern and print set-up, and with higher printing speed set-ups different behaviour should be expected. Furthermore, due to the flows within the pattern arising from progressive evaporation, AKD distribution is unlikely to be even within a given test sample.

For polyelectrolyte inks, 10 μm drop spacing setting was selected to ensure that the deposited ink would cover the full depth of the substrate. Nominal deposited dry polyelectrolyte amounts in relation to coating mass and internal pore surface area are shown in Table 5. Due to the very faint visibility of the printed polyelectrolyte on the coating, actual pattern spreading could not be reliably evaluated.

Table 5. Nominal ink consumption and ratios between deposited polyelectrolyte mass, per layer at 10 μm drop spacing, and coating properties, with 95 % confidence intervals.

Ink	Nominal ink consumption on printed area / $\text{cm}^3 \text{m}^{-2}$	Coating	Nominal printed polyelectrolyte to treated coating weight ratio / w/w	Nominal printed polyelectrolyte per treated coating pore surface area / mg m^{-2}
CMC	107 ± 11	Anionised	0.087 ± 0.013	8.7 ± 0.9
		Cationised	0.080 ± 0.018	9.9 ± 1.0
PEI	64 ± 6	Anionised	0.064 ± 0.009	6.4 ± 0.6
		Cationised	0.059 ± 0.013	7.3 ± 0.7
PolyDADMAC	127 ± 7	Anionised	0.128 ± 0.015	12.8 ± 0.5
		Cationised	0.118 ± 0.024	14.7 ± 0.6

3.4 Charge density measurements

Measured and theoretically calculated specific charge densities for the polyelectrolytes and model colorants are shown in Table 6. Charge density is expressed with the commonly employed unit of milli-equivalent (mEq), with $1 \text{ Eq g}^{-1} = e u^{-1} = 96485 \text{ C g}^{-1}$, where e stands for elementary charge and u for atomic mass unit. Theoretical maximum values have been calculated by dividing the theoretical maximum charge, obtained as the sum of counter-ion charges, or in case of PEI as the number of amine groups, on the molecular formula and dividing this by the respective molecular unit mass. For polyelectrolytes the theoretical maximum has been calculated for a single repeat unit, rather than the whole chain, thus not taking into account the effect of the end groups. In the case of CMC, the charge and mass of a repeat unit are dependent on the degree of substitution (ranging from 0 to 3), as will be explained in detail later in this section, and thus no values can be calculated unless the degree of substitution is known.

Table 6. Theoretical maximum and measured specific charge densities for tested colorants and polyelectrolytes, with 95 % confidence intervals where applicable.

Sample	Type	Property per molecule or repeat unit		Specific charge density / mEq g^{-1}	
		charge / e	mass / u	theoretical (max.)	measured
Tartrazine	Anionic	3	534.36	5.61	4.43 ± 0.63
Safranin O	Cationic	1	350.85	2.85	2.88 ± 0.22
Ferroin	Cationic	2	692.53	2.89	0.02 ± 0.01
PolyDADMAC (8.5 kDa M_w)	Cationic	1	161.67	6.19	5.67 ± 0.02
PolyDADMAC (100 kDa M_w)	Cationic	1	161.67	6.19	5.63 ± 0.08
Polyethyleneimine (branched)	Cationic	11	473.75	23.22	13.14 ± 0.59
Sodium polyacrylate	Anionic	1	94.05	10.63	9.44 ± 0.26
Carboxymethylcellulose	Anionic	Variable (0-3)	NA	NA	5.32 ± 0.07

The charge density of an electrolyte in aqueous solution can depend on environmental effects, such as the pH of the solution, which influence the dissociation of counter-ions from the parent molecule. In this study, the measurements were taken from samples dissolved in de-ionised water, and most of the measured charge densities range between 57-100 % of the calculated theoretical maximum. As an exception, ferroin has a measured charge density that is less than 1 % of the calculated maximum, suggesting very low dissociation of the SO_4^{2-} counter-ion.

The degree of substitution D of CMC, representing the average number of hydroxyl groups (from 0 to 3) substituted per repeat unit of cellulose chain, can be estimated from the charge density measurements. Based

on the molecular formula and assuming full counter-ion dissociation, charge q and mass m per repeat unit can be expressed as per Eqs. 1 and 2 in respect to the elementary charge e

$$q = De \quad (1)$$

$$m = a + bD \quad (2)$$

where a stands for the mass of a native cellulose repeat unit $C_6H_{10}O_5$ (162.142 u) and b for the mass increase due to substitution of a single hydrogen atom with a $-CH_2COONa$ group (80.018 u). Specific charge density, σ , of CMC, assuming insignificant end unit effect, can then be expressed as per Eq. 3

$$\sigma = \frac{q}{m} = \frac{De}{a+bD} \quad (3)$$

which can be solved to obtain D as a function of σ , as per Eq. 4.

$$D = \frac{a}{\sigma^{-1}e - b} \quad (4)$$

Thus, for the experimental CMC product employed in this study, degree of substitution can be estimated as approximately 1.5 according to Eq. 4. Meanwhile, for a CMC product with the maximum degree of substitution of 3, a specific charge density of 7.5 mEq g^{-1} would be expected according to Eq. 3.

3.5 Colorant separation on native and polyelectrolyte printed coatings

Fig. 3 displays examples of test pattern II samples eluted with model colorant solutions to the full channel length, thus demonstrating visually some of the separation effects depending on interaction of colorant, coating and printed polyelectrolyte. Fig. 4 shows measured values for the retardation factor R_F for different colorants and concentrations on native coatings.

Figure 3. Examples of pattern II samples eluted with 0.2 w/w% colorant solutions demonstrating (a) safranin O on anionised and (b) cationised coating, (c) tartrazine on anionised and (d) cationised coating, as well as (e) ferroin on anionised and (f) cationised coating. The number of ink layers (e.g. x1) shown at the foot of each channel.

Figure 4. Retardation factors, R_F , for ferroin, tartrazine and safranin O as a function of colorant concentration on unprinted anionised and cationised coatings, with 95 % confidence intervals. The values for ferroin and safranin O on cationised coating overlap.

Cationic safranin O shows no separation on the native cationised coating with concentrations of 0.1 w/w% or above, but shows separation at lower concentrations, while anionic tartrazine shows a level of separation at all concentrations on the anionised coating. Both of these colorants show significant levels of separation when applied on oppositely surface charged coatings, with the level of separation heavily dependent on the colorant concentration in the supersource, being greatest for the lowest concentrations. This concentration-dependent behaviour suggests that the charged colorant molecules can partially neutralise the separating

effect of the anionic/cationic nature of the coating, e.g. due to charge capture of colorant molecules on the pore walls, and thus the coating charge adsorption capacity becomes saturated.

In principle, such behaviour of concentration-dependent separation could be employed as a rough quantitative analytical method, where a sample is eluted a given length and then separation effect is measured to determine sample concentration. From the end-user perspective, this would resemble another published quantitative colorimetric analysis method employing length of a channel that changes colour in a reaction to determine analyte concentration [26]. However, the effectively measurable concentration range by the separation mechanism is limited by detection scale saturation at both ends, while the amount of variation in the results shown in Fig. 4 suggests limited precision. Furthermore, the slightly cationic ferroin shows a low degree of separation on anionised coating, thus demonstrating the limitations of the method, and with non-charged molecules no separation effect could be expected.

The anionised and cationised coatings demonstrated in this study are just two examples of what is possible, and other combinations of pigments, binders and additives can provide coatings with different separation properties. Though in this study only one single polyelectrolyte additive level was tested, it would be of interest to evaluate the effects of different polyelectrolyte concentration in the coating interactions. Besides anionised and cationised coatings, in principle it would also be possible to formulate coatings with no surface charge by coating the pigment particles with a layer of steric polymer binder. However, in case of FCC this could be counter-productive, since it might result in loss of the fine surface pores and native surface chemistry that are the authors' motives for studying this material for analytical applications in the first place.

In this study, surface charge of the coatings was further modified with the deposition of additional polyelectrolyte layers by inkjet printing. This allows both inclusion of polyelectrolytes that could not be added straight to coating formulations due to de-stabilisation, e.g. by flocculation of MFC binder, and selective application of polyelectrolyte onto specific areas of the substrate.

Fig. 5 displays the effects of printed CMC, PEI and polyDADMAC on the R_F of weakly cationic ferroin on pattern II samples. Due to the faint colour at low concentrations, ferroin was not studied with colorant concentrations lower than 0.1 w/w%. On the anionised coating, printing of CMC onto the channels significantly increased the separation of ferroin, though this effect was not further enhanced by jetting multiple layers, while printing of cationic polyDADMAC or PEI cationised the channels sufficiently to result in no separation between water and ferroin. On the cationised coating the addition of a layer of inkjet-printed CMC again resulted in a significant degree of separation, though the application of a second or third layer surprisingly seemed to partially reverse the effect and increase R_F , whereas opposite behaviour could have been logically expected. Potential free polymer effects might be at play due to exceeding the coating internal surface adsorption capacity.

Figure 5. Retardation factor, R_F , between cationic ferriin and water on polyelectrolyte printed channels on (a) anionised and (b) cationised coatings, with 95 % confidence intervals. Results for all polyDADMAC and PEI printed channels were effectively identical, and thus presented by a single entry.

Fig. 6 demonstrates the effects of printed polyelectrolytes on the R_F of cationic safranin O. On anionised coating, printed CMC reduced the R_F for this colorant, while cationic PEI and polyDADMAC increased it, both expected behaviour, though again the addition of second or third printed layer had no significant additional effect. On the cationised coating, a layer of printed CMC reduced R_F , though additional layers had no further effect, while inkjet-deposited PEI or polyDADMAC did not seem to have significant effect on the separation of safranin O.

Figure 6. Retardation factor, R_F , between cationic safranin O and water on polyelectrolyte printed channels on (a) anionised and (b) cationised coatings, with 95 % confidence intervals.

In the case of anionic tartrazine model colorant, polyDADMAC printed channels seemed to demonstrate two different colorant regions, a strong main colorant front and a significantly weaker leading colorant, with examples shown in Fig. 7. On both coatings, the intense (strong) main front on these samples had a reduced R_F compared to the native coating, while the faint (weak) leading front could have an even lower degree of separation than on the native coating itself. This faint leading front could be due to excess polyDADMAC, dissolving as free polymer, complexing with the tartrazine to form weakly charged molecules that transport differently to the native colorant. Multiple printed layers would result in larger amounts of free polymer being available, though some of this would be eluted ahead of tartrazine and, thus, not available to act with it.

Figure 7. Examples of the faint (weak) and intense (strong) fronts observed for 0.5 w/w% tartrazine on polyDADMAC printed channels on (a) anionised and (b) cationised coating.

Fig. 8 shows the effects of printed polyelectrolytes on tartrazine, with both weak and strong fronts shown for the polyDADMAC printed channels. In two cases (2 polyDADMAC layers on cationised coating and 3 polyDADMAC layers on anionised coating, respectively) no values are shown for samples tested with 0.01 w/w% colorant solution, due to these channels having been incompletely printed with polyelectrolyte on the samples. On anionised coating, the addition of printed CMC results in no separation of anionic tartrazine from water, while the addition of PEI increases the degree of separation, though again the effect is not dependent on the number of applied layers. On the cationised coating, printed CMC expectedly increases the R_F for tartrazine, while a layer of cationic PEI slightly reduces it.

Figure 8. Retardation factor, R_F , between anionic tartrazine and water on polyelectrolyte for all printed channels on (a) anionised and (b) cationised coating, and for the polyDADMAC printed channels on (c) anionised and (d) cationised coatings demonstrating the differences between the strong and weak fronts. Shown with 95 % confidence intervals. On (a) the results for CMC printed channels overlap.

In the case of printed polyDADMAC, the strong main front can be considered to be representative of the effect of adsorbed polyelectrolyte on the separation, and thus has been selected for comparison with CMC and PEI printed channels in Fig. 8(a) and (b), where similar separation effects can be observed for PEI and polyDADMAC printed channels. The weak fronts, as shown in Fig. 8(c) and (d) do not follow clear trends, and have high confidence intervals. The often very faint colour of these weak fronts required setting an arbitrary threshold for interpreting data; for this study $B \leq 250$ on the scanned RGB image was set as the threshold level for locating the leading edge.

Besides the described interaction with tartrazine, a curious effect on the polyDADMAC printed channels was observed also for ferroin and safranin O: these colorants did not always spread evenly across the channel, but instead formed swirly or tentacle-like shapes. These can be observed in Fig. 3(a), (b) and (f). This suggests inhomogeneous distribution of polyDADMAC within the channel, either due to uneven distribution during the drying, caused by Marangoni flows, or uneven distribution of re-dissolved polyDADMAC in the eluent. Confirming this hypothesis would require a method for measuring polyDADMAC distributions quantitatively across a sample, ideally during elution.

Overall, printing of anionic and cationic polyelectrolytes on the channels had the expected effect: anionic polyelectrolyte increases R_F for anionic compounds and decreases R_F for cationic compounds, and vice versa. However, in most cases the effect was independent of the number of layers applied, which suggests that there is a saturation effect for the amount of polyelectrolyte that can have effect. Furthermore, the amount of polyelectrolyte applied per layer was possibly moderately high, and the effect of lower applied polyelectrolyte amounts per layer would be worth investigation.

R_F of a molecule in solution on a native coating is a function of a number of variables, including the surface chemistries and proportions of the coating pigment, binder and additives, as well as the surface chemistry and concentration of the molecule in the solution. Inkjet-deposition of additional polyelectrolyte on the coating introduces additional variables, as polyelectrolyte adsorption modifies the pore surface chemistry according to the nature and quantity of the applied polyelectrolyte. Therefore, building a comprehensive model of the phenomenon would require a significant amount of experiments. Inversely, it could be of interest to build models for substrate charge capacities based on their interactions with various known solute charge concentrations.

3.6 Effect of printing on capillary transport

Besides having an effect on the retardation factors of the coatings, the inkjet deposited polyelectrolytes were also expected to slow down capillary transport in the pore network by partially filling smaller pores and pore throats. The times required for the water front to wet the printed channels fully are given in Table 7. Due to the uneven nature of the wetting front this time was usually somewhat longer than the time taken for the first part of the wetting front to reach the end of the channel.

Table 7. Transport times required to fill channels completely as a function of printed layers, with 95 % confidence intervals. Results for WE ink taken from three samples, others from ten samples.

Channel	Transport time / s	
	Anionised coating	Cationised coating
Unprinted	1 060 ± 160	1 700 ± 220
CMC, 1 layer	1 390 ± 130	970 ± 110
CMC, 2 layers	1 810 ± 150	890 ± 90
CMC, 3 layers	2 080 ± 270	880 ± 130
PolyDADMAC, 1 layer	1 140 ± 140	1 440 ± 120
PolyDADMAC, 2 layers	1 180 ± 130	1 440 ± 160
PolyDADMAC, 3 layers	1 140 ± 210	1 440 ± 180
PEI, 1 layer	1 170 ± 140	1 110 ± 140
PEI, 2 layers	1 140 ± 150	880 ± 110
PEI, 3 layers	1 130 ± 140	890 ± 190
WE, 1 layer	NA	1 190 ± 200
WE, 2 layers	NA	1 040 ± 120
WE, 3 layers	NA	1 000 ± 100

On the anionised coating, polyelectrolyte printed onto the channels increased travel times. In the case of polyDADMAC and PEI this effect was relatively small and not affected by the number of printed layers, while for the CMC printed channels the transport delay was more pronounced and increased as a function of printed layers.

Unexpectedly, on the cationised coating the opposite behaviour was observed, with the transport faster on all of the polyelectrolyte printed channels than on the native channel. The effect was most pronounced on CMC and PEI printed channels, less pronounced on polyDADMAC printed channels, and not significantly affected by the number of printed layers. This suggests that the solvent component of the inks dissolved the water-soluble PVOH binder and/or polyDADMAC additive present in the coating, and during the drying this was re-distributed in the channels, forming a more permeable pore network. To test this hypothesis, fully liquid WE ink was printed on three tests samples, with the results included in Table 7, demonstrating that the water-ethanol solvent mixture itself was capable of inkjet etching the cationised coating and thus speeding up wicking. As an alternative hypothesis, deposited polyelectrolytes could have affected surface energy by changing the zeta potential barrier effect to polar liquid by charge neutralisation, but this could not explain why the effect takes place also with purely solvent-based WE ink.

To test the separation of PVOH and polyDADMAC from the coating pigment, dry coating pigment was ground and mixed with water-ethanol mixture for 16 h, a time period expected to represent equilibrium conditions rather than the much shorter time scales involved in the printing and drying of the inks. Under these test conditions the majority of both PVOH and polyDADMAC were found to have dissolved into the supernatant. The amount of PVOH that remained on the pigment surface was estimated as $0.25 \pm 0.02 \text{ mg m}^{-2}$ compared to the original coating content of 0.91 mg m^{-2} , while with polyDADMAC only $0.008 \pm 0.006 \text{ mg m}^{-2}$ out of 0.09 mg m^{-2} remained on the pigment surface, i.e. $73 \pm 2 \text{ w/w\%}$ of PVOH and $91 \pm 7 \text{ w/w\%}$ of polyDADMAC dissolved from the coating to the supernatant.

Thus, the effects of speeded-up transport could be due to dissolving of either PVOH, polyDADMAC or both, and the effect could be further studied with simpler coating formulations containing just pigment and PVOH binder without polymeric additive. In contrast to the water-soluble PVOH binder on the cationised coating, the MFC binder on the anionised coating does not dissolve in water, and is therefore unlikely to re-distribute upon wetting of the coating, except for any minor amounts of nanocellulose component present which could migrate in suspension.

3.7 Transport of printed polyelectrolytes on elution

The prospect of printed polyelectrolytes re-dissolving and transporting upon elution was taken into consideration from the beginning of the study, with the test pattern III designed explicitly for this purpose. Possible polyelectrolyte transport was investigated with FTIR and Raman spectroscopy and ninhydrin indicator colour.

FTIR measured spectra were dominated by the FCC pigment, with only weak peaks discernible for printed polyelectrolytes. Printed CMC on coatings displayed peaks centred approximately at $1\,592$ and $1\,327\text{ cm}^{-1}$, printed PEI displayed peaks centred approximately at 815 cm^{-1} while for printed polyDADMAC no characteristic peaks could be detected against the coating background. Due to the weak nature of the peaks, eluted channels were measured close to the top only for those channels that had three layers of CMC or PEI printed, and, for these two, no indication of transported polyelectrolyte could be detected. However, considering the poor sensitivity of the set-up in detecting the polyelectrolytes against the coating background, this is not sufficient proof that no transport took place.

Raman spectra were also dominated by the strong background signal of the FCC pigment. Unlike with FTIR, no distinctive peaks could be detected for either PEI or CMC, even when measured from plain polyelectrolyte solution itself. For polyDADMAC solution, distinctive peaks could be observed, but when printed polyDADMAC was measured on the coating, peaks were no longer observable due to the strong background of the coating. Thus, it was not possible to study polyelectrolyte transport by this method.

Ninhydrin reactively changes colour on contact with PEI, but not with any of the other polyelectrolytes or coating components employed on this study. When ninhydrin solution was sprayed on coatings with PEI regions, a brown colour developed as shown in Fig. 9. The examples there clearly show that upon elution PEI has partially dissolved from printed regions and travelled the whole length of the channels, though also the original printed regions are still clearly visible. This suggests that some of the PEI adsorbed to the coating pore surfaces, while excess dissolved and was transported by the elution. However, the method does not lend itself to quantitative analysis due to the uneven nature of the manual spraying, which can also result in bleeding artefacts when excess amount of liquid spray is applied.

Figure 9. Pattern III samples printed with PEI and sprayed with ninhydrin solution, demonstrating (a) eluted anionised coating, (b) non-eluted anionised coating displaying colour change on original printed areas and (c) eluted cationised coating.

Thus, only transport of printed PEI by elution could be clearly confirmed, while for CMC and polyDADMAC no conclusive results could be achieved with the trialled methods. However, it became apparent that this kind of transport should be studied with methods that are not only sensitive to the polyelectrolyte, but also where the coating background does not mask the signal. In case of colorimetric

detection, e.g. with ninhydrin, the white coating is unlikely to mask the signal, except for reducing its colour intensity, but instead provides a strong contrast for detecting colour change.

4. Conclusions

This study followed-up investigation on the separation of cationic/anionic model colorants from water on speciality pigment coatings with anionised and cationised surface chemistries, designed to transport similarly charged molecules and separate oppositely charged ones. The charge modification was applied both universally, by adjusting the bulk coating slurry by a polyelectrolyte additive, and locally, by inkjet printing polyelectrolyte solution. The level of separation of oppositely charged colorants on the coatings depended on the colorant concentration, limiting the applicability of the method with high concentration samples, but, in turn, potentially offering a quantitative analytical method for concentration measurement.

Printed polyelectrolytes were observed to modify local surface chemistry effectively, though multiple ink layers were found not to have an additive effect, suggesting a saturation level reached by the first layer alone. Out of the tested polyelectrolyte inks, cationic PEI and anionic CMC lacked sufficiently reliable jetting for subsequent upscaling, though the polyDADMAC ink seemed to jet sufficiently stably to merit further investigation. Flocculation of MFC binder by polyDADMAC additive demonstrates that polyelectrolytes cannot always be included directly in coating slurries due to stability issues, though they can be printed subsequently on dry coatings.

Transport of the printed PEI within the coating by water elution was clearly observed, while in the case of suspected transport of CMC and polyDADMAC no firm conclusions could be reached. However, the solvent content of the inks was found to be sufficient to dissolve and re-deposit components of the cationised coating, thus affecting wicking times and analytical potential.

Glossary

Field-specific terms in coating, printing and porous media found in this work.

- Capillary transport: surface tension driven spontaneous transport of liquid in a capillary or porous media: also known as wicking.
- Coating slurry: dispersion of pigment and binder in a carrier liquid.
- Drop spacing (inkjet printing): centre-to-centre distance between adjacent drops on substrate in x - and y -directions.
- Functionalised calcium carbonate: calcium carbonate particles surrounded by a high surface area layer of hydroxylapatite.
- Pigment coating: layer of pigment and binder applied on a substrate.
- Substrate: a surface upon which material is applied in a coating or printing process.

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Declarations of interest

None.

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