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IMPROVEMENT OF INKJET PRINT QUALITY VIA HYDROPHILIC POLYMERS AND BASE PAPER

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ABSTRACT

Modified starches, grain flour and polyvinyl alcohols were used for surface treatment of base paper from virgin and recycled fibres in sizing press. The impact of base papers, and polymers on physical and printing properties of modelled papers was studied. The research found, that the base paper free surface energy and contact angle of inkjet ink had fundamental influence on colour gamut. Colour gamut significantly improved when the inkjet ink contact angle decreased below 28°. Application of grain flour and polyvinyl alcohols resulted in the lowest contact angle and the highest colour gamut. Grain flour and polyvinyl alcohols are suitable alternatives of low-viscous modified starches already from the point when their content is four times lower at 0.2-0.3 $g.m^{-2}$ in paper. High sharpness of print was reached by applying all polymers, especially the cationic starch. Virgin fibres swelling resulted in a decrease of print sharpness.

KEYWORDS: Surface treatment, polymers, inkjet printing, colour gamut, print sharpness, wettability.

INTRODUCTION

Surface treatment of paper is required for improvement of printing properties such as print sharpness, colour gamut area and optical density of printed area. Printing quality is significantly influenced by structural and chemical properties of the paper surface. Surface treatment is carried out in the sizing press either directly in the paper machine or separately. The deposition of the sizing agents must be perfectly uniform and this is achieved by the participation of sizing press as well as base paper. Viscosity can dramatically influence the uptake of the sizing agents.

The starch is normally used for surface treatment, with the main goal of improving paper surface resistance and printability. Oxidised or hydrolysed starches are increasingly used in combination with synthetic copolymers to enhance the effect of surface sizing by controlling hydrophility and affinity of paper surface towards different types of printing ink. Recently, the trend is to replace starches with cheaper food industry products, such as modified grain flours

(Mishra 2005). Modified grain flours also have lower environmental impact since the isolation of starch is an energy intensive process, which requires high water consumption, which in turn generates highly polluted waste water (Pluske et al. 2007). Using surface treatment with application of either 2 modified grain flours or 4 g.m^{-2} modified potato starch increased burst strength by approximately 50 % as well as short span compressive strength of fluting from recycled fibres (Schneider and Gigac 2006).

Polyvinyl alcohol is used for surface treatment due to many desired properties, which are needed to create a good quality papers. It has a great film-performing properties and good adhesion to fibres and fillers (Kuusisto 2014); and also delivers 2-2.5 times more UV brightness units when compared to starch. Dynamics of surface wetting and liquid penetration, surface roughness and porosity of papers significantly influence print quality (Gigac et al. 2011, 2014a, Stankovská et al. 2014).

The objective of this work is to evaluate the influence of base paper and hydrophilic polymers on wettability, colour gamut area, optical density and print sharpness of modelled papers.

MATERIAL AND METHODS

Base papers

Commercial paper from virgin fibres and commercial paper from recycled fibres were both used as base papers. The base paper from recycled fibres has higher surface roughness and lower free surface energy. Base paper properties are shown in Tab. 1.

Tab. 1: Physical and printing properties of base papers.

Properties	Virgin fibre base paper A	Recycled fibre base paper B
Base weight (g.m^{-2})	157	93
Apparent density (g.cm^{-3})	0.86	0.86
Roughness PPS (μm)	4.7	6.0
Free surface energy σ (mJ.m^{-2})	38.0	26.9

Polymers

The commercial agents on the base of hydrophilic natural and synthetic polymers were used in the experiment: oxidised starch OX (Perlsize 158, Lyckeby Amylex); cationic starch KS (Cerestar SP 05855, Cerestar Deutschland GmbH); modified weak-anionic grain flour GF (Ceresan LA, Ceresan Erfurt GmbH, Deutschland); polyvinyl alcohols PVOH-1 (Mowiol 28-99, Kuraray Specialisties Europe) and PVOH-2 (Mowiol 26-88, Hoechst AG, Deutschland).

Testing liquids

Deionized water, dye-based inks C,M,Y, K and pigmented black ink were used.

Preparation of polymer solutions for surface treatment

Starches and grain flour were dispersed in cold water and heated to 95°C. Cooking time at this temperature was 30 min. Polyvinyl alcohol was slowly added into cold water with constant mixing to the point of swelling of granules. The solution was then heated to 85-90°C with constant mixing in water bath. After 30 min of cooking at the maximum temperature, the solutions were cooled down to room temperature. Polymers solutions were prepared so that their viscosity measured by Ford cup No. 4 was within 12-15 s. This viscosity was found to be optimal for surface treatment in experimental sizing press (Gigac et al. 2008).

Surface treatment

Surface treatment of base papers was performed in a laboratory sizing press (Werner Mathis AG, Swizerland) at constant speed of paper of 5 $m.min^{-1}$ and linear pressure of 20 $kN.m^{-1}$. Modelled papers were then dried 3 min at a temperature of 105°C. Polymers solution properties recorded are included in Tab. 2. Polarity and specific charge density of polymers, dye-based inks and pigmented inks were determined by polyelectrolyte titration using the Streaming Current Detector (Waters Associates Inc., USA). Concentrations of cationic standard PDADMAC and anionic standard PVS were 0.001 $mol.l^{-1}$. The content of polymers was calculated from difference between the wet and dry base weight of paper and concentration of solutions. The content of polymers in modelled papers was found to be within 0.22-1.09 $g.m^{-2}$ depending upon type of polymer and base paper. The content of grain flour and polyvinyl alcohols was lower due to reaching desired viscosity even at the low solution concentration. Two types of used starches were modified for surface treatment so that their solution with higher concentration can be prepared. The polymers content in base papers are in Tab. 3.

Tab. 2: Polymers and their solution properties.

Polymer	KS	GF	OX	PVOH-1	PVOH-2
Labeling	**1**	**2**	**3**	**4**	**5**
Concentration (%)	15.2	3.9	14.8	4.0	3.5
pH	6.1	9.9	6.3	7.3	7.0
Viscosity Ford No. 4 (s)	14.4	14.0	13.8	14.5	12.9
Dynamic viscosity at 100 rpm (mPa.s)	35.3	57.7	43.4	51.2	25.4
Specific charge density ($\mu eq.g^{-1}$)	+ 370	- 150	-197	+ 5	- 12

Tab. 3: Polymers content in base papers.

Polymer	KS	GF	OX	PVOH-1	PVOH-2
Labeling	**1**	**2**	**3**	**4**	**5**
Polymer content in virgin fibre base paper ($g.m^{-2}$)	0.91	0.28	1.09	0.32	0.25
Polymer content in recycled fibre base paper ($g.m^{-2}$)	1.02	0.22	1.03	0.31	0.22

Inks properties

At the inkjet printing of the papers in the printer Canon PIXMA i7250, original dye-based inks CLI-521 Y, CLI-521 C, CLI-521 M, CLI-521 BK and pigmented ink PGI-520-BK were used. Their properties are in Tab. 4.

Tab. 4: Inks properties.

Liquids at temperature 23 °C	Cyan C	Magenta M	Yellow Y	Black K	Black pigmented
Specific charge density ($\mu eq.g^{-1}$)	-91	-112	-115	-229	-740
Free surface energy σ ($mJ.m^{-2}$)	37.4	37.7	38.2	39.8	43.6
Concentration (%)	0.30	0.28	0.30	0.28	0.04
Density ρ ($g.cm^{-3}$)	1.08	1.06	1.07	1.07	1.09

Dynamics of water absorption

Water absorption was measured by the ultrasound analyzer PDA C.02 (Emtec, Radnor, PA, USA) with frequency 2 MHz within time of 43 ms- 60 s. Deionized water has free surface energy of 72.80 $mJ.m^{-2}$ and dynamic viscosity of 0.9 mPa.s. The principle and procedure of measurement and the evaluation have already been described in scientific literature (Stankovská et al. 2014). In the experiment ultrasound signal intensity in time of 5 s (IR5water) for evaluation was used.

Wettability

Contact angles of base paper and modelled papers were measured by "Sessile drop" method using the optical tensiometer (OCA 35, Dataphysics Instruments GmbH, Germany). Contact angle changes were recorded by a CCD camera at the sequence of 20 frames per second. Deionized water and dye-based inkjet ink were used as the testing liquids. Contact angle was calculated as an average of ten parallel measurements. Within this study, the wetting contact angle in time of 5 seconds (CA_5^{water}, CA_5^{cyan}) was used. Contact angle measurement technique is fully described in publication (Gigac et al. 2011).

Inkjet printing

Base papers and modelled papers were printed in the thermal printer Canon PIXMA i7250 within the mode Plain paper. The printed side of paper contains full colour areas C (cyan), M (magenta), Y (yellow), K (black), G (green), B (blue), R (red) and O (orange) of dye inks; and the text printed by yellow dye ink on a black background. Colour area C, M, Y, K intensity was 100 % and G, O, B, R was 200 %.

Colour gamut area and optical density of black area

The colour gamut area CGA was calculated as the pentagram area from a* and b* colour coordinates of the C, M, Y, G and O blocks. Colour coordinates were measured by using the Elrepho spectrophotometer (Lorentzen & Wettre, Sweden). Print density of black area (OD_K) was measured by the QUIKDens 100 densitometer (X-Rite-GmbH, Czech Republic).

Print sharpness

The print sharpness was evaluated as a deformation of the small letter "s" in the text. The digitalized image of the printed surface area was captured using a CCD Coolpix E4500 camera with the adapter for homogenous lighting. For calculation of print object deformation, the software HarFA 5.3 for harmonic and fractal analysis (BOX Counting method) was used (Nežádal et al. 2000). Print object deformation POD was evaluated from the ratio r_p/r_a, where r_p is perimeter radius of the object and r_a is radius of the object area. Reduced print object deformation corresponds with improved print sharpness. Description of the method and evaluation was already published (Stankovská et al. 2014).

RESULTS AND DISCUSSION

Physical and printing properties of base papers and modelled papers with polymers KS, GF, OX, PVOH-1 and PVOH-2 are shown in Tabs 5 and 6.

Tab. 5: Modelled papers and virgin fibre base paper properties.

Polymer	**Base paper A**	**KS**	**GF**	**OX**	**PVOH-1**	**PVOH-2**
Labeling	**0**	**1**	**2**	**3**	**4**	**5**
Permeability resistance Gurley (s)	53	89	55	107	246	309
Wetting CA_5^{water} (°)	78	69	88	63	93	71

Penetration IR_5^{water} (%)	51	90	67	88	99	84
Wetting CA_5^{cyan} (°)	34	49	22	37	30	25
Colour gamut CGA	4402	4317	4676	4292	4432	4502
Print sharpness POD	12.8	10.0	10.9	12.2	10.9	8.2
Optical density of black colour OD_K	1.82	2.06	1.79	1.97	1.92	1.92

Tab. 6: Modelled papers and recycled fibre base paper properties.

Polymer	**Base paper B**	**KS**	**GF**	**OX**	**PVOH-1**	**PVOH-2**
Labeling	**0**	**1**	**2**	**3**	**4**	**5**
Permeability resistance Gurley (s)	84	210	113	278	1038	725
Wetting CA_5^{water} (°)	100	71	94	69	98	70
Penetration IR_5^{water} (%)	98	100	99	100	99	100
Wetting CA_5^{cyan} (°)	46	48	25	34	27	21
Colour gamut CGA	4721	4946	5171	5211	5395	5371
Print sharpness POD	22.9	11.1	15.7	12.4	13.0	12.9
Optical density of black colour OD_K	1.79	1.92	1.95	1.87	1.90	1.78

Porosity

Paper porosity was measured by the Gurley method as the air resistance permeability. It is presented in Tabs. 5 and 6 as the permeability resistance. Higher value of permeability resistance corresponds to lower porosity. More remarkable effect of polymers on the porosity was noticed at the base paper B. The most significant decrease of porosity was at the content 0.2-0.3 $g.m^{-2}$ of film-performing polyvinyl alcohol in the paper (Tab. 3), while grain flour GF didn't show a higher effect on the porosity. Low-viscous starches KS and OX did not affect porosity in such way as polyvinyl alcohols even with their four times higher content in the paper. Porosity of surface treated base paper B decreased in the order of polymers: GF > KS > OX > PVOH-2 > PVOH-1. Porosity of surface treated base paper A decreased in the order of polymers: GF > KS > OX > PVOH-1 > PVOH-2.

Wettability and dynamic penetration of water

Oxidised starch OX and cationic starch KS increased water wettability of papers surface treated on both base papers. The higher contact angle corresponds with reduced surface wetting. Wetting contact angle in time 5 s decreased from 78° (base paper A) to 63° and 69°, respectively, and from 100° (base paper B) to 69° and 71°, respectively (Tabs. 5 and 6). Surface treatment of the base paper A with grain flour GF and polyvinyl alcohol PVOH-1 decreased the wettability. Water penetration into surface treated base paper A slowed down with application of polymers in an order: GF > PVOH-2 > OX > KS = PVOH-1. By surface treatment of the base paper B water penetration was not changed (IR_5^{water} 98-100 %). In Fig. 1 is time course of ultrasound signal intensity at the contact of water with surface treated base paper A. The higher intensity IR corresponds to slower liquid penetration. Penetration was influenced by surface wetting and porosity. The slowest penetration was found in the case of modelled papers with PVOH-1 (curve 4). It was obtained by the combination of low porosity (Gurley 246 s) and low water wettability (CA_5^{water} 93°).

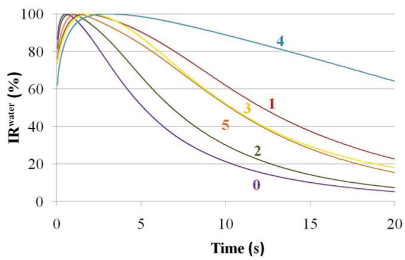

Fig. 1: Time course of ultrasound signal at the contact of modelled papers and base paper A (from virgin fibres) with water: 0–base paper; polymers: 1–cationic starch KS; 2–grain flour GF; 3–oxidised starch OX; 4–PVOH-1; 5–PVOH-2.

Wettability by inkjet cyan ink

Wetting contact angles of inkjet ink were 2-3 times higher than contact angles of water (Tabs. 5 and 6). Grain flour GF and polyvinyl alcohols increased wetting of the surface treated base papers A and B. While cationic starch reduced wetting of modelled papers on both base papers, oxidised starch increased wetting only in the case of base paper B. The wettability order of the surface treated base paper A with polymers was: KS < OX < base paper < PVOH-1 < PVOH-2 < GF; surface treated base paper B: KS < OX < base paper < PVOH-1 < GF < PVOH-2. High correlation between colour gamut area and ink wettability was found.

Colour gamut area

The highest colour gamut area (Tab. 6) was reached at the surface treated base paper B with both polyvinyl alcohols (CGA 5371 and 5395). In the case of base paper B (CGA 4721), colour gamut area of modelled papers was increased by application of all polymers in order: KS < GF < OX < PVOH-2 < PVOH-1. In the case of base paper A (Tab. 5) with colour gamut area 4402, the improvement was made only with application of grain flour GF (CGA 4676) and polyvinyl alcohol PVOH-2 (CGA 4502). Fig. 2 displays the recording of colour gamut area and dynamic

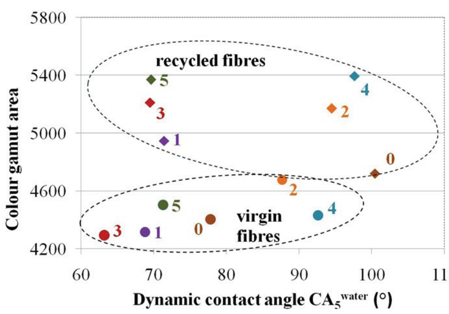

Fig. 2: Recording of colour gamut area of modelled papers and base papers from virgin A) and recycled B) fibres and dynamic water contact angle (0 – base paper; polymers: 1 – cationic starch KS; 2 – grain flour GF; 3 – oxidised starch OX; 4 – PVOH-1; 5 – PVOH-2).

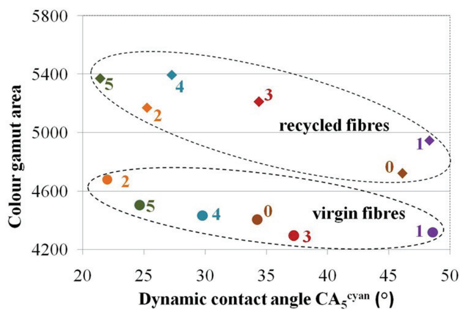

Fig. 3: Recording of colour gamut area of modelled papers and base papers from virgin A) and recycled B) fibres and dynamic cyan ink contact angle (0 – base paper; polymers: 1 – cationic starch KS; 2 – grain flour GF; 3 – oxidised starch OX; 4 – PVOH-1; 5 – PVOH-2).

water contact angle. Higher colour gamut area was achieved in the case of surface treated base paper B from recycled fibres. No correlation between colour gamut area and water contact angle was found. Fig. 3 presents the relationship between colour gamut area and dynamic cyan ink contact angle. Correlations between ink contact angle and colour gamut area were R 0.84 and 0.87, respectively. By decreasing the contact angle CA_5^{cyan} below 28°, colour gamut area of modelled papers improved.

Optical density of black area

The highest optical density (Tab. 5) was reached by surface treatment of base paper A (OD_K 1.82) with cationic starch (OD_K 2.06). Increased optical density was also reached with other polymers (OD_K 1.87-1.97), except the grain flour on base paper A and PVOH-2 on base paper B (Tab. 6). Optical density of surface treated base paper A increased in order of polymers: PVOH-1 = PVOH-2 < OX < KS and of base paper B increased in order of polymers: OX < PVOH-1 < KS < GF.

Print sharpness

The base paper A had higher print sharpness (Tab. 5) with reduced surface roughness. Surface treatment improved print sharpness of both base papers. Better print sharpness was achieved by surface treatment of base paper B (Tab. 6). Print object deformation POD dropped from 22.9 to 11.1-15.7, print sharpness increased in the order of polymers GF < PVOH-1 < PVOH-2 < OX < KS. The best print sharpness was reached by surface treatment of base paper A with polymers KS and PVOH-2 (POD dropped from 12.8 to 8.2 and 10.0, respectively). Less significant print sharpness improvement on base paper A is due to increases in surface roughness as result of virgin fibres swelling in aqueous solution during surface treatment. Hornified recycled fibres swell less in aqueous solutions, paper surface roughness does not increase and print sharpness improves. These conclusions are in accordance with previous results (Gigac et al. 2014b).

CONCLUSIONS

Colour gamut area, black ink optical density, print sharpness, porosity, surface wetting by water and inkjet ink, base paper fibrous matrix and surface roughness were used for evaluation of inkjet print quality. Free surface energy, surface roughness and fibrous matrix of base papers had significant impact on both colour gamut area as well as print sharpness of modelled papers. Base paper from recycled fibres with higher surface roughness and lower free surface energy had higher colour gamut area, lower wettability and lower print sharpness in comparison with base paper from virgin fibres.

The application of all polymers on surface of both base papers improved print sharpness. The conclusion is, that inkjet ink contact angle is suitable parameter for prediction of colour gamut area of inkjet paper. Colour gamut area of modelled papers significantly improved by reduction of inkjet ink contact angle below 28°.

By surface treatment of base papers with grain flour and polyvinyl alcohols, higher colour gamut area at the content 0.2-0.3 $g.m^{-2}$ of polymers in paper was achieved. Surface treated base paper from recycled fibres reached the greatest colour gamut area with film-performing polyvinyl alcohols where besides the decrease of contact angle, the paper surface was also enclosed and porosity was reduced. Surface treated base paper from virgin fibres achieved the best colour gamut area with grain flour. Grain flour did not change porosity, however it significantly decreased inkjet ink contact angle.

The results indicated that grain flour can be a suitable alternative of low-viscous modified starches. Inkjet papers with higher colour gamut area can be prepared already with significantly lower content of grain flour in paper. Four times higher content of low-viscous cationic starch in paper did not have a significant influence on colour gamut area. On the other hand, low-viscous cationic starch improved print sharpness and black ink optical density much more. Four times higher content of low-viscous oxidised starch improved colour gamut area and print sharpness only in the case of base paper from recycled fibres.

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