



Synergetic effect of cationic starch (ether/ester) and Pluronic for improving inkjet printing quality of office papers

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Abstract Improving the printability of paper is still a relevant challenge, despite the fast development of digital communications. While it is well-known that cationic starches enhance ink density, their commercial paper-grade forms are limited to ethers with low degree of substitution. This work addresses the underexplored potential of highly substituted cationic starch for paper coating and its combination with tri-block polymers, namely Pluronic (P123 and F127), taking advantage of their supramolecular interactions with amylose chains. For that purpose, cationic starch ether and ester (starch betainate), both with a degree of substitution of 0.3, were synthesized by alkaline etherification and by transesterification, respectively. Paper without any surface treatment was subjected to one-side bar coating with suspensions encompassing those products and Pluronic, besides other common

components. Black, cyan, yellow and magenta inks were printed on all coated papers through an inkjet printer. Key properties of printing quality such as the gamut area, gamut volume, optical density, print-through, inter-color bleed and circularity were measured in a controlled temperature-humidity environment. For instance, a formulation with cationic starch (ether/ester) and P123 improved the gamut area by 16–18% in comparison to native starch-coated paper sheets. Interestingly, the individual assessment of each component showed that cationic starch ether, starch betainate and P123 only improved the gamut area by 5.6%, 8.9% and 6.8%, respectively. Finally, but not less importantly, starch betainate was found to quench optical brightening agents to a lesser extent than cationic starch ethers.

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clearly more labile than ether bonds (Auzély-Velty and Rinaudo, 2003). Likewise, starch betainate (SB), a cationic starch ester, was suggested for the improvement of paper strength since the first work reporting its synthesis (Granö et al. 2000). However, as far as we know, no study has addressed the influence of SB on the printing properties of fine papers. This issue is addressed in the present work, evaluating coating formulations comprising SB and other interesting amphiphilic polymers, namely Pluronics.

Pluronics® is a BASF's trade name for the less commonly called poloxamers. This trade name comprises non-ionic, water-soluble, triblock copolymers of polyethylene oxide (PEO) and polypropylene oxide (PPO) units. Interestingly enough, they generally form inclusion complexes with starch in aqueous solution. This kind of binding has a significant effect on the dispersion performance and can be explained by hydrophobic interactions between hydrophobic parts of Pluronics macromolecules and the cavities of the amylose helix (Petkova-Olsson et al. 2017). Additionally, the micellar structure of these non-ionic surfactants also influences the adsorption onto the surface of cellulosic materials, which is enhanced in the presence of cationic polymers (Liu et al. 2010, 2011). Moreover, instead of becoming attached to the cellulosic substrate before printing, Pluronics can be directly included in the ink formulation, which is particularly useful for the inkjet printing of proteins (Mujawar et al. 2015).

In light of the aforementioned hypotheses and previous findings, paper sheets were coated using different concentrations of SB, HCS, Pluronics (P127 and F127), precipitated calcium carbonate (PCC), alkyl ketene dimer (AKD) and optical brightening agent (OBA). This study also illustrates the use of a statistical tool to design the coating experiments and to identify the most important factors to be considered for improving the paper printability. A comparison of HCS and SB coatings was also explored, discussing their influence on the whiteness of paper, given that the interaction between cationic polymers and OBAs, generally anionic, has been pointed out as a major cause of fluorescence quenching (Shi et al. 2012). All in all, this is the first work assessing the combination of cationic starches and Pluronics in paper coating, and it does so with an in-depth evaluation of their effects on optical, surface and printing properties.

Materials and methods

Materials

Native corn starch (NS), α -amylase (in standard buffer solution, pH 5.8), PCC, OBA and AKD were of industrial origin. 3-Chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC), Pluronics® P123 (MW ~ 5750 g mol⁻¹, PEO ~ 30 wt.% and CMC of 0.313 mM at 20 °C) (Alexandridis et al. 1994) and Pluronics® F127 (MW $\sim 12,600$ g mol⁻¹, PEO-70 wt.% and CMC of 0.56 mM at 25 °C) (Thapa et al. 2020) were purchased from Sigma-Aldrich. Betaine hydrochloride (99%) was purchased from Alfa Aesar and used as-is for transesterification. All solvents were purified or dried prior to use the standard procedures. Other commercially available compounds were used without further purification.

Figure 1 schematizes the methods, highlighting the aforementioned materials and displaying all the steps taken towards coated and inkjet-printed paper sheets.

Synthesis of HCS and SB

Native starch (NS) was mildly hydrolyzed with α -amylase (0.45 μ L g⁻¹ of starch), under continuous stirring, at 80 °C for 5 min. The temperature was raised up to 90–95 °C for 15 min. Then, the starch solution was cooled down and absolute ethanol was added to precipitate the polysaccharide, hereinafter referred to as “cooked starch”. Cooked starch was then vacuum filtered, dried and stored in an oven at 50 °C. This pretreatment is common to the synthesis of both HCS and SB.

HCS was synthesized as described elsewhere (Haack et al. 2002). Briefly, 10 g of cooked or native starch was converted into HCS using 33.5 mL of CHPTAC (60 wt.%) and 5.9 g of NaOH. The reaction was carried out for 24 h at 70 °C in 100 mL of distilled water. The reaction mixture was then neutralized with a 0.1% HCl solution.

Starch betainate (SB) was synthesized, as described in a previous paper (Sharma et al. 2021), through the transesterification of starch with methyl betainate (MeBetCl) in polar aprotic solvents. Briefly, 24 g of betaine hydrochloride was first esterified to synthesize MeBetCl using 11.3 mL of thionyl chloride and 75 mL of methanol, under reflux, for 4 h at 70 °C. MeBetCl was recovered through evaporation of

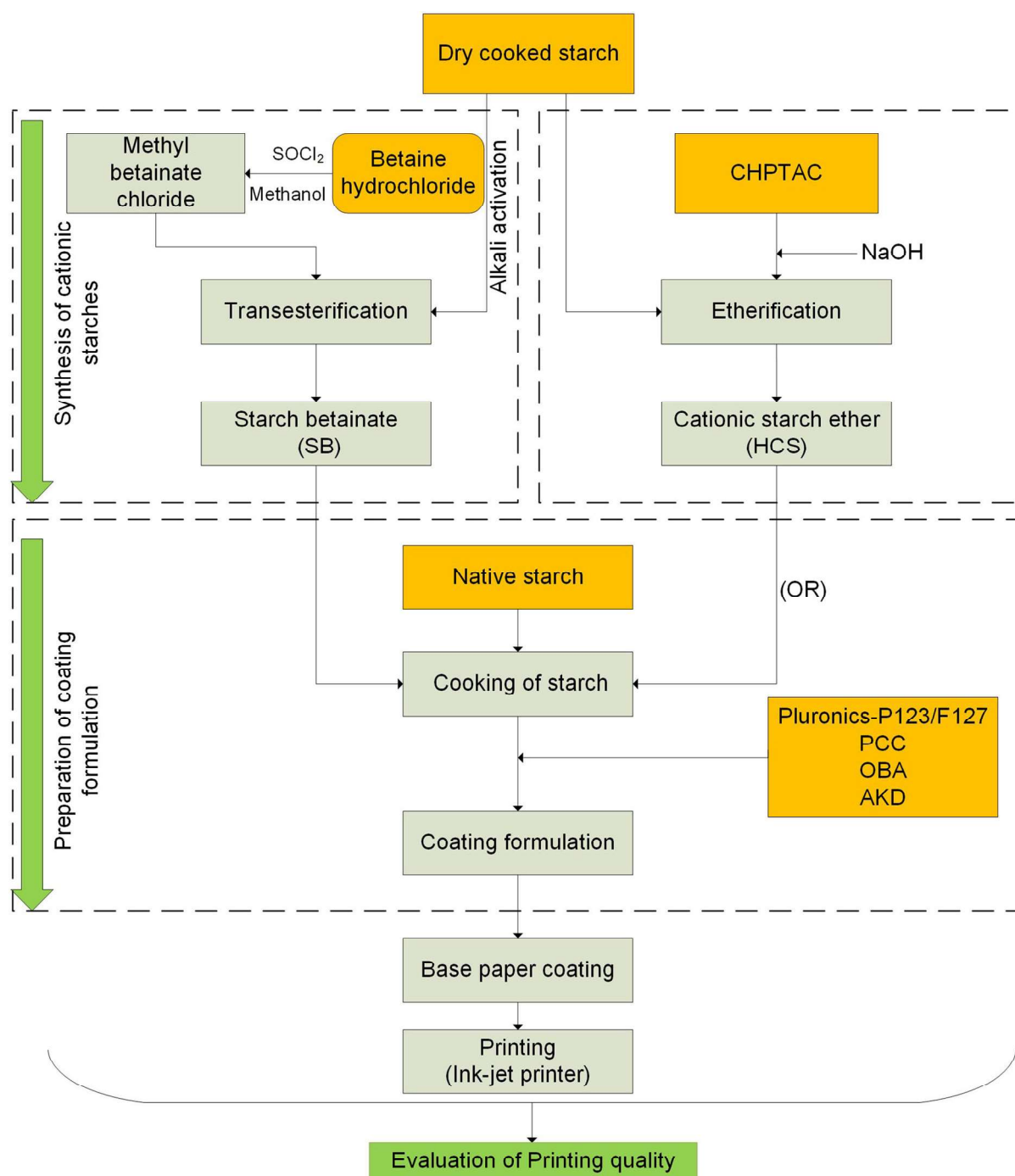


Fig. 1 Outline of the experimental procedure

methanol followed by trituration in diethyl ether and, finally, the crude product was dried under high vacuum. Then, 10 g of cooked starch were converted into SB using 20.8 g of MeBetCl in *N,N*-

dimethylformamide (DMF), 100 mL. Prior to transesterification, cooked starch was pre-activated in NaOH/ethanol. The reaction was carried out for 24 h at 70 °C.

HCS and SB were precipitated by adding ethanol (alcohol/water > 10, v/v), vacuum filtered and washed with absolute ethanol, followed by drying at 50 °C.

Characterization of synthesized cationic starches

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, ¹H-nuclear magnetic resonance (¹H-NMR) spectroscopy and viscometry analysis were performed to characterize the synthesized cationic starches. ATR-FTIR spectra were recorded by using an Agilent Cary 630 spectrometer, from 750 to 3000 cm⁻¹, at a resolution of 4 cm⁻¹ and 64 scans per sample. NMR spectra were obtained from a Bruker Biospin GmbH spectrometer, at 400 MHz, using D₂O as solvent. The degree of substitution was calculated from the area of the singlet assigned to the methyl protons of the quaternary ammonium group. The reliability of this result was confirmed by measuring the nitrogen percentage of samples on a Fisons Instruments EA 1108 CHNS-O elemental analyzer.

Paper coating

NS was used as a common component for preparing all formulations in this work. For that, NS was cooked as described earlier, and then cooled down to 50 °C instead of precipitated. An industrial calendered uncoated paper (base paper, BP), produced from bleached eucalyptus kraft pulp with a basis weight of ~ 78 g m⁻², was used as substrate for performing surface coating.

Coating of BP was performed using a Mathis laboratory coater, with a pre-drying infrared system coupled to an applicator bar (SVA-IR-B). The applicator roll with the diameter of 13 mm, in conjunction with a velocity of 6 m min⁻¹ and intermediate load at both sides, was used to achieve 1.5–3 g m⁻² per side, on the basis of dry coating weight. For all sheets, the coating time was 4 s/sheet. Afterwards, sheets were air dried at room temperature.

Besides NS, BP sheets were coated with SB, HCS, P123, F127, PCC, and combinations thereof. Coatings were performed using 8%, 16% and 24% of total solids coating weight of each of these components, and several combinations of them were tested at said concentrations. The coating compositions resulting

from individual components (with NS) and combinations thereof are shown in Tables 1 and 2, respectively.

The surface weight gain was calculated by the difference between basis weights (ISO standard 536:1995) of the air-dried coated paper sheet and the respective BP sheet. Before characterization, all coated papers were kept at controlled temperature (23 °C ± 1) and humidity (RH 50% ± 2). For each run, three numbers for paper sheets were coated, printed and characterized for evaluating the printing quality.

Paper properties

Bendtsen roughness (ISO 5636-3, 8791-2) and Gurley air permeability (ISO 5636/5) were measured for coated papers using appropriate testers from Frank-PTI. Whiteness (CIE W D65/10) of coated papers was measured using D65 illumination in the Elrepho spectrophotometer. The average value and the standard deviation of four independent measures are reported for Bendtsen roughness, Gurley permeability (also called Gurley porosity) and whiteness. The latter was related to the performance of OBA, as fluorescence emission spectra of solutions containing OBA were recorded by means of a FluoroMax 4 spectrofluorometer from Horiba.

Surface and cross-section micrographs of coated papers were obtained by means of a field emission scanning electron microscope (FE-SEM), Merlin (Carl Zeiss AG), including a Gemini II column and a secondary electron detector, and working at low acceleration voltage (2 kV). Furthermore, the average width of the coating layer was estimated by measuring the thickness of uncoated and coated paper sheets with a micrometer (ISO 534:1998).

Resistance to water

The surface hydrophilicity for SB-coated papers was evaluated by contact angle goniometry. The static water contact angle (SWCA) was measured in an OCA 20 goniometer (Dataphysics, Germany) using the sessile drop method. A droplet of deionized water (10 µL) was automatically poured onto the coated paper surface. After settling, the formed angle was measured by fitting the Young–Laplace equation to the drop profile. Likewise, the dynamic water contact

Table 1 Composition of coating components expressed as %w/w, on the basis of dry coating weight

Ingredients	Coating formulations													
	HCS/SB				P123			F127			PCC			Reference
HCS/SB	8	16	24	16										
P123					8	16	24							
F127								8	16	24				
PCC											8	16	24	
OBA	6	6	6		6	6	6	6	6	6	6	6	6	6
AKD	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
NS	85.6	77.6	69.6	83.6	85.6	77.6	69.6	85.6	77.6	69.6	85.6	77.6	69.6	93.6

Table 2 Composition of coating components for the interaction study, expressed as %w/w, on the basis of dry coating weight

Ingredients	Coating formulations									
	HCS/SB + P123				HCS/SB + P123 + PCC				Reference	
HCS/SB	16	16	16	16	16	16	16	16		
P123	8	16	24	16	8	16	24	16		
PCC					16	16	16	16		
OBA	6	6	6		6	6	6		6	
AKD	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
NS	69.6	61.6	53.6	67.6	53.6	45.6	37.6	51.6	93.6	99.6

angle (DWCA) was measured over periods of up to 60 s.

The time profile of water penetration through coated samples was plotted by means of an EST Surface and Sizing Tester from Emtec. Briefly, this device monitors the ultrasound absorption or scattering at the air–water interfaces of small bubbles, since air flows out from the pores of the sheet as water penetrates through it.

Viscosity and thermal degradation behavior

The kinematic viscosity was determined using a size 100 Cannon–Fenske viscometer in a thermostatic bath (TAMSON TV 2000) set at 40 °C. Measurements followed the ISO 3105 standard. Polymer solutions were prepared with a concentration of 5 mg cm^{−3} in 1 M NaOH/H₂O (for HCS) and DMSO (for SB).

The thermogravimetric analysis (TGA) was carried out on a thermo-microbalance TG 209 F3 Tarsus, from Netzsch Instruments. Samples were heated from 40 to 600 °C, under a flow of nitrogen (20 mL min^{−1}), with a heating rate of 10 °C min^{−1}. TGA was performed

for filter paper coated with P123, F127 and SB. A filter paper was cut into pieces (5 cm × 2 cm) and Pluronic P123/F127 were absorbed in this cellulosic substrate. This was carried out with a 10% Pluronic aqueous solution and a LayerBuilder dip coater from KSV. Cellulose substrates were dipped into the solution for 3 min, pulled out and air-dried. The same procedure was followed for 10% SB and 10% P123/F127 + 10% SB aqueous solutions.

Printing quality

Samples for measuring the printing quality were prepared as reported elsewhere (Lourenço et al., 2020). Briefly, the coated papers were printed using HP Officejet Pro 6230 inkjet printer in Max DPI mode (4800 × 1200 optimized DPI), having cyan, magenta, yellow, and black color ink cartridges. The printed sheets were air dried for 4 h under controlled conditions of temperature and humidity.

Gamut area and gamut volume

The GA is the area of the hexagon resulting from the a^* and b^* coordinates of six printed colors (red, green, blue, cyan, magenta, and yellow), where a^* axis represents the color from green to red and axis b^* represents the color from blue to yellow. It was determined by measuring the values of CIE $L^*a^*b^*$ coordinates for six color spots, including three base colors (cyan, magenta and yellow) and other three complimentary colors (red, green and blue). For that, the “X-Rite Eye One XTreme UV Cut” spectrophotometer was placed on each printed color spot, activating the UV light (D50, 2°). The readings were taken in the sequence of red, green, blue, cyan, magenta, and yellow color spots. Additionally, CIE $L^*a^*b^*$ values for black and white colors were measured to estimate the gamut volume (GV) of printed paper sheets.

Optical density, print-through, inter-color bleed, and circularity

In order to evaluate optical density (OD) and print-through (PT), the QEA PIAS-II spectrophotometer was used with a low-resolution optical module (33 $\mu\text{m}/\text{pixel}$ with visual area of 21.3 mm $\times$ 16 mm), along with the software PIAS II, based on ISO 13660 quality standards, for processing the images. The PT of a printed paper requires the measurement of $L^*a^*b^*$ values on the opposite side of printed areas, in contrast with the non-printed area of the same paper sheet. The transmitted light intensity from a specific area of each color (black, white, cyan, magenta, and yellow) was measured using QEA PIAS-II, and thus PT and OD were calculated from the following equations:

$$\text{OD} = \log_{10}(\text{Incident light}/\text{Transmitted light}) \quad (1)$$

$$\text{PT} = \sqrt{(L_p^* - L_u^*)^2 + (a_p^* - a_u^*)^2 + (b_p^* - b_u^*)^2} \quad (2)$$

where L^* , a^* , b^* are the CIE chromatic coordinates, and the subscripts u and p refer to areas of unprinted and back of the printed black spot, respectively.

The other printing properties, namely inter-color bleed (ITCB) and circularity (black), were also evaluated by means of QEA PIAS-II with high-resolution module (5 $\mu\text{m}/\text{pixel}$ with 3.2 mm $\times$ 2.4 mm). This was used to measure the raggedness, which

can be defined as the geometric distortion of the line and dots, given by the standard deviation of the residue from the lines and dots adjusted to their ideal limit. The higher the raggedness, the worse the ITCB and circularity.

Statistical analysis

In order to observe the interactions between coating components and their impact on the printing quality of coated papers, TIBCO's Statistica software was used as a statistical tool for the design of experiments and data analysis. In this study, four continuous factors, namely HCS, P123, PCC and OBA, were selected, each at two levels (0 and 16%), and a full factorial design with two center points was chosen to design the coating experiments. A total number of 18 runs were performed to evaluate the effect of these factors and their interactions on the printing quality, namely: GA; OD for cyan, magenta, yellow, and black; PT; ITCB and circularity for black color in the responses.

Results and discussion

Synthesis of SB and HCS

Figure 2a presents the ATR-FTIR spectra for synthesized cationic starches from etherification and transesterification, using respectively CHPTAC and betaine hydrochloride, in comparison to the NS spectrum. The absorption peaks at 3300 cm^{-1} , 2912 cm^{-1} , 1648 cm^{-1} can be assigned to the $-\text{OH}$, $-\text{CH}_2$ stretching vibrations, and H_2O bending vibration due to water sorption, respectively. Additionally, peaks at 994 cm^{-1} can be attributed to the ether bonds and the absorption band at 897 cm^{-1} can be assigned to C1-H bending in starch. Compared to cooked starch, a new prominent peak at 1473 cm^{-1} can be observed due to the quaternary ammonium group attached to the anhydroglucose unit (AGU) (Wang and Cheng 2009; Hebeish et al. 2010). Furthermore, the absorption band at 1750 cm^{-1} is assigned to the ester bond in SB.

Figure 2b shows the ^1H -NMR spectra for HCS and SB, compared to the spectrum of cooked starch. The singlet at 3.28 ppm is assigned to the nine hydrogens of methyl groups of the quaternary ammonium. The resonances from 3.5 to 4 ppm represent the hydrogens

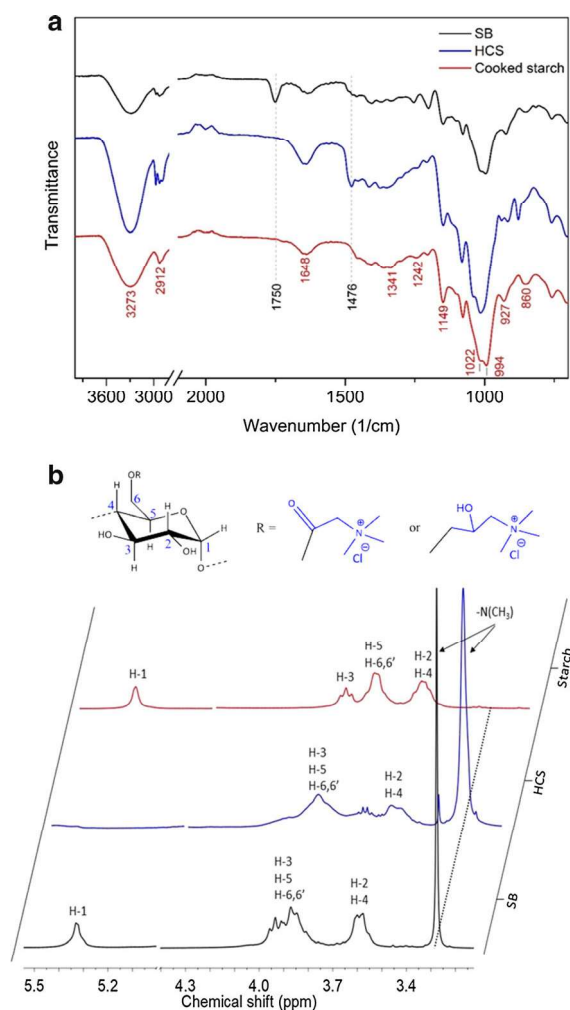


Fig. 2 ATR-FTIR (a) and ¹H-NMR (b) spectra for cationic starch ether and starch betainate, compared to cooked starch

attached to carbons 2, 4, 5, 6 (H-6 and H-6'), and 3 of AGU, typically in that order. The doublet for the H-1(α) anomeric proton lies downfield (5.35 ppm). There was a certain shift upfield and broadening of all signals upon cationization. No impurities were detected in SB, but the HCS spectrum displayed a singlet at 3.33 ppm and a quadruplet at 3.65 ppm, none of which belong to the canonical structure of cationic starches. The former could be due to quaternary ammonium groups arising from substitution on hydroxypropyl chains, instead of the hydroxyl groups of AGU.

An important hypothesis regarding the reaction is that enzymatic cooking improves its efficiency. Figure 3a shows the effect of cooking and reaction time

on the DS of the synthesized HCS. It can be observed that the DS increases from 0.20 to 0.33 and from 0.34 to 0.43 with the increase in the reaction time from 3 to 24 h, when native and cooked starches were used as raw materials for the etherification reactions, respectively. This is likely due to the formation of more porous starch granules, which facilitates the access of the reagent to hydroxyl groups (Huber and BeMiller 2001). It was also observed that the cooking of starch enables the homogeneous dispersion of starch granules in the solvent by increasing the solubility and decreasing its viscosity, as seen in Fig. 3b (Gao et al. 2012).

Undoubtedly, due to the cleavage of 1–4 α -D-glucopyranosyl linkages of amylose and amylopectin, the inherent viscosity decreases with the enzymatic pre-treatment, from 199.4 cm³ g⁻¹ (NS) to 151.8 cm³ g⁻¹ (cooked starch). The viscosity was further reduced by 43–45% when using them in etherification. Likewise, the hydrolysis of starch molecules in highly alkaline media and at high temperature is evidenced by a loss of viscosity after functionalization. Nonetheless, after reaction times beyond 3 h, further hydrolysis is either negligible or compensated by the effects of cationization on polymer–solvent interactions.

Like etherification, the increase in DS and decrease in viscosity were also observed in the synthesis of SB. However, DS increased much more abruptly, from 0.01 to 0.33, when using NS and cooked starch in the transesterification reaction, respectively, proving the poor reaction efficiency with NS. Given that the inherent viscosity decreased by $\sim 73\%$, starch faced higher depolymerization during functionalization, mostly due to the previous alkalization of starch at high temperature.

Properties of coated sheets

Micrographs of BP and coated paper sheets are displayed in Fig. 4. None of those formulations involved PCC, so the characteristic hexagonal crystals that can be appreciated correspond to the starting material, i.e., PCC that had been added to the pulp before the formation of the paper web. As expected, the PCC particles close to the surface and nearby cellulosic fibers become strongly bound by HCS (Fig. 4b) and SB (Fig. 4d). Then, the addition of Pluronics, specifically P123, resulted in less binder (HCS and SB) at the surface (Fig. 4c and, more

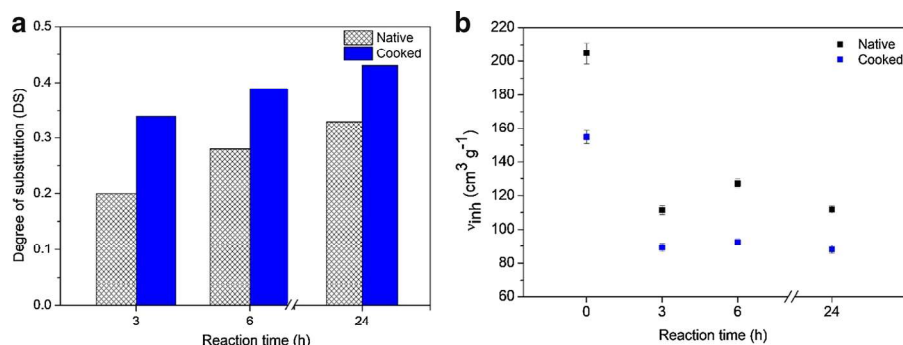


Fig. 3 Effect of reaction time and enzymatic cooking on degree of substitution (a) and inherent viscosity (b) of HCS

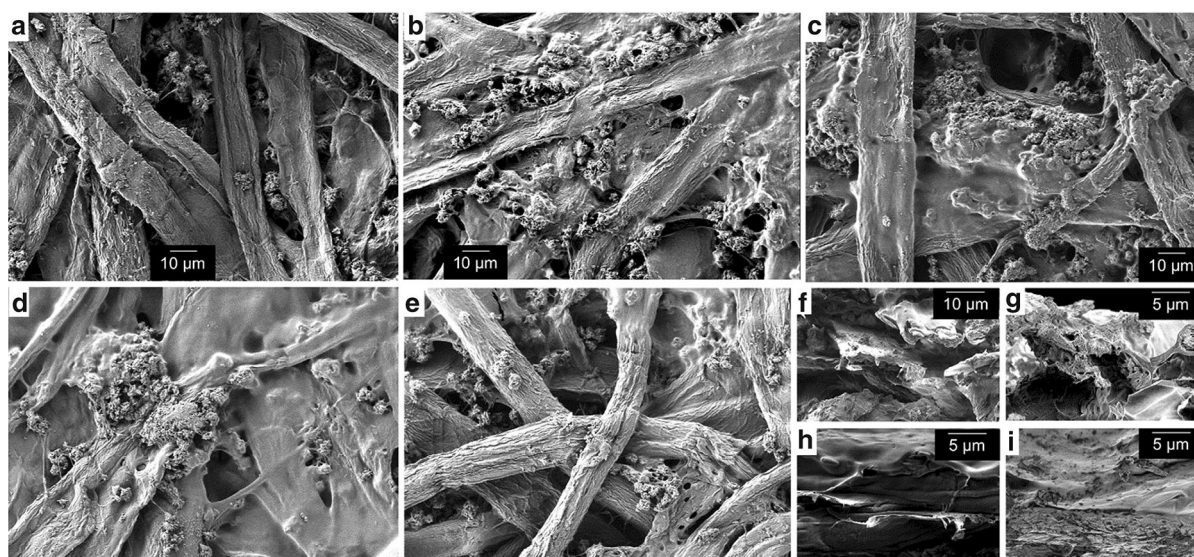


Fig. 4 SEM images of the surface of uncoated paper (a), and of the surface (b–e) and cross-section (f–i) of paper sheets that underwent different surface treatments: with HCS (b, f), with HCS and P123 (c, e), with SB (d, h), and with SB and P123 (e, i)

clearly, 4e). Instead, the presence of this amphiphilic copolymer favors the penetration of binder through the cross-section of paper (Fig. 4f–i). This effect is more evident for SB, going from a thin layer over fibers (Fig. 4h) to an apparent depth of at least 15 μm (Fig. 4i). This is more than three times the nominal thickness gain of sheets, which is shown in Table 3.

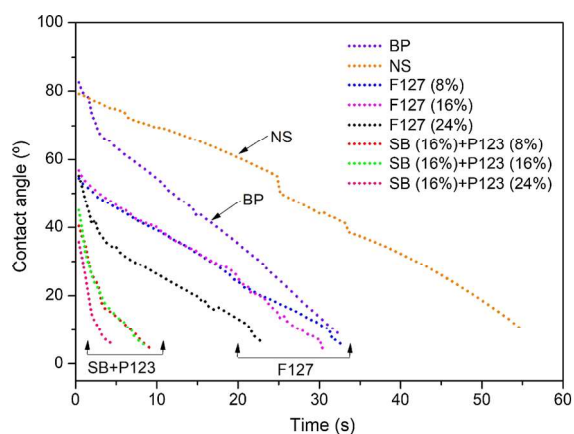
Table 3 also displays the Bendtsen roughness, the Gurley permeability, and the SWCA values for papers coated with SB, Pluronics and/or PCC. For instance, addition of SB decreased the permeability of the paper surface and increased its smoothness. It can be appreciated that porosity was generally lower in the printed areas, although differences are not significant when P123 and SB were combined.

The static contact angle increased, although slightly, with SB or PCC. As intended, the interaction with non-ionic surfactants (Pluronics) decreased this angle. This increase in surface hydrophilicity was mimicked or even made more evident by the DWCA profiles and the water penetration plot (Figs. 5, S1 and S2). Through the process of wetting paper sheets coated with SB and Pluronics for 1 min, water drops reached contact angles below 5° after less than 20 s. Furthermore, liquid penetration was practically instantaneous when those sheets were immersed in water. Hence, Pluronics are expected to enhance the penetration, and thus fixation, of any polar ink.

In order to clarify the interactions between components, it should be noted that PCC, Pluronics, OBA

Table 3 Properties of coated papers using different concentrations of SB, Pluronic (P123 and F127), and their combination in coating formulations

	Conc. (%)	Roughness (mL/min)	Gurley(mL/min)		SWCA (°)	Coating thickness (μm)	Whiteness	Gamut volume/10 ³	Weight gain (g/m ²)
			Unprinted	Printed					
Reference (NS)		329 ± 13	318 ± 07	320	72 ± 1	3	162.8 ± 1.3	132 ± 1	1.8 ± 0.3
SB	8	324 ± 14	379 ± 14	363	75 ± 2	4	162.3 ± 0.5	146 ± 1	2.5 ± 0.2
	16	311 ± 07	397 ± 04	364	77 ± 2	5	164.5 ± 0.3	151 ± 1	1.9 ± 0.2
	24	376 ± 09	420 ± 16	366	79 ± 1	4	164.1 ± 0.7	153 ± 1	2.3 ± 0.3
P123	8	368 ± 09	407 ± 06	378	50 ± 3	5	165.1 ± 0.2	153 ± 1	2.9 ± 0.2
	16	379 ± 30	381 ± 05	368	43 ± 2	5	165.6 ± 0.2	152 ± 2	2.9 ± 0.1
	24	357 ± 09	354 ± 09	320	47 ± 1	6	165.8 ± 0.4	150 ± 2	3.0 ± 0.2
F127	8	378 ± 38	356 ± 05	313	63 ± 3	4	163.6 ± 0.6	145 ± 2	2.4 ± 0.2
	16	363 ± 28	325 ± 50	325	57 ± 1	4	163.4 ± 0.4	141 ± 3	2.7 ± 0.1
	24	329 ± 18	444 ± 13	388	53 ± 2	6	162.2 ± 0.7	150 ± 1	2.7 ± 0.2
PCC	8	414 ± 37	347 ± 05	296	75 ± 2	3	160.9 ± 0.3	149 ± 1	2.5 ± 0.3
	16	370 ± 15	381 ± 11	319	83 ± 2	4	161.3 ± 0.1	146 ± 1	2.5 ± 0.2
	24	365 ± 05	367 ± 02	370	80 ± 2	5	162.5 ± 1.1	143 ± 1	2.7 ± 0.1
P123 (with SB)	8	375 ± 22	376 ± 21	358	51 ± 3	3	164.9 ± 1.7	162 ± 3	2.4 ± 0.1
	16	383 ± 36	321 ± 09	354	48 ± 2	5	165.4 ± 0.8	161 ± 2	2.8 ± 0.1
	24	368 ± 13	374 ± 13	372	40 ± 3	4	163.6 ± 0.5	164 ± 2	2.7 ± 0.1

**Fig. 5** Effect of Pluronic (P123 and F127) on the dynamic contact angle

and AKD were always added after cooling down the starch solution to 50 °C. It should also be stressed that P123 and F127 have critical micelle concentrations of 0.313 mM (20 °C) and 0.56 mM (25 °C), respectively. These values are lower than the concentration of Pluronic used in the experiments reported here; additionally, the critical micelle temperatures of these

surfactants are well below 50 °C, which also support the idea that Pluronic are found as micelles (He and Alexandridis 2018).

TGA contributes to understand the adsorption of Pluronic in the presence of a cationic polymer. Figure 6 represents the TGA and DTG curves of dip-coated paper samples. It can be seen that the major decomposition areas can be divided into three zones, 275–350 °C, 300–350 °C and 325–400 °C for SB coatings, filter papers and Pluronic coatings, respectively. Interestingly, an increase in the major decomposition area of both Pluronic was observed when filter papers were coated with SB and Pluronic, indicating that the former favors the adsorption of the latter.

Paper printing properties

Gamut area

It was observed that the GA, presented in Fig. 7a, increased by 8.6%, 9% and 12.5% using 8%, 16% and 24% dry solids content of SB, respectively, compared

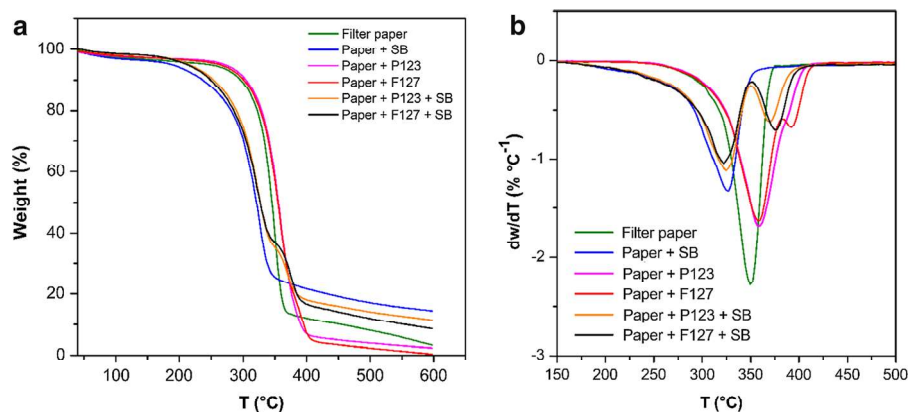


Fig. 6 TGA (a) and DTG (b) curves for filter paper, paper + SB, paper + P123, paper + F127, paper + P123 + SB and paper + F127 + SB

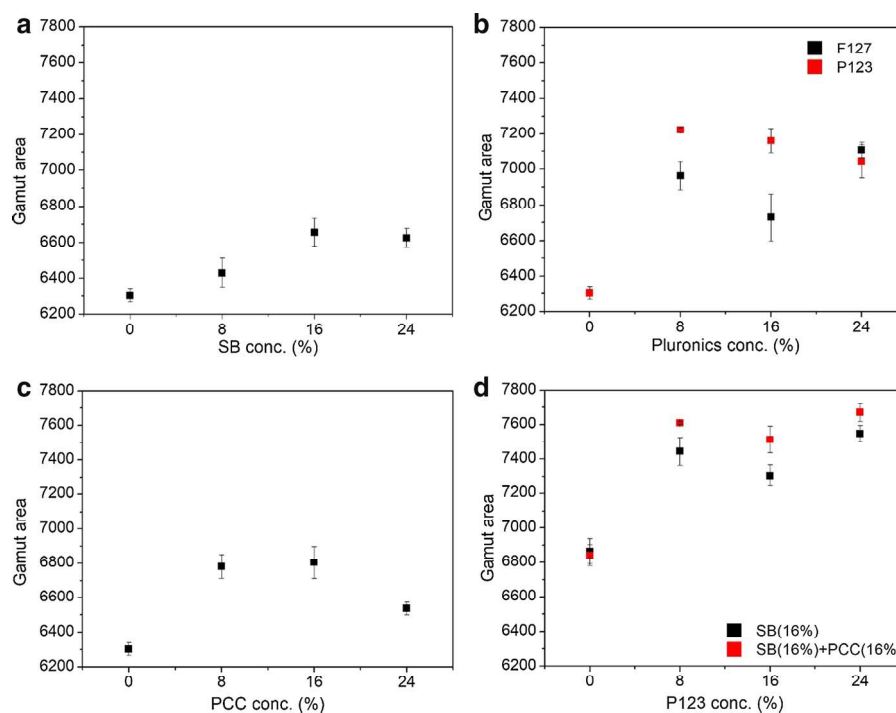


Fig. 7 Effect of different concentrations of SB (a), Plurionics (b), PCC (c), and their combinations (d) on GA

to NS coating. Plausibly, the high DS led to higher deposition of SB on the paper surface, resulting into improved GA (Gigac et al. 2016b; Niegelhell et al. 2018).

Similar to GA, GV, which considers the color luminance L , besides a and b , also increased with increasing SB concentration. The maximum increase was 16.4%, using 24% of SB, compared to NS coating (Table 3).

In Fig. 7b, the GA for different concentrations of Plurionics P123 and F127 is presented. GA was improved by 14.6% using 8% of P123 in the coating solution; however, the GA was further reduced by increasing the P123 concentration from 8 up to 24%. For F127, the 8% addition improved the GA by 10.5%, but further increase in the concentration of F127, from 8 up to 16%, reduced the GA as well. However, the use of 24% of F127 showed almost equal GA increase as

24% of P123, 11.8% and 12.8%, respectively. The increase of GA can be explained by the amphiphilic nature of Pluronics, which facilitates the strong adsorption of these components on cellulosic surfaces (Liu et al. 2010). Additionally, Pluronics form inclusive complexes with starches, leading to the formation of self-supporting flocs in the coating formulation, and enhancing the dispersion of other coating components (Petkova-Olsson et al. 2016, 2017). Remarkably, the lowest amount of P123 and F127 (8%) was found to be more favorable to improve GA. This area was also improved by $\sim 7.9\%$ in the presence of PCC at a concentration of 8% or 16% (Fig. 7c), which is related to the gain in hydrophobicity of the paper surface. However, roughness increased with the presence of PCC and GA was further decreased by 3.7% with a large content of PCC (24%) in the coating formulation.

The effect of P123 coatings in combination with SB (16%) and SB (16%)/PCC (16%) is displayed in Fig. 7d. It is observed that GA increases by 8.5–9% using P123 or a mixture of P123 and PCC. It was further improved significantly by 16–20% and 19–22% with the presence of SB/P123 and SB/P123/PCC, respectively. This enhancement can be explained by the sorption of Pluronics on the cellulosic surface, which increases in combination with a highly cationic polymer (Liu et al. 2011, 2010). Moreover, formation of amylose-Pluronics inclusion complexes may also facilitates the immobilization of the ink pigments on the coated paper surface, improving GA.

Optical density

Figure 8 presents the OD of the black color with increasing concentration of SB (A), Pluronics (B), PCC (C) and SB/P123/PCC (D). Figure 8c shows the effect of PCC concentration on OD. OD for PCC coating correlates with the Gurley permeability, attaining deeper tones as the sheet became more resistant to air flow (Kasmani et al. 2013). The highest improvement was observed at 8% of PCC. Likewise, OD followed the same trends as GA, and thus it increased with increasing concentration of SB and P123/F127. Above all, Fig. 8d shows that the highest increase in OD was achieved with the combination of SB-P123-PCC in the coating formulation.

Inter-color bleed (ITCB), print-through (PT) and circularity for black color

Figure 9 presents the ITCB, PT and circularity (black dots) of SB, PCC, P123, SB/P123 and SB/P123/PCC coated papers. Similar to GA, ITCB was also improved (*i.e.*, reduced) upon the addition of these components. The highest decrease in ITCB, 15.9%, was observed with SB/P123/PCC coatings. Unlike GA and ITCB, PT of SB/P123 or SB/P123/PCC-coated paper showed a higher PT at the concentrations used in this work, due to decrease in viscosity of the coating formulation, letting the formulation go deeper into the cellulose matrix, which increased the show-through of ink from the other (non-coated) side of the paper. The presence of PCC on the cellulosic surface provided a better improvement in the PT compared to SB or P123 coated papers. Circularity of black dots generally correlates with the ITCB, improving with the formulation containing SB and P123, due to better fixation of ink particles onto the surface.

Whiteness and fluorescence quenching

Whiteness, positively correlated with ISO brightness, represents a paper's ability to equally reflect a balance of all wavelengths of light across the visible spectrum (Hu et al. 2017). The addition of OBA on the paper surface is a cost-effective solution in papermaking to increase the whiteness of printing and writing papers (Shi et al. 2012). Therefore, the interaction between OBA and the other coating components is important. From Table 4, it can be noted that the presence of OBA improved the whiteness of the coated paper but the presence of HCS quenched this agent, resulting in lower whiteness (Fig. S2). It is also worth mentioning that the presence of P123 and PCC did not show any further improvement in the whiteness.

In comparison to NS coatings, whiteness increased by 11% with the addition of OBA. As aforementioned, HCS (with OBA) reduced the whiteness of coated papers by $\sim 10.85\%$ due to the OBA quenching, irrespective of the presence of any other components. Interestingly, such loss of whiteness was not observed when SB was used instead of the cationic starch ether (Fig. S2).

To understand the OBA quenching effect in the presence of HCS and SB, fluorescence emission spectra were recorded for solutions containing OBA

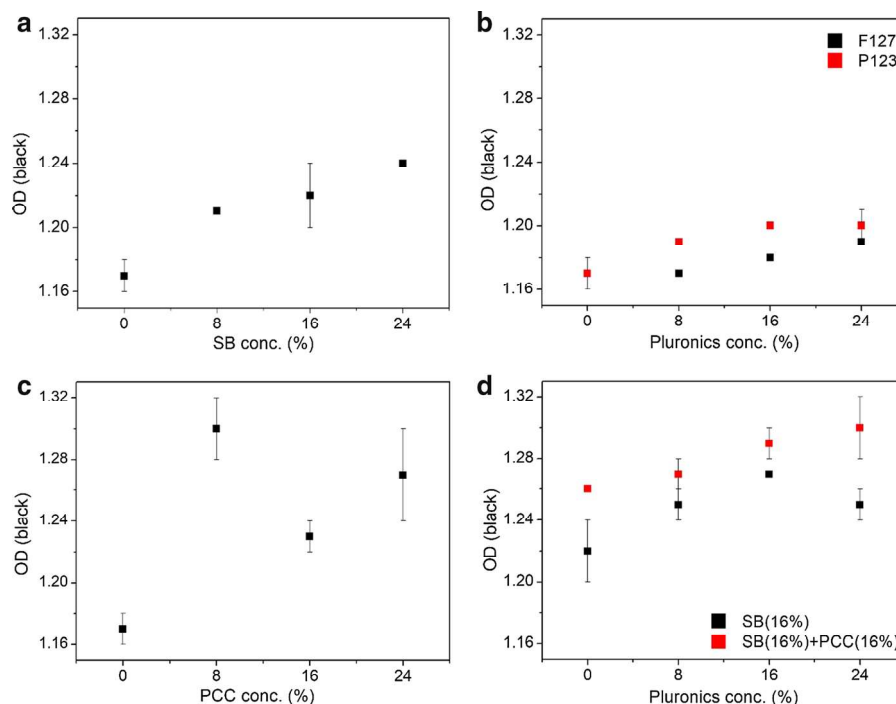


Fig. 8 Effect of different concentrations of SB (a), Pluronic (b), PCC (c) and their combinations (d) on OD (0%: reference coating using NS)

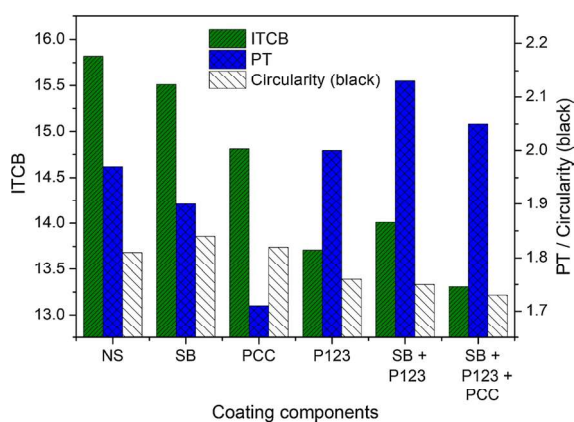


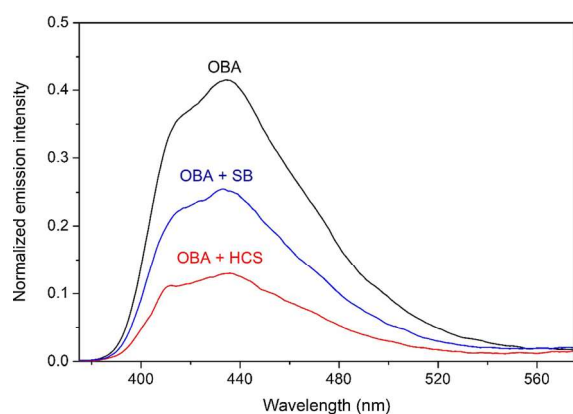
Fig. 9 Effect of different coating components on ITCB, PT and circularity of black color

(1.84 ppm) and either cationic starch (6.1 ppm), so as to keep the same ratio as in coating formulations (6% OBA/16% CS). Fluorescence quenching was clear in the presence of all cationic starches but, in the case of HCS, the intensity of the emission of blue light (~ 440 nm) decreased almost by a factor of 4 (Fig. 10).

Quenching was possibly due to the formation of a non-fluorescent complex, where the sulfonate groups of OBA donate electrons to the quaternary ammonium groups of HCS. Still, the most plausible explanation is the aggregation-caused quenching, where aggregation is promoted by electrostatic interactions. The reason for this is that solutions at higher concentration, such as 9.2 ppm OBA/24.4 ppm HCS, showed Rayleigh scattering to such extent that no reliable spectrum could be obtained, even though a concentration of 24.4 ppm lies much below the solubility limit of HCS. In other words, there was a phase transition from solution to dispersion when both solutions, each of them displaying negligible light scattering, were mixed. However, regardless of the quenching mechanism, neither this aggregation nor that extent of quenching was observed when using SB/OBA at the same concentrations, supporting the previously described retention of paper whiteness. Given that SB and HCS had the same DS, it may be concluded that the cationic starch ester possesses a key advantage over its ether counterpart. This advantage should, undoubtedly, be further explored.

Table 4 Study of interactions among factors. Percentages are related to the total solids content (on the basis of dry weight) of coating formulations

HCS (%)	P123 (%)	PCC (%)	OBA (%)	GA	OD (cyan)	OD (magenta)	OD (yellow)	OD (black)	PT	ITCB	Circularity (black)	Whiteness
0	0	0	0	6512	0.76	0.87	1.31	1.23	1.6	15.5	1.95	146
0	0	0	6	6301	0.74	0.84	1.31	1.17	1.97	15.8	1.81	162
0	0	16	0	6596	0.76	0.88	1.33	1.20	1.56	15.4	1.98	146
0	0	16	6	7074	0.80	0.91	1.36	1.21	1.76	14.4	1.81	162
0	16	0	0	6758	0.79	0.89	1.33	1.22	1.76	14.5	1.80	146
0	16	0	6	6922	0.80	0.90	1.34	1.20	1.86	13.7	1.76	162
0	16	16	0	7004	0.81	0.90	1.34	1.20	1.80	14.2	1.74	146
0	16	16	6	6802	0.81	0.90	1.33	1.21	1.69	14.0	1.71	163
8	8	8	3	7122	0.82	0.90	1.34	1.19	1.65	13.8	1.80	148
8	8	8	3	7212	0.82	0.91	1.33	1.20	1.69	14.2	1.81	147
16	0	0	0	6610	0.80	0.78	1.33	1.25	1.99	16.0	1.79	144
16	0	0	6	6656	0.74	0.77	1.37	1.24	1.78	16.2	1.79	145
16	0	16	0	6971	0.77	0.88	1.31	1.20	1.82	15.6	1.95	144
16	0	16	6	6739	0.79	0.78	1.31	1.23	1.82	15.6	1.84	146
16	16	0	0	7479	0.83	0.92	1.36	1.22	1.80	12.7	1.83	146
16	16	0	6	7443	0.86	0.85	1.50	1.42	1.66	16.3	1.89	146
16	16	16	0	7427	0.83	0.91	1.35	1.20	1.72	13.9	1.76	145
16	16	16	6	7670	0.85	0.93	1.37	1.22	1.84	13.2	1.71	148

**Fig. 10** Fluorescence emission spectrum of OBA in presence of HCS and SB. An excitation wavelength of 350 nm was used to record all spectra

Statistical analysis

Under the hypothesis that the presence of HCS, P123, PCC and OBA in coating formulations would have a positive influence on printing quality parameters, TIBCO's Statistica software allowed to discriminate

between those four factors. An in-depth and detailed assessment can be found in the Supplementary Information, including different statistical parameters (such as Fisher–Snedecor's F , Student's t , and β probability) and model validation plots.

Briefly, after processing the results of Table 4, the most relevant variables for the improvement of GA were found to be HCS concentration ($p = 0.005$), P123 concentration ($p = 0.0006$), and their binary interaction ($p = 0.05$). The presence of PCC and OBA and their interactions with other variables did not significantly affect the GA. Regarding OD for cyan, influential factors were, once again, the concentrations of HCS ($p = 0.04$) and P123 ($p < 0.0003$). Nonetheless, the OD for magenta was only influenced in a significant way by P123 ($p = 0.005$). Likewise, only P123 ($p < 0.005$) exerted a significant impact on ITCB. For whiteness, the most significant effect was provided by OBA ($p < 0.001$), HCS and their interaction.

An alternative experimental design, considering three levels for each factor (instead of two), resulted in

significant correlations for the OD of yellow, the OD of black and circularity (Table S1), three responses for which the aforementioned model failed to do so. For instance, circularity was found to be significantly improved by P123 ($p < 0.0005$) and OBA ($p < 0.02$). Other than that, there was a high degree of agreement with the two-level case, highlighting the importance of HCS and P123.

Conclusions

The effect of an unconventional combination of coating components, highly substituted cationic starch and Pluronic, on the printing quality of office papers was investigated. As a key novelty, cationic starch refers not only to its typical ether form, but also to starch betainate, an ester that has been suggested for bulk addition in sheet forming but not (as far as the authors are concerned) for paper coating. A 24% coating weight of starch betainate increased the gamut area by 12.5%, whilst Pluronic P123 and F127 (8% coating weight) attain improvements of 14.6% and 11.8%, respectively. Both cationic starches, ether and ester, showed the same outcome for improving the paper printing properties in presence and absence of Pluronic. Nonetheless, while the ether caused a certain loss of whiteness, as it quenches the fluorescence emission of the optical agent, such loss was not found when starch betainate was used. The ability of starch betainate of keeping the whiteness gain of an anionic brightening agent is a key finding of this work.

Remarkably, the statistical analysis indicated that besides the aforementioned individual effects of cationic starch and Pluronic, the binary interaction thereof had a significantly positive influence on the gamut area. Furthermore, the optical density (cyan, magenta, yellow and black), inter-color bleed and circularity were successfully correlated with the independent variables. Overall, the combination of cationic starch and Pluronic, accounting for a total solids content of 16%, was found to exert a great impact on the global printing quality.

Authors' contributions All authors made substantial contributions to the conception of the work, the acquisition and interpretation of data, and writing. All authors approve the manuscript. All authors agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or

integrity of any part of the work are appropriately investigated and resolved.

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Code availability Not applicable.

Declarations

Conflict of interest The authors declare that there is no conflict of interest and that they do not have competing interests.

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Consent to participate Not applicable. No studies involving humans and/or animals.

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