

Research article

Dynamic Penetration Profile of Starch Betainate, Pluronic and PCC Coated Papers

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Abstract.

Despite changes in optical and printing properties, the applied coating components on the paper surface have a significant impact on the surface chemistry of office paper. Depending on the use, such as ink penetration for printing and writing papers, an optimal hydrophobic and hydrophilic balance may be beneficial. In this study, several coating components including starch betainate, Pluronic, and precipitated calcium carbonate were employed to coat base paper (paper without any surface treatment). The influence of these components on water penetration was investigated using dynamic penetration. When compared to native starch coated papers, paper coated with starch betainate (a cationic starch ester) showed reduction in hydrophobicity and increased water penetration. Moreover, this effect was further enhanced with the use of Pluronic. Likewise, hydrophobicity decreased as the concentration of starch betainate, precipitated calcium carbonate and Pluronic increased. Furthermore, water penetrated even more quickly when the combination of these components compared with the individual component coatings.

Keywords: hydrophobicity, PCC, Pluronic, starch betainate, water penetration

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1. Introduction

Papers are generally coated with starch to, among other purposes, enhance the surface hydrophobicity, and thus to exhibit controlled water absorption in high moisture environment. Nevertheless, certain paper properties, such as the printing quality, often demand a quick penetration of carrier solvents for water-based inks [1]. Some other factors such as sufficient positive charge on the surface and a more closed surface can also help to improve the printing quality by retaining the ink pigments on the paper surface [2–4]. In this sense, starch betainate (a cationic starch ester), Pluronic (triblock co-polymers) and precipitated calcium carbonate (PCC) were identified as good coating components to produce papers with superior printing quality [5,6].

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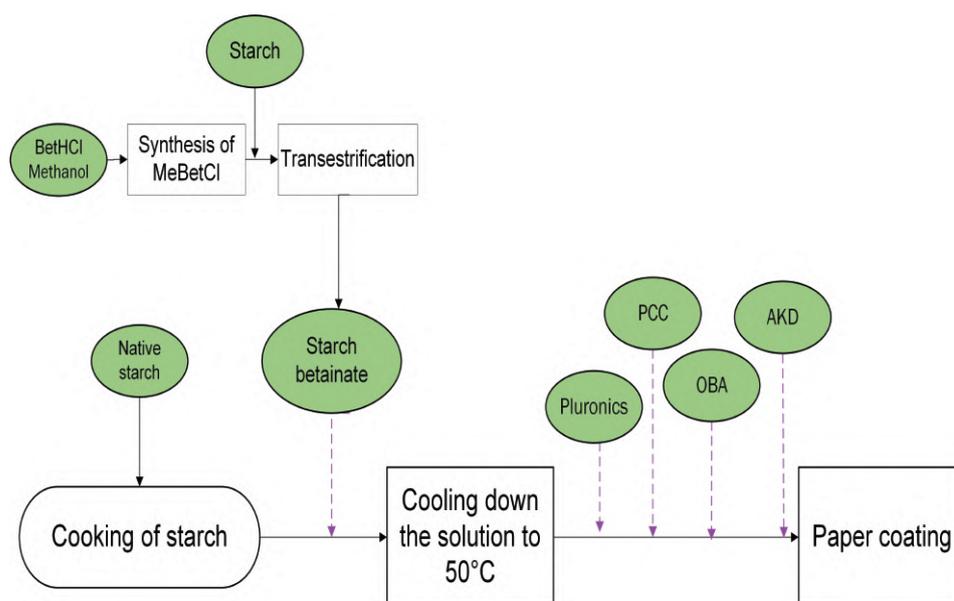


Figure 1: Outline of the experimental methodology.

In this study, paper sheets were coated with different concentrations of coating components, namely starch betainate, Pluronics and PCC. The effect of these components on the surface hydrophobicity and water absorption of coated papers were measured by water penetration profiles.

2. Methods

An industrial calendered uncoated paper (base paper, BP), produced from bleached eucalyptus kraft pulp with a basis weight of $\sim 78 \text{ g m}^{-2}$, was used as substrate for performing surface coating. A laboratory coater from Mathis AG was used to coat the base papers. An applicator roll (coupled with the coater) was used to achieve 1.5 to 3 g m^{-2} per side, on the basis of dry coating weight (ISO standard 536:1995). Pre-drying was performed using a pre-installed infrared system. Besides native starch (NS, used as reference), base papers were coated with starch betainate (SB), Pluronics with different degrees of hydrophilicity (P123, F127), PCC, and combinations thereof. The concentrations of coating components are shown in Table 1 and Table 2. Starch was used as host component for all coatings and a schematic representation of experimental procedure is shown in Fig. 1.

A Surface & Sizing Tester from Emtec was used to obtain the water penetration profile. This device detects the ultrasound absorption or scattering from the air-water interfaces of small bubbles, since air flows out from the pores of the sheet as water penetrates through it. The dynamic water contact angle (DWCA) was measured up to 60 s on an

OCA 20 goniometer (Dataphysics, Germany) using the sessile drop method. A droplet of deionized water (10 μ L) was automatically poured onto the coated paper surface.

TABLE 1: Composition of formulations for starch betainate (SB), Pluronics and PCC coatings expressed as %w/w, on the basis of dry coating weight.

Ingredients	Coating formulations				
	SB coatings	P123 coatings	F127 coatings	PCC coatings	Ref. coatings
Starch betainate	8 / 16 / 24	–	–	–	–
Pluronics P123	–	8 / 16 / 24	–	–	–
Pluronics F127	–	–	8 / 16 / 24	–	–
PCC	–	–	–	8 / 16 / 24	–
Native starch	85.6 / 77.6				93.6
OBA / AKD	6 / 0.4				

TABLE 2: Composition of formulations containing starch betainate (SB), Pluronics and PCC in combination expressed as %w/w, on the basis of dry coating weight.

Ingredients	Coating formulations		
	SB and Pluronics-P123 coatings	SB, Pluronics-F127 and PCC coatings	Ref. coatings
Starch betainate	16	16	–
Pluronics P123	8 / 16 / 24	8 / 16 / 24	–
PCC	–	16	–
Native starch	69.6 / 61.6 / 53.6	53.6 / 45.6 / 37.6	93.6
OBA / AKD	6 / 0.4		

3. Results

It was found that the native starch coating showed the lowest water absorption (highest sizing degree) compared to any other coatings which further increases with the use of PCC, starch betainate (SB), Pluronics (F127 and P123) and the combination thereof. Papers coated using the combination of SB, Pluronics and PCC showed high absorption of water (lowest sizing degree).

Water penetration can also be inversely correlated to the t_{95} , time at which ultrasonic intensity decreases to 95% of the maximum value. This time was higher for native starch-coated paper (0.29 s) than for BP (0.14 s). With the use of 8% ($t_{95} = 0.17$ s), 16% ($t_{95} = 0.21$ s) and 24% ($t_{95} = 0.24$ s) of SB, a negative influence of concentration was observed on the water penetration (Fig. 2A). A similar effect of concentration was also observed when varied concentrations of PCC were used on paper surface ($t_{95} = 0.15, 0.15$ and 0.19 s for 8, 16, 24 % of PCC in the formulations, respectively) (Fig. 2B). Further, t_{95} was not

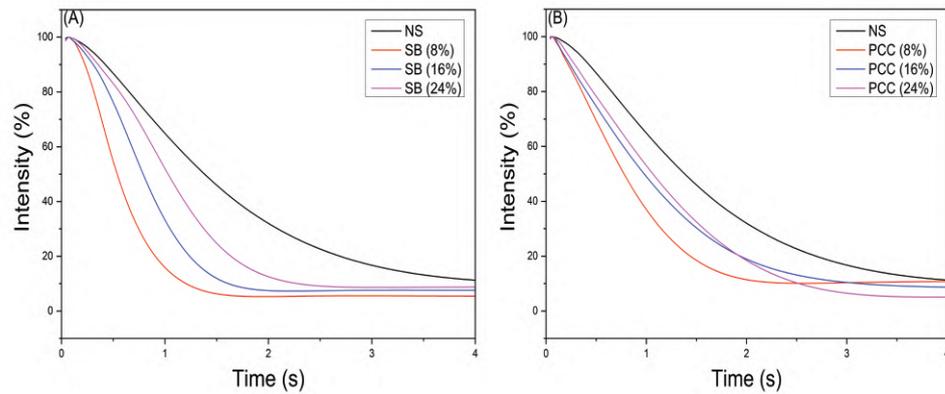


Figure 2: Dynamics of water penetration through paper sheets coated with NS, SB (A) and PCC (B).

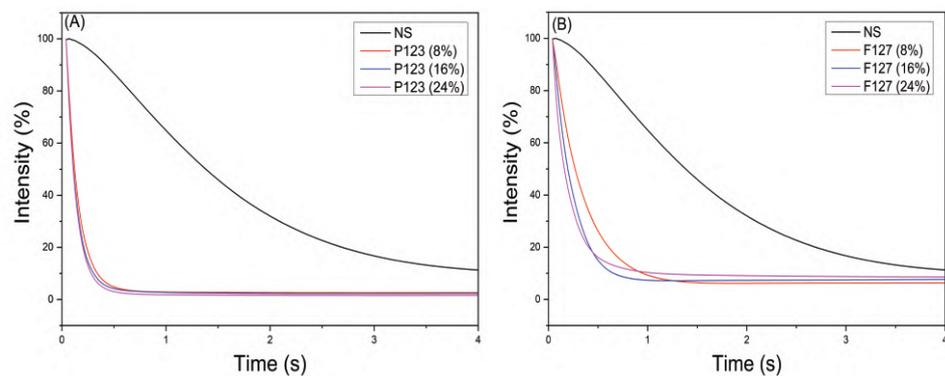


Figure 3: Dynamics of water penetration through paper sheets coated with NS, Pluronic-P127 (A) and Pluronic-F127 (B).

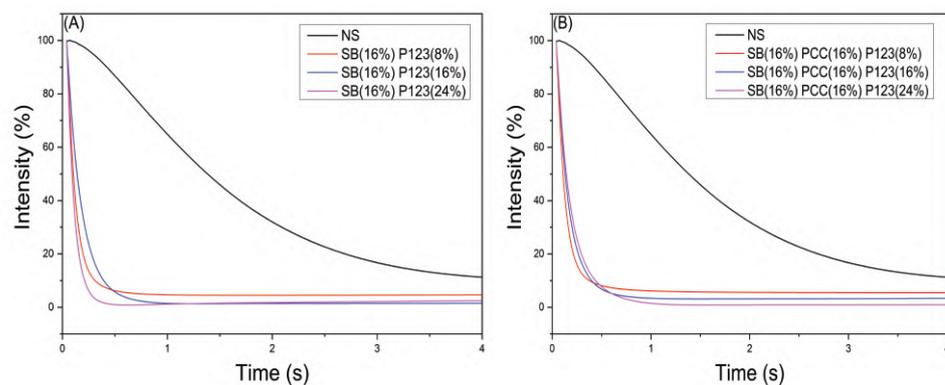


Figure 4: Dynamics of water penetration through paper sheets coated with NS, SB and Pluronic-P123 (A); and NS, SB, Pluronic-P123 and PCC (B).

measurable due to quick absorption for P123 coated papers and it was 0.06 and 0.05 for 8 and 16% of F127, respectively, whereas 24% of F127 showed a quick absorption of water. Also, coating formulation containing combination of SB, P123 and PCC showed non-measurable t_{95} due to quick absorption of water in PDA (Fig. 3A, 3B, 4A and 4B).

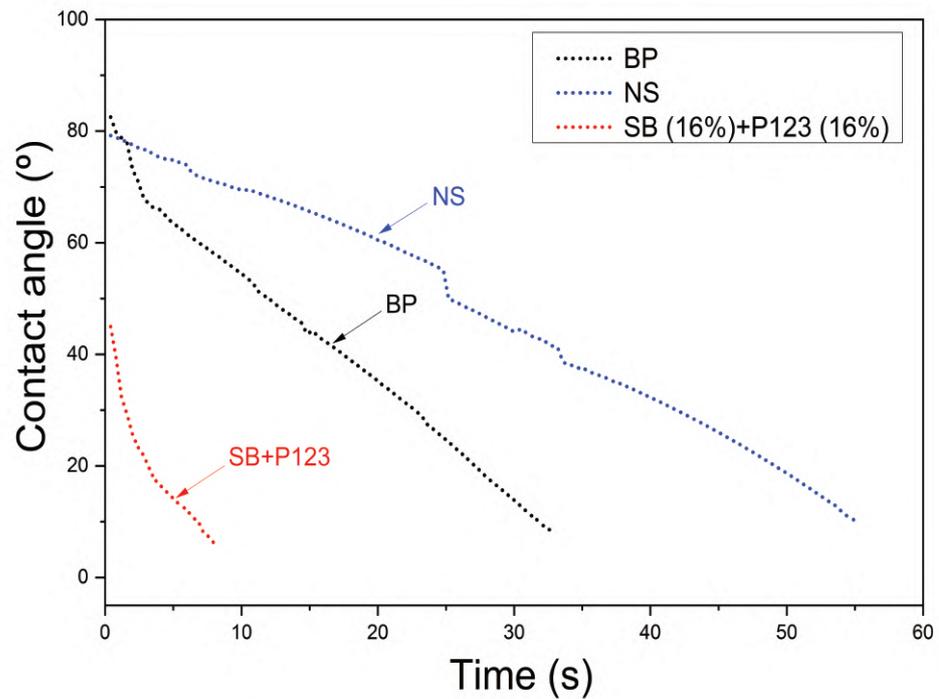


Figure 5: Effect of SB-Pluronics (P123) coating on hydrophobicity of coated paper surface.

As also evidenced by the contact angle, surface of starch coated papers (NS) showed higher time to absorb a water drop, whereas SB (16%) enhanced the static water contact angle (SWCA) from 72 ± 1 (°) (for NS coating) to 77 ± 1 (°). Similar trend was also observed with PCC, increasing SWCA to 83 ± 1 (°). However, Pluronics (P123 and F127) showed remarkably lower SWCA—43 to 63 (°)—compared to NS or SB coated paper. Also, surface of SB and P123 coated papers were also highly hydrophilic with SWCA values of 48 ± 2 (°) for 16% of each component (Fig. 5).

Addition of SB in the coating formulation decreased the presence of hydroxyl groups on the surface of coated papers, thus increased the hydrophobicity of the coated paper surface. The amphiphilic nature of Pluronics, nonionic triblock copolymers of polyethylene oxide (PEO) and polypropylene (PPO), facilitates the absorption of these components on the cellulosic surfaces, additionally, Pluronics forms inclusive complexes with the starches, leading to form self-supporting supramolecular assemblies in formulations, thus enhanced the dispersion of other coating components [7–9]. Apart from this, Pluronics also increased the hydrophilicity of the coated surface, as long as their concentration in the coating formulations was higher than the critical micelle concentration.

4. Conclusions.

The delay in water absorption was correlated with the surface hydrophobicity for coated papers. Native starch coated papers take around 60 s to absorb a single drop of water whereas for the papers coated with starch betainate, Pluronic and PCC the absorption time was reduced to 5-10 s (Fig. 5). A similar trend of water penetration was observed with a high amount of water in the dynamic penetration analyzer. Coatings with these components can be useful for the application such as paper printing quality where a proper hydrophilic/hydrophobic balance is desirable, along with a good water penetration property.

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References

- [1] Sharma M, Aguado R, Murtinho D, Valente AJM, De Sousa APM, Ferreira PJT. A review on cationic starch and nanocellulose as paper coating components, *International Journal of Biological Macromolecules* 2020;162:578–598. <https://doi.org/10.1016/j.ijbiomac.2020.06.131>
- [2] Lee HL, Shin JY, Koh C-H, Ryu H, Lee D-J, Sohn C. Surface sizing with cationic starch: Its effect on paper quality and the papermaking process. *Tappi Journal* 2002;1:34–40.
- [3] Lamminmäki TT, Kettle JP, Gane PAC. Absorption and adsorption of dye-based inkjet inks by coating layer components and the implications for print quality. *Colloids Surfaces A: Physicochemical. Engineering Aspects* 2011;380:79–88.

- [4] Gigac J, Stankovská M, Opálená E, Pažitný A. The effect of pigments and binders on inkjet print quality. *Wood Research* 2016;61:215–226.
- [5] Sharma M, Aguado R, Murtinho D, Valente AJM, Ferreira PJT. Novel approach on the synthesis of starch betainate by transesterification, *International Journal of Biological Macromolecules* 2021;182:1681–1689. <https://doi.org/10.1016/j.ijbiomac.2021.05.175>
- [6] Sharma M, Aguado R, Murtinho D, Valente AJM, Ferreira PJT. Synergetic effect of cationic starch (ether/ester) and Pluronic for improving inkjet printing quality of office papers. *Cellulose*. 2021;28:10609–10624. <https://doi.org/10.1007/s10570-021-04206-w>
- [7] Liu X, Wu D, Turgman-Cohen S, Genzer J, Theyson TW, Rojas OJ. Adsorption of a nonionic symmetric triblock copolymer on surfaces with different hydrophobicity. *Langmuir* 2010; 26(12):9565-74. <https://doi.org/10.1021/la100156a>
- [8] Petkova-Olsson Y, Ullsten H, Järnström L. Thermosensitive silica-Pluronic-starch model coating dispersion-part I: The effect of Pluronic block copolymer adsorption on the colloidal stability and rheology. *Colloids Surfaces A: Physicochemical Engineering Aspects* 2016;506:245–253. <https://doi.org/10.1016/j.colsurfa.2016.06.032>
- [9] Petkova-Olsson Y, Altun S, Ullsten H, Järnström L. Temperature effect on the complex formation between Pluronic F127 and starch. *Carbohydrate Polymer* 2017;166:264–270.