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Partial Replacement of Cationic Starch by Cationic Hardwood Kraft Lignin Does Not Compromise Key Paper Properties

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Abstract: Competition issues with food industry have recently boosted the exploration of alternative solutions capable of replacing starch in papermaking to a certain extent. Covalent grafting of quaternary ammonium groups onto LignoBoost® *Eucalyptus* kraft lignin has recently shown promise in this regard as the cationic products feature excellent water solubility across the entire pH scale. Considering these suitable properties, cationic kraft lignin was applied and evaluated, for the first time, in the perspective of partial substitution of cationic starch in papermaking, using bleached *Eucalyptus* kraft pulp. Based on an assessment of key paper properties, such as mechanical (tensile, bursting, and tearing indexes), structural (roughness, capillarity rise, air resistance, internal strength, and water contact angle), and optical ones (brightness, opacity, and relative color change), it is safe to conclude that the partial replacement of conventional cationic starch by cationic lignin does not compromise these features. The results also show that properties can be fine-tuned by varying the degree of lignin derivatization, providing paper-specific solutions for replacing starch by lignin potentially available at large-scale at the pulp and paper industry, closing the loop within the circular economy concept.

Keywords: cationic starch; cationic lignin; hardwood kraft pulp; papermaking; water-soluble kraft lignin; bulk paper modification

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1. Introduction

Starch is one of the most valued macromolecular gifts of our ecosphere. In addition to being used for food, starch has long had a multitude of non-food applications [1], including papermaking, where it is today one of the most abundant additives used either in native or modified form [2]. Depending on its mode of application and desired function, starch in papermaking is classified into wet-end starch (e.g., retention agent and dry strength agent), sizing starch (e.g., coating binder and adhesive), and spray starch (e.g., dry strength agent) [3,4]. Advanced compatibility with paper and specific properties can be imparted to starch by various chemical and physical modification approaches [5]. Cationic starch, which is added to the pulp slurry at the wet-end of a paper machine (0.05 to 0.25 wt.%) [6], is a typical example in this regard. Since the fibrous raw material (cellulosic pulp) and many of the fillers are negatively charged, cationic starch acts as a binder of these components by electrostatic interaction, even at the low degrees of substitution (DS ca. 0.06) commonly used. This is additionally boosted by the excellent water solubility of cationic starch and its structural similarity with cellulose, which ensure intimate access to both fiber and filler surfaces. As a result, faster water drainage and better retention of fines and fillers during papermaking are achieved, translating into enhanced paper mechanical properties and reduced wastewater pollution [3,4,7,8].

Current efforts to accelerate the transition from linear towards an even more focused circular bioeconomy is transversal to the pulp and paper industry. In this context, we have demonstrated that the grafting of quaternary ammonium groups onto LignoBoost® *Eucalyptus* kraft lignin affords a cationic product that features excellent water solubility across the entire pH scale, comparable to that of lignosulfonates [9], which could pave way for a much better material usage of kraft lignins. Consequently, we pursue here the idea of re-integrating kraft lignin into the papermaking process, using its cationic derivative as a partial starch replacement, adding thus significant value to a hitherto underutilized byproduct of the kraft pulping process. The idea of re-integrating lignin into paper is not entirely new as it has been recently shown that the enzymatic (laccase) polymerization of lignosulfonates can replace fossil-based styrene-butadiene latex binders in paper [10].

Similar to starch, the cationization of lignin can be accomplished in various ways using either amines or quaternary ammonium compounds that additionally carry a suitable reactive group for covalent grafting, such as glycidyl moieties. Commonly, the partial etherification of aliphatic or phenolic hydroxyl groups is preferred along with the introduction of quaternary ammonium groups as the latter provide far-reaching inertness towards undesired onward reactions and availability of the positive charge across the entire pH scale. Among the range of compounds (Figure 1) that have been used for small or larger scale modification of biopolymers such as starch, chitosan, or cellulose, 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride (CHPTAC) is by far the most frequently used cationization reagent, due to its relatively low price and environmental impact [11,12]. Therefore, CHPTAC has been also used for grafting quaternary ammonium groups onto kraft lignin to impart high water solubility across the entire pH scale. With regard to sustainability, it is worth noting that CHPTAC is derived from epichlorohydrin, which can be produced from glycerol using the solventless, atom-efficient, and environmentally friendly DOW GTE process. Glycerol is nowadays quite cheap and almost exclusively produced from renewable resources, such as by transesterification in the biodiesel process or by the fermentation of sugars. The epichlorohydrin is then reacted at ambient conditions with trimethylamine hydrochloride in the presence of a catalyst such as choline [13]. With regard to the principles of the green chemistry philosophy it is important to add that also the final grafting of CHPTAC onto the respective biopolymers can be conducted in aqueous alkaline medium and does not require organic solvents. In addition to wet cationization, "dry" approaches also exist, with the starch surface being impregnated with small quantities of alkaline CHPTAC solution [14].

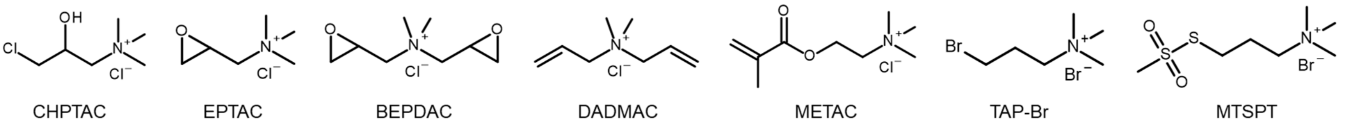

Figure 1. Selection of commercially available reagents for covalent grafting of quaternary ammonium groups onto biopolymers.

The high water-solubility of cationic LignoBoost® *Eucalyptus* kraft lignin across the full pH scale along with further features inherent to lignin, such as the potent absorption of UV light, antimicrobial activity or trapping of oxidants [15], literally invite their own use in a wide range of applications [9,16–18].

Therefore, this work investigated for the first time whether and to what extent cationic starch—an essential additive in papermaking to increase fiber and ash retention, accelerate dewatering, and improve process runnability—can be replaced by this novel type of cationic kraft lignin. At the example of handsheets made from bleached *Eucalyptus* kraft pulp, key paper mechanical (tensile, bursting, and tearing indexes), structural (roughness, capillarity rise, air resistance, internal strength, and water contact angle) and optical properties (brightness, opacity, and relative color change) were compared for different levels of starch replacement. As the results will suggest, reintegration of lignin into the papermaking process is a feasible option that could release significant quantities of starch without compromising key paper properties concomitantly meeting the targets of circular bioeconomy, as well as that of the cradle-to-cradle and green chemistry philosophies.

2. Materials and Methods

2.1. Materials

Industrially bleached *Eucalyptus* kraft pulp (BEKP) with a refining degree of 33°SR was used as raw material for the preparation of handsheets. *Eucalyptus* kraft lignin was isolated from the black liquor of a pulp mill using the LignoBoost® pilot plant facilities of RISE (Stockholm, Sweden). Both of the products were kindly provided by a Portuguese pulp mill. Industrial cationic starch having a degree of substitution (DS) of 0.04–0.05, was bought from Roquette Frères (Lestrem, France).

3-Chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC, 65 wt.% in H_2O) was purchased from TCI Europe N.V. (Zwijndrecht, Belgium). Phosphorus pentoxide ($\geq$99%, P_4O_{10}) was bought from Acros Organics (Geel, Belgium). Sodium chloride, sodium hydroxide and sulfuric acid were all ACS grade and supplied by Fisher Chemical (Loughborough, UK). Dialysis tubing (benzoylated cellulose, cut-off 2000 Da) was obtained from Sigma-Aldrich (Lisbon, Portugal). All chemicals were used as received if not mentioned otherwise. Ultra-pure water (Simplicity® UV, Millipore, Molsheim, France) was used in all experiments.

2.2. Preparation and Characterization of Cationic Lignins

Synthesis of the cationic kraft lignins were accomplished as detailed elsewhere [9]. In brief, solutions of 5.0 g of kraft lignin (24 mmol C9) in 50 mL of 1 M NaOH (50 mmol) were placed in two nitrogen flushed 3-necked round bottom flasks equipped with gas inlet, condenser and rubber sealing. The aqueous alkaline kraft lignin solutions were heated to 70 °C. Defined amounts of CHPTAC (4.4 g and 8.6 g) were slowly added within a time period of 15 min and the reaction mixtures were kept under continued stirring for three hours. After rapid cooling to near room temperature (ca. 15 min), the solutions were neutralized using semi-dilute sulfuric acid. Prior to dialysis, the product mixtures were centrifuged using a Sorvall ST 16R centrifuge (Thermo Fisher Scientific, Osterode am Harz, Germany) to remove insolubles. The supernatants were transferred into dialysis membranes (cut-off of 2000 Da) and dialyzed against dilute brine at room temperature for 24 h. The purified solutions of cationic lignins were then freeze-dried using a Lyovapor L-200 (Büchi, Flawil, Switzerland) and kept in a desiccator over phosphorous pentoxide until further use. The two cationic lignins were produced using a CHPTAC-to-kraft lignin molar ratio of 0.6 and 1.3, and herein noted as CL-A and CL-B, respectively.

Elemental analyses were performed on an Elementar vario MAX cube elemental analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany) to determine the content of nitrogen. The degree of substitution (DS) representing the count of quaternary ammonium moieties introduced per "C9 repeating unit" [19] was calculated from the nitrogen elemental contents according to Equation (1).

$$DS = \frac{211.4\left(\text{g mol}^{-1}\right) \cdot N(\%)}{\left[14\left(\text{g mol}^{-1}\right) \cdot 100(\%)\right] - \left[151.6\left(\text{g mol}^{-1}\right) \cdot N(\%)\right]}, \tag{1}$$

In this equation, 211.4 represents the C9 molecular weight of the used *Eucalyptus* kraft lignin (g mol^{-1}) [20]; N, the nitrogen content determined by elemental analysis (wt.%); 14, the molecular weight of elemental nitrogen (g mol^{-1}), and 151.6, the molecular weight of the newly introduced cationic substituent (g mol^{-1}).

The charge densities of the cationic lignins were determined by potentiometric polyelectrolyte titration using a Mütek PCD-05 titrator (BTG Instruments AB, Säffle, Sweden). Aliquots of 10 mL were taken from the aqueous solutions of the cationic lignins (0.5 g L^{-1}) and then titrated against a sodium polyethylene sulfonate (Pes-Na, 0.001 N) solution. The results were expressed as average values.

The ζ-potentials of the 0.2 g L^{-1} solutions of cationic lignins were measured using a Malvern zetasizer NANO-ZS ZEN 3600 (Malvern Instruments Ltd., Malvern, UK). Duplicate measurements were performed and average values were reported.

2.3. Preparation and Characterization of Handsheets

Defined amounts of cationic starch powder were added to 250 mL of ultra-pure water to prepare solutions meeting the concentration range of industrial application (Table 1). These solutions were then heated under continuous stirring and kept at 95 °C for 15 min. After the onset of gelatinization, different amounts of cationic lignin pre-dissolved in ultra-pure water were added (cf. Table 1). The resulting mixtures were combined with pre-heated (65 °C) aqueous suspensions (0.6 wt.%) of bleached *Eucalyptus* pulp (33 °SR) under continuous stirring. After maintaining temperature and stirring for another five minutes, the mixtures were forced to quickly cool down to about 20 °C. If required, small losses of water were compensated by adding ultra-pure water at 65 °C. Aiming to minimize degradation, preparation of the starch/lignin formulations was accomplished only shortly before they were added to the BEKP suspensions.

Table 1. Composition of the additive formulations used for the preparation of the handsheets.

Formulation Code	**Formulation Composition [kg ton^{-1}]**		
	Cationic Starch	***Type of Cationic Lignin***	
		CL-A	***CL-B***
CS-100%	10	-	-
CL-A-10%	9	1	-
CL-A-30%	7	3	-
CL-A-50%	5	5	-
CL-A-100%	-	10	-
CL-B-10%	9	-	1
CL-B-30%	7	-	3
CL-B-50%	5	-	5
CL-B-100%	-	-	10

For each experiment, 12 handsheets with a target grammage of 80 g m^{-2} were formed in a semi-automatic TMI 300-1 sheet former (Testing Machines Inc., Delaware, NJ, USA), followed by pressing and drying according to ISO standard 5269-1 [21]. The handsheets were conditioned at 23 ± 1 °C and 50 ± 2% RH for 24 h according to the TAPPI T 402 norm [22].

2.4. Mechanical Properties

All handsheets were characterized with regard to properties comprising grammage (ISO 536) [23], thickness, and apparent density (ISO 534) [24]. Furthermore, tensile testing according to ISO 1924-2 [25] was conducted, using a TH1 Alwetron tensile tester (ABB, Zurich, Switzerland) to determine respective tensile strength, stiffness, tensile energy adsorption (TEA), and tensile strain. Burst strength (TAPPI T 403/ISO 2758) [26,27] and tear strength (TAPPI T 414/ISO 1974) [28,29] were measured using a FRANK-PTI burst tester (FRANK-PTI GmbH, Birkenau, Germany) and an L&W tearing tester (ABB, Zurich, Switzerland), respectively. Burst and tear index values were calculated from the respective critical pressure and force values normalized for the grammage of the handsheets.

2.5. Structural Properties

This set of investigations comprised measurements of air resistance (Gurley method; ISO 5636-5) [30], surface roughness (Bendtsen method; ISO 8791-2) [31], capillarity rise (ISO 8787) [32], and internal bond strength (TAPPI T 569) [33]. Furthermore, water contact angle measurements (sessile drop method, 20 °C) were conducted using an OCA 200 instrument (DataPhysics Instruments GmbH, Filderstadt, Germany), equipped with a CCD camera and SCA20 software. Ten drops of water, each having a volume of 1 µL, were randomly deposited on the surface of the handsheets and the decrease in the water contact angle θ was immediately measured.

2.6. Optical Properties

All handsheets were subjected to optical analyses, including opacity (ISO 2471), [34] whiteness, brightness (ISO 2470-1 and ISO 2470-2) [35,36], and position within the CIE color space (ISO 11664-4) [37]. The respective spectrophotometric measurements were conducted using an L&W Elrepho SE 070-1 instrument (ABB, Zurich, Switzerland), calibrated to standard black and white tiles prior to the analyses. The three spatial coordinates, L^*, a^*, and b^*, of the CIE colour space represent the following components: L^* quantifies the lightness of the handsheets, ranging from full-light absorption (black, $L^* = 0$) to perfect reflective diffusion (white, $L^* = 100$). The chromatic coordinates a^* and b^* follow the transitions from red to green and yellow to blue. If their positions equal zero, the handsheets are achromatic. The Euclidean distance ΔE representing the color distance between two handsheets within the CIE color space was calculated from the respective differences in lightness (ΔL^*) and color transitions (Δa^*, Δb^*) using Equation (2) (Euronorm EN ISO 11664-4) [37].

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

With $\Delta L^* = |L_2^* - L_1^*|$, $\Delta a^* = |a_2^* - a_1^*|$, $\Delta b^* = |b_2^* - b_1^*|$.

2.7. Light Transmittance

The light transmittance of all the samples was studied in the wavelength range between 200 and 600 nm of each sample using a Thermo Scientific Multiskan GO microplate spectrophotometer (Thermo Fisher Scientific, Vantaa, Finland).

3. Results and Discussion

3.1. Preparation and Characterization of Cationic Lignins

Previously, it has been shown that the covalent modification of LignoBoost® *Eucalyptus globulus* kraft lignin with 3-chloro-2-hydroxy-propyl-trimethylammonium chloride (CHPTAC) affords cationic products that can feature excellent water solubility (>750 g L^{-1}) across the entire pH scale, provided that a sufficiently high percentage of the free phenolic hydroxyl groups is etherified by reaction with CHPTAC (Figure 2). This critical degree of substitution is around 1.0, depending on variation in lignin macromolecular composition and synthesis conditions. Solubilization in water is also possible below that threshold value; however, it is either restricted to partial solubilization or a certain fraction of the pH scale. For practical reasons, two cationic lignins were tested in the scope of this study: one featuring minimum DS (CL-A) for being sufficiently water soluble at pH 7 to prepare the handsheets series from lignin type CL-A, and one offering high solubility at all pH values (750 g L^{-1}, CL-B) [9].

The synthesis of the modified kraft lignins was accomplished in the aqueous alkaline medium (10 wt.% lignin, 1 mol L^{-1} NaOH) at an elevated temperature (70 °C, 3 h), using nitrogen atmosphere to prevent the phenolic substrate from excessive oxidation. CHPTAC-to-lignin molar ratios of 0.6 (CL-A) and 1.3 (CL-B) were used. The products obtained after neutralization, 24 h dialysis (cut-off 2000 Da), and freeze-drying had a DS of 0.7 and 1.2 according to elemental analysis (cf. Table 2), molecular weight analysis, and quantitative ^{13}C NMR data [9]. The ^{1}H and ^{13}C NMR analyses of the modified lignin as well as of the products obtained from pure CHPTAC under comparable conditions also suggested that no polymeric compounds were formed, which could have remained in the product after dialysis. Based on the signal ratios of C3 and C5 carbon atoms neighboring free and etherified phenolic hydroxyl groups at C4 positions in guaiacyl and syringyl-type moieties, as well as taking into account the nitrogen elemental contents, it was concluded that about 70–80% of the available free hydroxyl groups had been reacted, next to a smaller portion of aliphatic hydroxyl groups [9]. The absence of any malodorous volatile amino compounds in the products after dialysis and freeze-drying, furthermore, suggests that both of the products were free of Hoffmann-type degradation products. The latter could have formed under the strongly alkaline reaction conditions, and it would have been highly undesired in a paper additive. Next to the results of the elemental analyses and NMR spectroscopy, the introduction of the cationic moieties has also been indirectly confirmed by the observed increases of charge density, as determined by the potentiometric polyelectrolyte titration (CL-A: 202 μeq L^{-1}; CL-B: 494 μeq L^{-1}) and zeta potential (CL-A: +12.9 mV; CL-B: +22.4 mV).

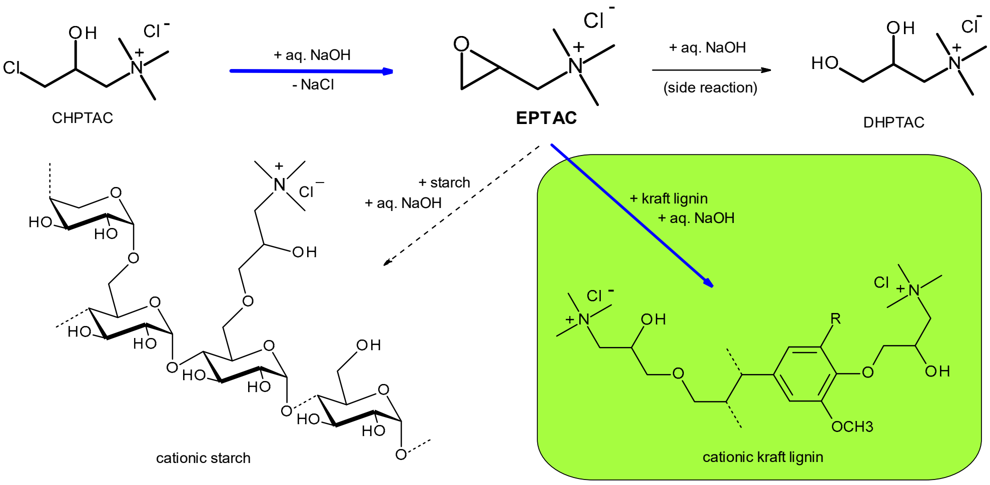

Figure 2. Synthesis of cationic kraft lignin from low-toxic CHPTAC for partial substitution of cationic starch in papermaking.

Table 2. Selected properties of the cationic lignins tested as paper additives.

Cationic Lignin	CHPTAC-To-Kraft Lignin Molar Ratio	Nitrogen Content	Degree of Substitution	Charge Concentration	Zeta Potential
		[wt.%]	[mol mol^{-1}]	[μ_{eq} L^{-1}]	[mV]
CL-A	0.6	3.2	0.7	202 ± 2	+12.9 ± 0.5
CL-B	1.3	4.2	1.2	494 ± 5	+22.4 ± 1.5

3.2. Preparation of Handsheets under Replacement of Cationic Starch by Cationic Lignins

3.2.1. Mechanical Properties

Aiming to assess the potential of cationic hardwood kraft lignin as a wet-end additive for replacement of cationic starch in papermaking, respective control and reference handsheets were first prepared. These specimens were included in all paper analytics to obtain benchmark values for the respective mechanical, structural, and optical properties investigated. While the control series of handsheets were prepared from bleached *Eucalyptus* kraft pulp (BEKP), only the reference series of handsheets contained additionally cationic starch, with an estimated degree of substitution between 0.04 and 0.05, at a common application rate of 10 kg of cationic starch per metric ton of BEKP (CS-100%). The effects of starch replacement by lignin were investigated using series of handsheets (n = 10) of decreasing starch-to-lignin ratio until a final application rate of 10 kg of cationic lignin per metric ton of BEKP was reached (quantitative starch replacement, Table 1). The preparation of the handsheets was accomplished by: (i) Mixing the defined volumes of the aqueous solutions of either of the two cationic lignin synthesized (Table 2) with that of the commercial cationic starch pre-gelatinized at 95 °C (15 min, then cooled to 60 °C); and (ii) Incorporating the thus prepared clear mixtures into pre-heated (65 °C) suspensions of bleached and homogenized *Eucalyptus* kraft pulp. Immediately after being forced to cool to 20 °C, handsheets were prepared using a semi-automatic sheet former. Prior to characterization, all specimens were equilibrated at 23 ± 1 °C and 50 ± 2% RH for 24 h. A visual inspection of the papers prepared confirmed excellent homogeneity and the absence of aggregates.

Apparent bulk density measurements confirmed that all handsheets prepared were largely similar with regard to grammage (83.4–87.1 g m^{-2}). Compared to the control paper solely made of BEKP, as well as to the reference handsheets containing cationic starch as the only additive (CS-100%), all handsheets representing the partial replacement of starch by lignin had similar bulk properties in terms of thickness, apparent density, and specific volume (Table 3). Even though slight variation in grammage was noticed, a direct comparison of these values for variants CS-100% and CL-A-100% (CL-B-100%) suggests good retention of the cationic lignin inside the fibrillar cellulose networks. Furthermore, there is evidence from all parameters in Table 3 that the higher net surface charge of the cationic lignins entails a slightly enhanced compaction of the handsheets by physical interaction with negative surface charges on cellulose.

Table 3. Properties of handsheets targeting partial substitution of cationic starch by lignin (cf. Table 1). Sample noted as control represents handsheets solely prepared from BEKP.

Sample Code	Grammage [g m^{-2}]	Thickness [µm]	Density [g cm^{-3}]	Specific Volume [cm^3 g^{-1}]
Control	85.9 ± 0.01	114 ± 1	0.75	1.33
CS-100%	86.1 ± 0.02	118 ± 1	0.73	1.37
CL-A-10%	85.5 ± 0.02	115 ± 1	0.74	1.34
CL-A-30%	87.0 ± 0.02	121 ± 1	0.72	1.39
CL-A-50%	83.4 ± 0.02	112 ± 1	0.74	1.34
CL-A-100%	87.1 ± 0.03	118 ± 1	0.74	1.35
CL-B-10%	84.0 ± 0.01	113 ± 1	0.74	1.35
CL-B-30%	86.3 ± 0.01	119 ± 1	0.73	1.38
CL-B-50%	86.6 ± 0.03	117 ± 1	0.74	1.35
CL-B-100%	87.0 ± 0.05	115 ± 1	0.75	1.33

In-depth sensitive mechanical characterization is one of the main pillars in paper analysis to gain valuable information about the chemical and morphological aspects of the cellulosic fiber networks formed during papermaking. Therefore, all the handsheets of this study (cf. Table 1) were comprehensively analyzed with regard to tensile, burst, and tear strength. Handsheets without cationic additives (“control”) and those containing 10 kg per ton of cationic starch (“reference”; sample CS-100%) were used to derive benchmark values for selected mechanical, structural, and optical properties. The properties of both “control” and “reference” handsheets (cf. Table 4) were in agreement with values reported elsewhere [3,4].

Table 4. Mechanical properties of handsheets prepared with the addition of cationic starch and cationic lignins in replacement of cationic starch. Sample noted as control represents handsheets prepared with BEKP without any additive.

Sample Code	Tensile Index [kN m kg^{-1}]	TEA Index [J g^{-1}]	Tensile Stiffness [kN m^{-1}]	Strain [%]	Burst Index [kPa m^2 g^{-1}]	Tear Index [mN m^2 g^{-1}]	Breaking Length [km]
Control	77.9 ± 2.3	2.2 ± 0.1	724 ± 27	4.3 ± 0.1	5.6 ± 0.4	9.6 ± 0.8	10.5 ± 0.3
CS-100%	78.9 ± 2.4	2.5 ± 0.1	690 ± 19	4.7 ± 0.2	6.5 ± 0.2	9.6 ± 0.5	10.7 ± 0.3
CL-A-10%	79.6 ± 4.7	2.5 ± 0.1	706 ± 33	4.6 ± 0.2	6.6 ± 0.2	10.1 ± 0.5	10.7 ± 0.6
CL-A-30%	76.6 ± 3.0	2.3 ± 0.1	712 ± 27	4.5 ± 0.2	6.1 ± 0.3	10.2 ± 0.5	10.4 ± 0.4
CL-A-50%	79.6 ± 3.8	2.5 ± 0.1	701 ± 26	4.5 ± 0.2	6.3 ± 0.3	9.9 ± 0.4	10.4 ± 0.5
CL-A-100%	73.8 ± 2.6	2.0 ± 0.1	730 ± 24	4.0 ± 0.2	5.5 ± 0.3	9.7 ± 0.6	10.1 ± 0.4
CL-B-10%	80.6 ± 3.2	2.5 ± 0.1	698 ± 30	4.6 ± 0.2	6.4 ± 0.5	9.9 ± 0.4	10.6 ± 0.4
CL-B-30%	75.7 ± 4.4	2.3 ± 0.1	699 ± 22	4.6 ± 0.2	6.2 ± 0.3	10.0 ± 0.5	10.2 ± 0.6
CL-B-50%	73.4 ± 3.5	2.2 ± 0.1	686 ± 24	4.5 ± 0.2	6.3 ± 0.2	9.5 ± 0.2	10.0 ± 0.5
CL-B-100%	71.5 ± 3.3	2.0 ± 0.1	735 ± 26	4.0 ± 0.2	5.4 ± 0.3	9.4 ± 0.7	9.7 ± 0.4

Tensile properties: The results compiled in Table 4 show that both tensile strength (maximum stress to break a strip of paper) and tensile energy absorption (TEA, durability of paper under repetitive or dynamic stressing) respond in a quite similar manner to the addition of cationic starch (relative to the additive-free control specimens) and to the incremental replacement of starch by cationic kraft lignin (relative to the reference handsheets). This is by no means a matter of course in industrial papermaking, where various factors, such as anisotropic fiber orientation, fiber dimensions, degrees of crystallinity and entanglement, and type and quantity of additives, govern the mechanical properties of the dense fiber networks formed. Particularly for packaging paper, it is known that their TEA values correlate better with favorable drop tests and low-failure rates than tensile strength data. Since packaging could be one possible application for paper containing the brownish cationic kraft lignin as a starch substitute, but also for the sake of clarity, only the TEA values will be discussed here as they represent the toughness of the supposedly anisotropic handsheets very well. The data in Table 4 clearly demonstrate that up to 30% of cationic starch can be safely replaced by cationic kraft lignin without compromising the durability of the respective papers as expressed by the TEA values, i.e., the area under the load-elongation curve. It is worth noting that the extent of starch replacement can be even as high as 50 wt.% at virtually the full preservation of the paper's toughness (reference sample CS-100%), if a cationic kraft lignin of lower degree of substitution is used, such as sample CL-A (DS 0.6) (cf. Figure 3). Cationic kraft lignins with DS values ≥1.0 (e.g., sample CL-B), however, reach only somewhat less than 90% of the TEA performance relative to the reference sample CS-100% at this high level of replacement.

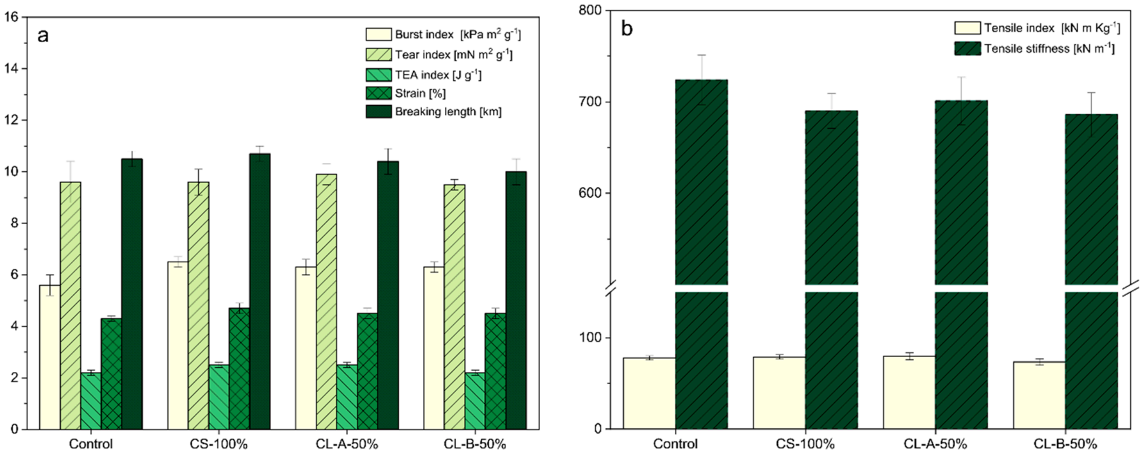

Figure 3. Effect of partial replacement (50%) of cationic starch by cationic *Eucalyptus* LignoBoost kraft lignin on: (**a**) Burst, tear, TEA indexes, strain and breaking length properties; and (**b**) Tensile index and tensile stiffness of handsheets compared to a starch/lignin-free control and reference specimens containing cationic starch only (CS−100%).

A similarly good preservation, if not improvement of paper mechanical properties, achieved through replacement of cationic starch by cationic kraft lignin is evident from the results of tensile stiffness measurements. The latter provide valuable information about the resistance of a sheet towards converting forces, such as bending. According to TAPPI standard T 494 [38], tensile stiffness represents the ratio of tensile force per unit width to tensile strain within the elastic region of the tensile–strain relationship, being equivalent to the product of Young's modulus and sheet thickness. The data in Table 4 suggest a slight gain of tensile stiffness for all handsheets, increasing with the degree of starch replacement by lignin. At 100% starch substitution, the highest values of tensile stiffness were measured for both types of cationic lignin (DS 0.7 or 1.2; Table 4). These findings are in good agreement with a previous study [39] investigating the impact of residual lignin on the tensile properties of single wood fibers at the cellular level. The authors were able to show that the modulus of elasticity (and hence, the tensile stiffness) of single fibers decreases with the reduction in lignin content, while both tensile strength and elongation increase. Despite the principal differences in lignin-to-polysaccharide bonding that exist between the materials of the cited work and our study, there is evidence also from paper structural study (Table 5, discussion below) that the physical bonding of cationic lignin within the cellulosic network occurs, causing a somewhat enhanced tensile stiffness.

Table 5. Structural and surface properties of the handsheets prepared testing partial replacement of cationic starch by cationic kraft lignin. Sample noted as control represents handsheets prepared from BEKP only.

Sample Code	**Roughness (Bendtsen) [mL min^{-1}]**	**Capillarity Rise (Klemm) [mm 10 min^{-1}]**	**Air Resistance (Gurley) [s 100 mL^{-1}]**	**Internal Bond Strength (Scott) [J m^{-2}]**	**Contact Angle [°]**
Control	82 ± 8	37 ± 3	22.2 ± 2.4	369 ± 28	64 ± 5
CS-100%	78 ± 8	40 ± 1	13.6 ± 1.1	470 ± 50	62 ± 5
CL-A-10%	85 ± 11	41 ± 1	15.1 ± 1.6	429 ± 18	68 ± 9
CL-A-30%	106 ± 8	41 ± 1	12.7 ± 1.0	393 ± 14	74 ± 4
CL-A-50%	78 ± 6	36 ± 1	16.7 ± 1.2	525 ± 24	73 ± 9
CL-A-100%	72 ± 10	35 ± 1	22.7 ± 2.3	418 ± 23	70 ± 7
CL-B-10%	72 ± 10	44 ± 1	15.4 ±1.8	427 ± 52	72 ± 7
CL-B-30%	91 ± 11	40 ± 1	15.8 ± 1.3	453 ± 41	76 ± 8
CL-B-50%	81 ± 7	38 ± 1	13.5 ± 0.9	518 ± 44	82 ± 8
CL-B-100%	57 ± 7	31 ± 2	25.6 ± 1.1	396 ± 30	73 ± 4

Burst and tearing properties: The calculation of the burst index (bursting strength divided by basis weight; kPa m^2 g^{-1}) and burst factor (dimensionless, bursting strength divided by basis weight)—both are relevant parameters particularly for packaging applications—revealed that the resistance of the handsheets towards rapture remains largely the same up to 50% replacement of cationic starch by cationic kraft lignin. Only at full substitution of starch by either of the two types of the cationic lignin tested, burst performance dropped significantly to reach that of the control handsheets (Table 4).

Complementing bursting characteristics, all handsheets were also subjected to Elmendorf tear testing (TAPPI standard T 414) [28], which reports the internal resistance of a paper towards tearing, more specifically, the force necessary to impact the plane of a paper in perpendicular direction to tear a single sheet through a specific distance after the tear has been started already [40]. The results reveal that similar as with most of the other mechanical parameters, the partial replacement of cationic starch by cationic lignin had no negative impact on the internal tearing resistance of the paper formed. It is worth mentioning that slightly higher tear indexes were obtained for all substitution variants tested with lignin sample CL-A. This was also the case for CL-B but up to 30% starch replacement only. Since tear characteristics are largely affected by fiber entanglement and bonding next to grammage, length, and strength of individual fibers, the obtained results suggest that the tested cationic lignins contribute to a somewhat enhanced bonding of the cellulose fiber networks.

These results fit well with the measured data of breaking length, representing the strength of the handsheets by reporting the maximum length of a column of the respective paper that can support its own weight without rupture. The results clearly show that at 10 wt.% substitution of cationic starch by cationic lignin, virtually no loss of breaking length is obtained (cf. Table 4). Only at higher degrees of starch replacement, such as at 50 wt.% (CL-A: 10.4 km, CL-B: 10.0 km), is breaking length slightly inferior to that of the control specimens (10.5 km) and the papers of variant CS-100% (10.7 km). This slight reduction in breaking length for the highest levels of starch replacement is accompanied by somewhat declining values of fracture strain, i.e., elongation at break, implying small losses of elasticity. However, only non-significant differences were observed up to 50 wt.% starch substitution as evident from a comparison with the strain values of variant CS-100% (4.5% vs. 4.7%; Table 4).

In summary, the results of mechanical testing provide clear evidence that except for the scenario of quantitative starch replacement, the incorporation of cationic lignins (CL-A: DS = 0.7; CL-B: DS = 1.2) into BEKP had no negative impact on the properties of the paper specimens formed. Compared to the control assay (free of starch or/and lignin), it reversely suggests that, similar to the handsheets made from wet-end cationic starch [4,8,41], the electrostatic interaction between the quaternary ammonium groups of lignin and the negative charges on the surface of pulp fibers are responsible for the slightly enhanced mechanical properties obtained.

Impact of degree of substitution by cationic groups: A comparison of the two handsheet series prepared from cationic lignins of different degree of substitution (DS 0.7 vs. DS 1.2) revealed that up to 50% starch replacement consistently somewhat lower values of tensile energy adsorption, breaking length, and tensile strain were obtained for the lignin featuring the higher density of quaternary ammonium groups (CL-B). This might be surprising at a first glance since it is known that tensile performance is largely dependent on the extent of inter-fiber bonding [42,43] next to the strength of individual fibers [8]. However, it should be taken into account that the over-saturation of the negative surface charges by cationic lignin can increasingly lead to electrostatic repulsion, reduced lignin adsorption, increased inter-fibril distances, and, hence, loss of mechanical performance. Obviously, this point is reached for CL-B already somewhat below 30% starch replacement, as evident from a 10% TEA loss for sample CL-B-30%, while the CL-A data suggest no loss up to 50% starch replacement (CL-A-50%). The same effect was demonstrated by Hedborg et al. [44] for the incorporation of cationic starch of an increasing degree of substitution (DS = 0.015–0.050) into bleached softwood kraft pulp. The authors concluded that lignin adsorption is driven by electrostatic interaction up to charge neutrality, while oversaturation leads to reduced bonding and may increase inter-fibril distances. This is in good agreement with another study [45] showing that better adsorption onto bleached kraft pulp and higher strength of handsheets is obtained when cationic dextran of lower charge density was used.

The somewhat lower mechanical performance obtained with the higher substituted lignin sample CL-B, evident particularly at quantitative starch replacement, could be also caused by secondary phenomena, such as: (1) The formation of charge-shielding $\pi \rightarrow$ cation complexes by interaction of quaternary ammonium groups with phenolic moieties [46]; and (2) The nanoscale phase separation by the formation of extended lignin aggregates through π-π stacking, which is known to occur in both the solution state [47] and on cellulosic surfaces [48].

3.2.2. Structural Properties

Ten sets of handsheets (two types of cationic lignin, each tested at four levels of starch replacement; reference, representing the common practice of cationic starch addition; control, containing no cationic additive) were subjected to standard tests assessing the structural properties of paper. These tests comprised Bendtsen roughness, Klemm capillary rise, Gurley air resistance, Scott internal strength, and water contact angle measurements (Table 5).

Bendtsen roughness (ISO 8791-2) [31] represents the rate ($mL{\cdot}min^{-1}$) at which pressurized air (1.47 kPa) passes between a flat circular land and a sheet of paper or board. High values are indicative for high surface roughness negatively impacting printability in terms of resolution, gloss or amount of coating required for graphical papers. Bendtsen roughness testing is still widely applied as a facile off-line monitoring method in paper production. It is particularly used for uncoated and non-calendared papers, where it is considered to give more precise values than the Parker print surf (PPS) analysis [49]. The data in Table 5 and in particular those obtained for sample CL-B (DS 1.2) reveal that the replacement of starch by lignin does not increase surface roughness (Figure 4). Instead, a significantly lower roughness was obtained for variant CL-A-100% compared to variant CS-100% (57 ± 7 vs. 78 ± 8 $mL\ min^{-1}$). For lignin sample CL-A (DS 0.7), a statistically significant higher roughness was obtained at the 30% starch replacement only; the differences at all other levels of replacement were not significant and a tendency towards smoother surfaces compared to the CS-100% reference was also observed here. The results support the above conclusion that cationic lignins can be well-dispersed within the fibrous matrix and feature a similarly good bonding despite having significantly lower molecular weight.

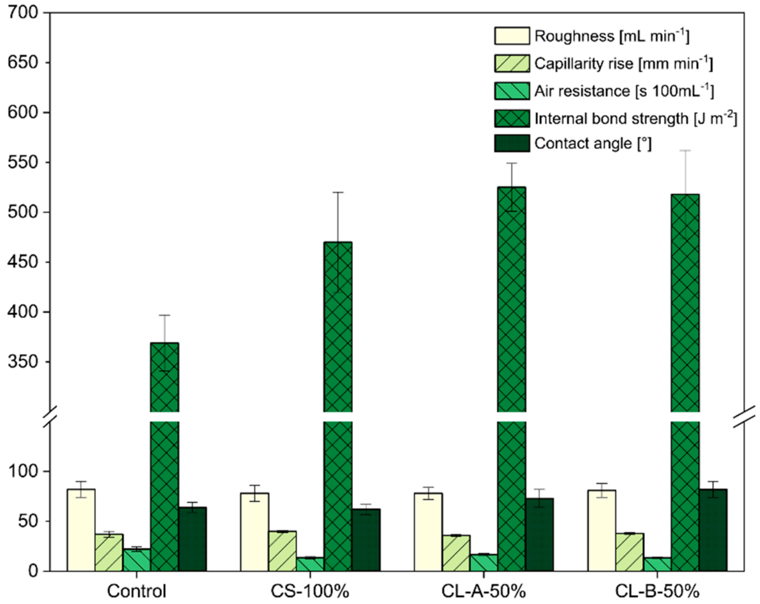

Figure 4. Partial replacement (50%) of cationic starch by cationic Eucalyptus LignoBoost® kraft lignin: Effects on mechanical and structural properties of respective handsheets in comparison to a starch/lignin-free control sample and reference handsheets containing cationic starch only (CS−100%).

Klemm capillarity rise test (ISO 8787) [32] investigates water adsorption by evaluating the capillary rise (mm) in the respective paper. Stripes cut from the latter are suspended and fixed by clamps in such a manner that the bottom parts of the strips can be immersed in a water-filled bowl at a defined start time, causing the water to ascent a certain distance within a predefined time. Good water absorbency by the paper that is to be tested is a prerequisite (capillary rise ≥ 5 mm per 10 min), which was definitely given for all specimens of this study (35–44 mm per 10 min). The values in Table 5 demonstrate that the replacement of cationic starch by up to 30% of cationic lignin fully preserves, if not slightly increases, the absorptivity of the handsheets prepared, independent of whether CL-A (DS 0.7) or CL-B (DS 1.2) were tested. The water absorption rate at 50% starch substitution by either of the two cationic lignins was slightly lower than for the reference paper; however, it was still higher than for the additive-free control specimens. Only for handsheets representing 100% starch replacement, a clearly reduced capillary rise was observed for both of the cationic lignins tested. This is in good agreement with increasing air resistance (Gurley test, cf. below) and decreasing surface roughness (Bendtsen test, cf. above), both supporting the assumption that the added lignin promotes water repellency by joint hydrophobization and the narrowing of capillaries.

Gurley air resistance of paper (ISO 5636-5) [30] measures the resistance of paper to the passage of air, which largely depends on various structural features, including fiber dimensions, grammage, porosity, type and content of fillers or additives. Air resistance is quantified based on the time required for a certain volume of air to pass through a defined cross-sectional area of paper at constant air flow, temperature, and relative humidity. In addition to air resistance, the test allows also for assessing paper drainability. Similar to other parameters, the replacement of starch by lignin had no significant effect on air resistance up to 50%. This is evident from a comparison of the respective values of the reference handsheets (10 kg cationic starch per ton of pulp) with that prepared from a pulp, which contained 5 kg ton^{-1} of each, cationic lignin and cationic starch, revealing marginal differences only (CS-100%: 13.6 s/100 mL; CL-B-50%: 13.5 s/100 mL). The values for all other variants were quite similar, varying in the range of 12.7–16.7 s per 100 mL of air, and being clearly lower than the air resistance values of the starch/lignin-free control handsheets (22.2 s/100 mL). This is in good agreement with a previous study demonstrating that the cationization of lignocellulosic pulp fibers decreases drainage time during sheet formation as reflected by the low air resistance [50]. Only at quantitative replacement of starch, a somewhat higher air resistance (CL-A-100%: 22.7 ± 2.3; CL-B-100%: 25.6 ± 1.1 s/100 mL) similar to that of the control specimens (22.2 ± 2.4 s/100 mL), was measured.

Scott internal strength (TAPPI T 569 standard) [33] determines the energy required to rapidly delaminate a given test sheet with a pendulum of controlled mass and high velocity. Prerequisites for the test to deliver meaningful results is a paper basis weight higher than 40 g m^{-2} and a moderate strength, excluding very strong (bonded or card stock paper) and very soft materials such as tissue. Since the pendulum's energy is absorbed by the elongation and stretching of the fiber networks, Scott internal strength assesses the semi-elastic nature of the test material, quantifying strain energy per sample area (J·m^{-2}). The results compiled in Table 5 reveal a significant gain in Scott internal strength for all handsheets containing cationic starch and/or cationic lignin compared to the control variant. This is in good agreement with previous findings reporting a 60% increase in Scott internal bond strength in thermo-mechanical pulp after cationic moieties had been grafted onto the cellulose and hemicellulose fractions [51]. For the handsheets of this study it is worth noting that at 50% replacement of cationic starch by cationic hardwood lignin, an even somewhat higher Scott-type internal bond strength compared to the CS-100% reference handsheets, is obtained.

Water contact angle measurements were conducted to complement the analysis of structural properties and to assess the impact of starch replacement by lignin on the hydrophilicity of the test handsheets. The data in Table 5 show that compared to variant CS-100% ($\theta = 62°$), the water contact angle increases with the extent of starch replacement by either of the two lignins tested. This is illustrated with the examples of CL-A-30% and CL-B-50%, which featured water contact angles of $\theta = 74°$ and $\theta = 82°$, respectively. This increase in hydrophobicity is surprising since the DS of cationic lignin, and hence the density of quaternary ammonium groups, is significantly higher than that of the cationic starch used in this study. Similarly, it was also not anticipated that the contact angle of handsheets containing the higher substituted lignin (CL-B-100%, DS 1.2, θ=73°) would be higher than for the lignin carrying fewer quaternary ammonium groups (CL-A-100%, DS 0.7, $\theta = 70°$). This observation was made for 100% starch replacement; however, it is in agreement with a recent study [52] that reported an increase in paper hydrophobicity when chitosan was added (1–4 wt.%, protonated form) to a bleached mixed kraft pulp (70% softwood, 30% hardwood) prior to handsheets formation. These congruent results suggest that quaternary ammonium atoms are engaged in bonding to oppositely charged deprotonated hydroxyl groups of cellulose to form ion pairs imparting enhanced lipophilicity compared to the free ions. Other than with starch, a considerable fraction of quaternary ammonium groups grafted onto lignin could be additionally masked by $\pi \rightarrow$ cation interactions with the aromatic moieties of lignin, increasing net lipophilicity.

In view of all structural properties analyzed it can be concluded that up to 50% of cationic mass starch can be safely replaced by cationic lignin without compromising any of the respective paper features.

3.2.3. Optical Properties

Different from native lignin, technical lignins are commonly intensely colored, which can be unwelcome for a range of applications. This is due to the formation of small quantities of chromophores during pulping and lignin isolation [53], with *o*- and *p*-quinones and quinone methides being the most dominant ones, complemented by stilbenoquinones, conjugated phenolics, aromatic ketones, metal complexes, and stable oxygen radical structures. The central role of quinoid structures can be demonstrated at the example of spruce milled wood lignin. Despite its low content of *o*-quinoid structures (about 0.7 wt.%), it has been shown that the latter accounts for 35–60% of blue light absorption at 457 nm [54]. There is consent that the formation of these key chromophores is the result of nucleophilic side-chain attacks by both hydroxide and bisulfide ions. The subsequent demethylation of guaiacyl and syringyl moieties leads to the formation of catechol derivatives, which readily undergo autoxidation to yield colored *o*-quinoid structures [55]. As a side note, it should be mentioned that leucochromophores, including hydroquinones, dihydroxystilbene or *p*-hydroxybenzyl alcohol, can be formed as well, which potentially can add color under certain conditions [56].

Various approaches have been investigated aiming to suppress the engagement of free phenolic hydroxyl groups in *o*-quinone formation by blocking this position with appropriate moieties. This included also the derivatization agents of the general structure X-$(CH_2)_n$-Y, with X and Y representing a wide variety of functional groups and (n) an integer from 1 to 5 [57]. The variation of X also included a halohydrin group, and that of Y a tertiary amine, which, at the precondition of n = 1, matches with the structure of CHPTAC and, hence, with the substitution pattern of the cationic lignin investigated here. This is insofar interesting, as all efforts of the above study, the intensive brown color of the LignoBoost kraft lignin in the aqueous solution state was not significantly altered by modification with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC).

The successful incorporation of the cationic lignins was, therefore, evident already by the visual inspection of the prepared handsheets. Depending on the extent of starch replacement, the color depth increased, starting with a brownish hue for the paper with the lowest quantity of lignin added (10 wt.%) to the clearly brown color perception typical for packaging paper (Figure 5a). Full-scan spectrophotometric analysis confirms that with the increasing replacement of cationic starch by either of the two cationic lignins tested, the transmission of the handsheets for near-ultraviolet (300–400 nm) and violet (380–436) light is considerably reduced (Figure 5b). These differences decrease at a higher wavelength; however, a 15% lower transmittance was still observed at about 500 nm (blue-green transition) for sample CL-A-100% compared to the reference (CS-100%).

Aiming to describe the optical differences in a more quantitative manner, respective handsheets were tested for opacity (diffuse reflectance, ISO 2471) [34], brightness (R457 value representing the percentage of blue light reflected from the surface of the handsheets, measured at $\lambda = 457$ nm, ISO 2470-1) [35], whiteness (D65 brightness according to the ISO 2470-2 [36] reflectance of the outdoor average north sky daylight illumination = CIE standard illuminant D65, which represents a greater UV energy compared to ISO 2470-1) [35], and relative color change within the CIE 1931 RGB color space (ISO 11664-4) [37].

The optical data compiled in Table 6 confirm that the opacity of all handsheets increases with the extent of starch replacement by lignin. Additionally, consistently for all levels of starch replacement, somewhat lower transmittance values were obtained for handsheets that were prepared using the cationic lignin of a higher degree of substitution (CL-B; DS 1.2). This further supports the assumption that $\pi \rightarrow$ cation complex formation between the quaternary ammonium groups of the grafted CHPTAC and the phenolic lignin moieties takes place, similar to potassium ions in aqueous media [58]. This phenomenon could also explain why the higher substituted lignin caused a stronger drop in brightness than its lower substituted counterpart at the same level of starch replacement. Compared to the control (92.3%) and starch-only variants (89.7%, CS-100%), brightness decreased to 59.9% (CL-A-100%) and 53.3% (CL-B-100%) at quantitative starch replacement. However, it is noteworthy that the brightness values at higher levels of starch replacement and handsheet coloration are less reliable since ISO 2470-1 [35] is limited in its scope to white and near-white pulps, papers, and boards. No difference was observed between R457 and D65 values, since the added lignin obviously does not feature optical brightening activity.

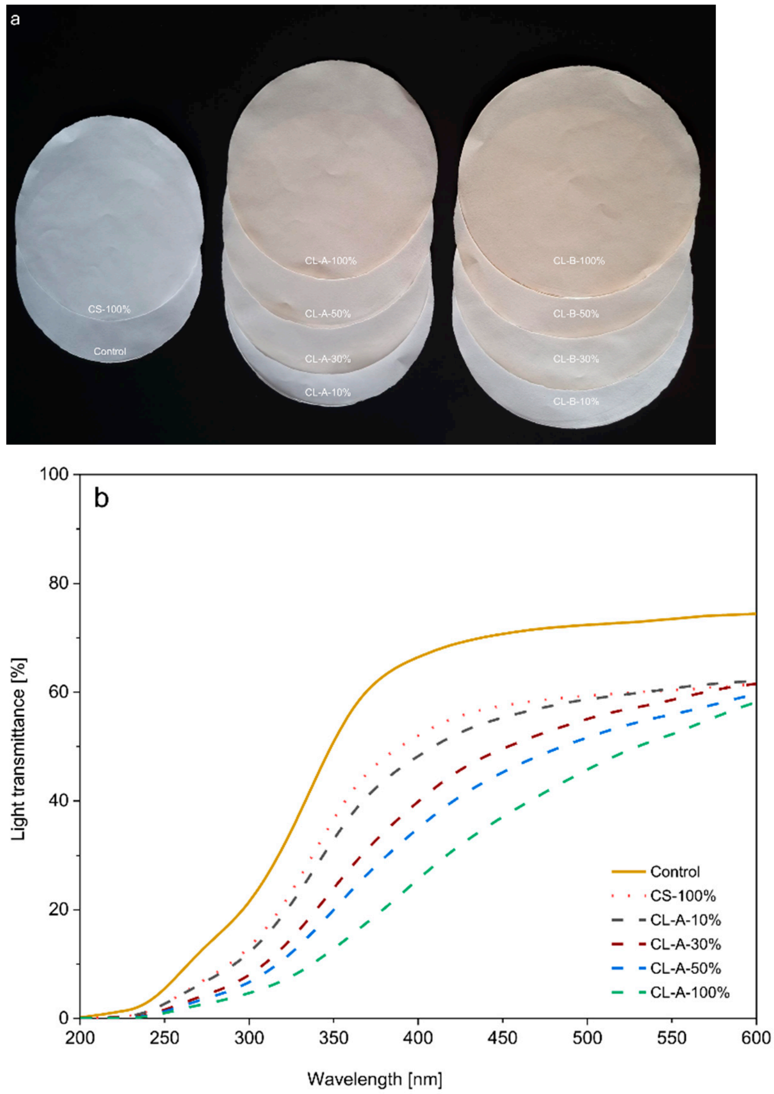

Figure 5. Pictures of handsheets of increasing degree of starch replacement by lignin (**a**); and their light transmittance spectra (**b**).

Table 6. Optical and colorimetric properties of handsheets prepared with the addition of cationic starch and cationic lignins in replacement of cationic starch. Sample noted as control represents handsheets prepared with BEKP without any additive.

Sample Code	Opacity	Brightness	L^*	a^*	b^*	ΔE
	[%]	R457 D65	D65/10	D65/10	D65/10	
Control	79.0	92.3	97.1	0.3	0.3	-
CS-100%	81.8	89.7	96.6	0.0	1.4	1.2
CL-A-10%	85.1	82.7	94.5	0.6	2.9	3.7
CL-A-30%	89.2	75.7	92.3	0.9	4.8	6.6
CL-A-50%	90.1	70.3	90.5	1.2	6.2	8.9
CL-A-100%	93.3	59.9	86.7	1.8	9.1	13.6
CL-B-10%	86.0	80.1	94.0	0.6	4.2	5.0
CL-B-30%	90.4	70.6	90.9	1.1	6.8	8.9
CL-B-50%	92.2	64.5	88.8	1.4	8.4	11.6
CL-B-100%	94.9	53.3	84.4	2.2	11.7	17.1

Therefore, only D65 white light standard illumination was used to determine the color vectors L^*, a^*, and b^* at a 10° viewing angle (D65/10 notation in Table 6) within the device-independent CIE 1931 RGB color space: lightness L^* with values between zero and

100, color gradient a^* varying from green to red ($-50 \leq a^* \leq +50$), color gradient b^* varying from blue to yellow ($-50 \leq b^* \leq +50$).

The results in Table 6 confirm the color change of handsheets noticed by visual perception, i.e., the shift from whitish (CS-100%) to brownish color depth (Euclidean distance), increasing with the extent of starch replacement by lignin. The changes in lightness and along the blue-to-yellow transition vector contribute more than those of the green-to-red transition. The overall color change was more pronounced—consistently for all levels of starch replacement—when lignin CL-B (DS 1.2) was used, which additionally supports the assumption that the formation of cation-π-complexes is here more pronounced.

4. Conclusions

This study demonstrates that cationic Eucalyptus kraft lignin featuring excellent water solubility across the entire pH scale has the potential to replace up to 50% of cationic starch dosage applied in paper production without compromising key paper mechanical and structural properties. In addition, the partial replacement of cationic starch by cationic lignin in paper materials allows better control of moisture permeability, which is critical both for printing and packaging papers, thus also reducing the need for sizing agents. Furthermore, improving the paper's resistance to delamination with the addition of cationic lignin may favor some printing properties (e.g., offset printing) and coating performances. In view of the relatively large quantities of kraft lignin that could be made available and its hitherto limited material usage, the outcome of this work is considered to have the potential to further promote the desired transition from linear to circular economy, which is of high societal priority.

5. Patents

P.I.F., Pinto, P.C.R Pinto, D. Evtuguin, F. Liebner. Processo químico de introdução de grupos carregados positivamente em lenhinas kraft para produção de lenhinas solúveis em água, em toda a escala de pH, lenhinas kraft obtidas e seus usos. Publication no.: PT117481. September 2021.

P.I.F., Pinto, P.C.R Pinto, D. Evtuguin, F. Liebner. Cationization of eucalyptus kraft lignin. Publication no.: EP22020453. September 2022

Author Contributions: Conceptualization, P.I.F.P., D.V.E. and F.L.; methodology, P.C.R.P., F.L. and D.V.E.; validation, D.V.E., F.L. and P.C.R.P.; formal analysis, P.I.F.P.; investigation, P.I.F.P.; resources, P.C.R.P., D.V.E.; data curation, P.I.F.P.; writing—original draft preparation, P.I.F.P.; writing—review and editing, F.L. and P.I.F.P.; visualization, P.I.F.P. and F.L.; supervision, P.C.R.P., D.V.E., F.L.; project administration, P.C.R.P.; funding acquisition, P.C.R.P. All authors have read and agreed to the published version of the manuscript.

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