

Addition of Ascorbic Acid or Purified Kraft Lignin in Pulp Refining: Effects on Chemical Characteristics, Handsheet Properties, and Thermal Stability

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The effects of two pulp pretreatments, impregnation with ascorbic acid (AA) or purified kraft lignin (KL), on bleached pulp refining were investigated by examining and testing handsheets made from these pulps. The AA pretreatment of the pulp amplified the depolymerization of the cellulose and notably impaired the strength properties of the pulp handsheets. The effects were enhanced upon the combination of the AA pretreatment and intensive refining. Furthermore, heat treatments (at 225 °C, 30 min, in water vapor atmospheres of 1 and 75% (v/v)) promoted the depolymerization of cellulose and the total color difference in the AA impregnated handsheets more than for the KL impregnated and reference handsheets. In contrast to AA, the KL pretreatment of the pulp improved the burst index stability of the refined pulp handsheets after the humid thermal treatment (75% (v/v)). In addition, the total color difference of the KL impregnated handsheets was lower than the AA impregnated and reference handsheets.

Keywords: Ascorbic acid; DP; Lignin; Pulp; Radical scavenger; Refining; Thermal degradation; UVR; XPS

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INTRODUCTION

Free radicals have been shown to play a significant role in the degradation chemistry of cellulose when subjected to mechanical treatments (Hon 1979; Hon and Srinivasan 1983; Hon 1983; Kuzuya 1999). Furthermore, several studies have indicated the formation of mechanoradicals in the course of Masuko refining (Solala *et al.* 2012), microfluidization (Ferrer *et al.* 2012; Rojo *et al.* 2015), and intensive refining (Vänskä and Vuorinen 2015) of cellulosic pulps. The objective of this work was to introduce the known antioxidant properties of ascorbic acid (AA) (Brand-Williams *et al.* 1995; Gregory 1996; Arrigoni and De Tullio 2002) and lignin (Dizhbite *et al.* 2004; Ugartondo *et al.* 2008; Arshanitsa *et al.* 2013) to intensive pulp refining to examine their effects on the properties of refined handsheet. Kraft lignin is a dark, partially hydrophobic material, whereas ascorbic acid is an acidic material with substantial buffering capacity (Niki 1991; Antonsson *et al.* 2008). In principle, the antioxidant capacity of low-cost lignin could be exploited to inhibit the adverse effects of radical formation in paper production to enhance the durability of fiber-based products.

AA is a non-phenolic antioxidant. Its antioxidant capacity has been widely investigated against the photo-oxidized yellowing of mechanical pulps (Schmidt and Heitner 1991; Ragauskas 1994; Pan *et al.* 1996). However, evidence of a reverse impact also exists, suggesting that AA promotes the thermal discoloration (Ragauskas 1994). The

significances of other natural antioxidants in the accelerated ageing of cellulosic materials have been also reported (Fagerlund *et al.* 2003; Peng *et al.* 2015). Earlier studies have revealed that heat enhances the degradation of AA (Brand-Williams *et al.* 1995; Gregory 1996). Furthermore, the thermal degradation of AA results in the formation of furan compounds, which are generally known as browning products in nutriment (Hodge 1953; Kurata *et al.* 1967; Tatum *et al.* 1969). Furan compounds have also been connected to the degradation products of electrical insulating papers impregnated with transformer oils (Unsworth and Mitchell 1990; Lelekakis *et al.* 2012). Furthermore, the pro-oxidant activity of AA in the presence of metal ions is well established (Kanner *et al.* 1977; Ivanova *et al.* 2013), leading to questioning the total antioxidant value of AA.

The phenolic groups of lignins have been found to stabilize radical species (Dizhbite *et al.* 2004; Kang *et al.* 2011; Arshanitsa *et al.* 2013). Phenolic groups in lignin are hydrogen donors and are oxidized to phenoxy radicals. These radicals have been suggested to generate quinone methide intermediates in the presence of heat (Cui *et al.* 2013). Furthermore, similar chromophore formation reactions have been associated within lignin structures after heat and light treatments (Paulsson and Ragauskas 1998). Despite the fact that lignin initiates chromophore formation, several studies have shown the beneficial effect of residual lignin in fibers on the final properties of fiber-based products (Schmidt *et al.* 1995; Spence *et al.* 2010; Ferrer *et al.* 2012; Vänskä *et al.* 2014; Rojo *et al.* 2015; Vänskä *et al.* 2015).

In this study, the impact of impregnating pulps with AA and kraft lignin (KL) on pulp refining was studied *via* UV resonance Raman (UVR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The depolymerization of the cellulose in the pulps was monitored *via* intrinsic viscosity measurements before and after intensive refining and thermal treatments (at 225 °C, 30 min, in water vapor atmospheres of 1 and 75% (v/v)). The chemical composition of the untreated and thermally treated, reference and KL impregnated pulp handsheets was determined by carbohydrate composition analysis. The physical properties of the reference, AA and KL impregnated pulp handsheets were assessed *via* tensile and burst strengths measurements, along with optical properties, including CIE $L^*a^*b^*$ color coordinates. Finally, scanning electron microscopy (SEM) imaging was employed to verify the presence of lignin deposits on the surface of the KL impregnated pulp fibers.

EXPERIMENTAL

Materials

Two differently pretreated pulps were studied and compared to a fully bleached reference kraft pulp, henceforth referred to as “FBP,” which was provided by Metsä Fibre Oy (Rauma mill, Finland). In the first treatment, the FBP (80% to 90% pine and 10% to 20% spruce) that was mill-bleached by the D(EP)DP sequence was suspended into an alkali lignin solution, henceforth referred to as “FBP+L”. In the second treatment, the FBP was suspended into an aqueous ascorbic acid solution, henceforth referred to as “FBP+A”. The sample set was chosen in order to provide information on the antioxidant effect of the kraft lignin on bleached pulp sheet properties.

Black liquor was supplied by Metsä Fibre Oy, (Rauma mill, Finland) from a bulk delignification stage. KL was separated and precipitated at pH 5 by the step-wise addition of sulfuric acid. The general features of the precipitated KL were as follows: 91.2% total

lignin, 3.4% carbohydrates, 7.9% sulfur, 14.3% methoxy groups, and 4.4 mmol/g phenols (Alekhina *et al.* 2015). L-Ascorbic acid was ordered from Sigma-Aldrich Finland Oy (Vantaa, Finland) with a $\geq 99.5\%$ purity.

Methods

Pulp pretreatments

KL was purified to remove mainly ash in a regenerated cellulose dialysis membrane tubing with a molecular weight cut-off (MWCO) of 1000. Subsequently, KL yield in the purified aqueous lignin suspension was determined *via* dry matter content using ISO 638 (2008).

After preparing a caustic solution (10 L) of alkali lignin (12.1 g (oven-dried)) at pH 13, 600 g of the oven-dried FBP was dispersed in the solution and left to soak for 3 h with hourly stirring. Next, the pH of the FBP+L suspension was decreased to 6.4 with 0.98 M sulfuric acid to precipitate the KL onto the surface of the fibers. Finally, the pulp was diluted to 4% solids content in distilled water and stored at 4 °C overnight.

The second approach consisted of an AA pretreatment of the FBP, henceforth referred to as “FBP+A”. The FBP+A (12.1 g of AA) and FBP suspensions were processed similarly as the KL pretreated suspension, with the exception of the addition of alkali lignin and pH adjustments.

Refining

Prior to a 90-min Hollander refining, the pulp suspensions were divided in half and diluted to 1.57% refining consistency with distilled water (0.08% of KL or AA). The refining level of the pulps was determined with Schopper-Riegler number (°SR) according to ISO 5267-1 (1999). To evaluate the effect of the pretreatments on the pulp swelling, the water retention values (WRV) of the pulps were analyzed with a GR 4.22 centrifuge (Jouan, Saint-Herblain, France), as described in the work of Pönni *et al.* (2014).

Pulp handsheet preparation

Prior to pulp handsheet preparation, the pH of all pulps was adjusted to approximately 7. Pulp handsheets were prepared with a target grammage of 65 g/m² following ISO 5269-1 (2005) at Labtium Oy (Espoo, Finland). The obtained handsheets were conditioned at 23 °C and 50% RH, according to ISO 187 (1990).

Thermal treatments

The thermal treatment procedure of Vänskä *et al.* (2014) was adapted to evaluate the thermal durability of the handsheets. A 30-min thermal treatment was applied for four conditioned pulp handsheets per sample at 225 °C in water vapor atmospheres of 1 and 75% (v/v). Water vapor atmosphere was provided by an automatic steam generator. A lambda sensor measured the proportion of oxygen in the oven and transferred it into the water vapor atmosphere (75% (v/v)) of the chamber.

Chemical characterization

To monitor the depolymerization of cellulose during refining and thermal treatments, the intrinsic viscosity of the cellulose content of handsheets was measured according to SCAN-CM 15:99 (1999) with a minor modification. Deviating from the standard, the dry handsheets were disintegrated with a blunt blade grinder (for approximately 30 s) prior to the viscosity measurements. The viscosity-based degree of

polymerization (DP) of cellulose was calculated *via* the Mark-Houwink-Sakurada equation,

$$[\eta] = K_p(DP_v)^a \quad (1)$$

where the constants $K_p = 1.7 \text{ mL/g}$ and $a = 0.80$ were chosen as suggested by Kasaai (2002) for the 0.5 M cupric ethylenediamine (CED) cellulose solvent.

Ultraviolet resonance Raman (UVR) spectroscopy is a feasible method for studying chemical changes induced by AA, lignin (Halttunen *et al.* 2001), and thermal treatments because of the strong aromatic and C=C signal enhancement in the UVR spectra (Vänskä *et al.* 2014). Before the measurements, the handsheets were dried overnight at approximately 40 °C and afterwards flattened using a hydraulic press. The UVR spectra measurements were collected over 60 s with a Renishaw 1000 UV Raman spectrometer (Coherent Inc., CA, USA) at 40-times magnification and a laser power of 10 mW at an excitation wavelength of 244 nm. The obtained spectral data were processed with Grams AI software (Thermo Fisher Scientific Inc., USA) by setting the baselines of spectra to zero after a linear function was fitted to calculated average values. The band heights were normalized to the cellulose-related band at $\sim 1093 \text{ cm}^{-1}$ (= 1 a.u.). The final spectral data represent the average of at least three spectra.

Quantitative saccharification *via* acid hydrolysis (Sluiter *et al.* 2011) was performed for the determination of the chemical composition of the refined FBP and FBP+L handsheets before and after the thermal treatment (30 min, 225 °C, 75% (v/v)). Prior to the analyses, the handsheets were milled with a Wiley mill and extracted with acetone for approximately 6 h in a Soxhlet apparatus. The individual monosaccharides were assayed using a high performance anion exchange chromatography with a pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 system (Dionex Corp., Sunnyvale, CA, USA) (Borrega *et al.* 2013). In the chemical composition results, heat-induced weight losses for the handsheets were calculated after weighing four handsheets prior to and after the thermal treatment according to the following equation,

$$WL(\%) = 100x(m_0 - m_1)/m_0 \quad (2)$$

where m_0 is the initial weight of the four handsheets and m_1 the weight of the same handsheets after the 30-min thermal treatment.

The surface chemistry of the refined pulp handsheets was also investigated using an AXIS ULTRA electron spectrometer (Kratos Analytical Ltd., UK) with a monochromatic Al $K\alpha$ X-ray source operating at 100 W with a neutralizer. Both low-resolution survey scans and high-resolution regions of C 1s and O 1s were recorded. Data from an *in-situ* reference (100% cellulose) were also recorded with each sample batch to evaluate ultra-high vacuum (UHV) conditions (Johansson and Campbell 2004). The spectra were obtained from areas less than 1 mm in diameter, and three to seven data sets were acquired for each sample handsheet. Afterwards, the acquisitioned data were analyzed with the Casa XPS program (Casa Software Ltd., UK) using compound parameters tailored for XPS cellulose studies. The reported results are primarily based on the analysis of high-resolution carbon regions recorded from acetone extracted samples (which were extracted in a Soxhlet apparatus for 6 h). The surface content of KL, Φ_{lignin} , was evaluated according to the equation proposed by Koljonen *et al.* (2003),

$$\Phi_{\text{lignin}} = (C1_{\text{extracted pulp}} - a) \times 100\%/49\% \quad (3)$$

where $C1_{extracted\ pulp}$ is the relative amount of the C–C bond component in the C 1s spectrum of the FBP+L handsheet and a is the corresponding value for reference (FBP) handsheet.

Physical properties

The grammage and caliper of the handsheets were measured in accordance with ISO 5270 (2012) and 534 (2005). The grammage and caliper results are the average of ten and four handsheets before and after thermal treatments, respectively. The apparent bulk density of the handsheet was calculated by dividing the sample's grammage by its caliper according to ISO 5270 (2012). The tensile and burst strength indices were measured before and after the thermal treatments according to ISO 1924-2 (1994) and SCAN-P 24:77 (1977), respectively, with minor modifications. Differing from the standards, the burst strength values were reported as an average of four measurements. The obtained strength results were normalized to the handsheets' grammage to yield respected indices.

The presence of KL deposits in the FBP+L handsheets was confirmed by means of SEM. The sample ($\sim 1.0\text{ cm}^2$) from the FBP+L handsheet was sputter-coated with a thin layer of gold to enhance the sample's conductivity. The SEM micrographs were taken using a scanning electron microscope (Hitachi TM-1000, Japan) operating at an acceleration voltage of 15 kV.

Colorimetric analysis

The thermal yellowing of the handsheets was evaluated with the CIE $L^*a^*b^*$ color coordinates. The color coordinates were measured with a SE 070R Elrepho spectrophotometer (Ab Lorentzen & Wettre, Sweden) operating at a wavelength of 457 nm in accordance with ISO 5631 (2000). The results represent the averages of five measurements from ten and four handsheets before and after the thermal treatments, respectively. The total color difference (ΔE^*) of the handsheets after the thermal treatments was calculated according to the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (4)$$

RESULTS AND DISCUSSION

Effect of Pretreatments on Pulp Refining

Table 1 shows the pH and extent of refining as measured by drainage ($^{\circ}\text{SR}$) for the FBP, FBP+A, and FBP+L. In addition, the consequences of the AA and KL pretreatments on the water uptake of the pulps were evaluated with the WRV test.

Table 1. Effect of the AA and KL Pretreatments and Refining on the pH, $^{\circ}\text{SR}$, and WRV (\pm Standard Deviation) of the Pulp

Pulp	pH	$^{\circ}\text{SR}$	WRV (g water \cdot g $^{-1}$ pulp)
Unrefined FBP	7.0	13.9	2.5 \pm 0.1
Refined FBP *	7.4	91.9	
Unrefined FBP+A	6.2	12.9	2.5 \pm 0.0
Refined FBP+A *	5.8	92.4	
Unrefined FBP+L	6.4	13.1	2.4 \pm 0.0
Refined FBP+L *	5.7	88.5	

* The fully bleached, AA, and KL pretreated pulps (FBP, FBP+A, and FBP+L, respectively) were refined for 90 min in a Hollander refiner

Although the pH of the pretreated pulps (FBP+A and FBP+L) was lower than that of the reference pulp (FBP) during refining, Table 1 shows that neither the AA nor KL pretreatment had a great impact on the WRV of the pulp prior to refining. This was expected because of the low amount of AA and KL (~0.08%) in the pulp suspensions. Furthermore, the finding indicated that regardless of the alkali lignin pretreatment, the water uptake and fiber swelling of the pulp remained comparable during the treatment (Shao and Li 2006; Hubbe and Heitmann 2007).

Chemical Characterization of Handsheets

Depolymerization of cellulose

Figure 1 shows the effect of the AA and KL pretreatments, refining, and thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) on the decrease in degree of polymerization of the cellulose of the handsheets.

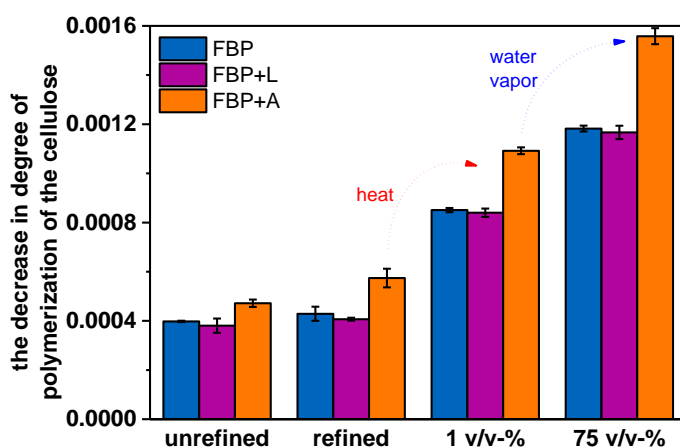


Fig. 1. Effect of the AA (FBP+A) and KL (FBP+L) pretreatments, refining and thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) on the decrease in degree of polymerization of the cellulose. Error bars show standard deviation. The pulps were refined for 90 min in a Hollander refiner.

Figure 1 indicates that the AA pretreatment already led to the depolymerization of cellulose prior to refining. Furthermore, the depolymerization of cellulose was enhanced during refining. The random cleavage of cellulose chains has been indicated to occur during the refining process of kraft pulps (Vänskä and Vuorinen 2015). This kind of chain cleavage produces hydrocarbon radicals. AA may donate a hydrogen radical, which suppresses the recombination reactions of these hydrocarbon radicals, thus explaining the high susceptibility of the FBP+A towards mechanical degradation.

The heat treatments showed their greatest impact on the DP of the cellulose in the FBP+A handsheets because of the initial low DP. However, the effect of the KL pretreatment on the DP of the FBP+L handsheets was less clear. In the previous study, the residual lignin in the pulp was shown to be an essential prohibitive factor against the cleavage of glycosidic bonds of cellulose upon thermal treatment (Vänskä *et al.* 2015). The location of lignin is most probably of relevance for its protective effect for the carbohydrates. In addition, the depolymerization of the cellulose seemed to be faster in the previous study (Vänskä *et al.* 2015), which accounted for the severe industrial refining process. Finally, Fig. 1 demonstrated the dramatic influence of water vapor on the thermal

degradation process. Water enhanced the hydrolytic degradation reactions of carbohydrates (Huang *et al.* 2014; Vänskä *et al.* 2014; Vänskä and Vuorinen 2015; Vänskä *et al.* 2015).

Chemical composition

To explicate the impact of the KL pretreatment on the DP of the FBP+L handsheets, the change in the chemical composition of the refined FBP and FBP+L handsheets upon the thermal treatment (30 min, 225 °C, 75% (v/v)) was investigated further (Table 2).

Table 2. Effect of the KL Pretreatment and Thermal treatment (30 min, 225 °C, 75% (v/v)) on the Chemical Composition (% on Original Unextracted Pulp ± Standard Deviation) of the Refined Pulp Handsheets

Chemical composition	FBP * initial	FBP * 75% (v/v)	FBP+L * initial	FBP+L * 75% (v/v)
Glucose	83.7±9.9	76.6±0.5	83.4±8.8	76.7±2.9
Xylose	7.4±1.0	6.3±0.2	7.5±0.7	6.0±0.9
Mannose	7.4±0.8	6.3±0.1	7.6±0.7	6.7±0.1
Arabinose	0.7±0.1	0.5±0.0	0.7±0.0	0.5±0.1
Galactose	0.3±0.0	0.2±0.1	0.2±0.0	0.2±0.0
Acetone extract	0.1±0.0	0.0±0.0	0.1±0.0	0.1±0.0
Lignin	0.4±0.0	0.4±0.0	0.4±0.0	0.5±0.0

* The fully bleached and KL pretreated pulp handsheets (FBP and FBP+L, respectively) were refined for 90 minutes in a Hollander refiner
Heat induced mass losses for FBP and FBP+L handsheets were 9.5% and 9.4%, respectively.

The essential finding in Table 2 was that the KL pretreatment did not change the relative chemical composition of the refined pulp handsheets (see also Table 1). Furthermore, the heat induced reactivity towards the cellulose in Fig. 1 was accompanied by a modest decrease in the amount of glucose units in the pulp handsheets in Table 2. Also, the hemicelluloses, xylose and mannose, showed slight sensitivity towards the thermal process, while no marked change in the lignin content occurred upon the thermal treatment. However, statistical difference between chemical composition before and after the thermal treatment was limited. Similar findings have been reported earlier in the presence of residual lignin during heat treatments of cellulosic materials (Nuopponen *et al.* 2004; Huang *et al.* 2014; Vänskä *et al.* 2014, 2015).

Spectroscopical data (UVR)

The changes in the chemistry of the unrefined and refined FBP, FBP+A, and FBP+L handsheets were further investigated to elucidate the influences of AA and KL pretreatments on pulp refining (Fig. 2).

Lignin is known to lead to distinct resonantly enhanced Raman scattering at ~1600 cm⁻¹ when UV excitation is used (Halttunen *et al.* 2001). Although the direct chemical analysis was not sensitive enough to show any change in the lignin content of the handsheets (Table 2), UVR spectroscopy verified that the lignin content increased by 10% to 20% with the KL pretreatment, which depended upon the extent of refining (Fig. 2). Refining without the added KL led to a small decrease in the lignin content. In Fig. 2, the refining of the FBP showed an increase in the band intensity at ~1650 cm⁻¹. No similar change was observed with the refining of the AA and KL pretreated pulps. It is plausible that this signal results from oxidized carbohydrate or lignin structures and is diminished because of the antioxidant capacity of AA and KL upon refining.

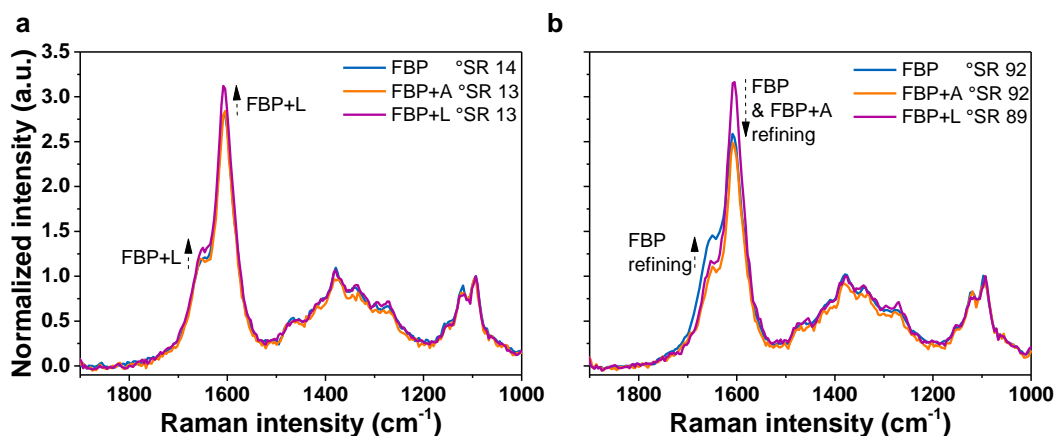


Fig. 2. (a) UVRR spectra of fully bleached (FBP), AA pretreated (FBP+A), and KL pretreated (FBP+L) handsheets. (b) UVRR spectra of FBP, FBP+A, and FBP+L refined handsheets (90 min in a Hollander refiner). The heights of the spectra were normalized at $\sim 1093 \text{ cm}^{-1}$.

Surface chemistry (XPS)

The chemical effects of the pretreatments and refining on the surfaces of the pulp fibers were also evaluated by XPS. In this technique, the data are collected from only the topmost few nanometers. Because of the extreme surface sensitivity, XPS can also be utilized indirectly in evaluation of surface activity (Johansson *et al.* 2011). According to XPS survey scans, all sample surfaces studied were clean and typical of cellulose. However, while survey spectra indicated similar atomic compositions, there were several small, but consistent, chemical changes in high resolution carbon data (Table 3). Examples for survey as well as component fitted high resolution C 1s spectra are given in the appendix (Supplementary Material) in Fig. S1.

Table 3. High Resolution XPS C 1s Data for Extracted Pulp Handsheets, Given as Percentages of Total Carbon Content at the Surface

Carbon components	C–C (%)	C–O (%)	O–C–O (%)	O–C=O (%)
FBP unrefined	3.5±0.3	76.1±0.1	18.9±0.1	1.6±0.1
FBP refined *	5.4±0.6	74.4±0.6	18.5±0.1	1.7±0.0
FBP+A unrefined	3.4±0.0	76.0±0.1	19.0±0.1	1.6±0.1
FBP+A refined *	4.5±1.3	75.2±1.0	18.7±0.3	1.6±0.1
FBP+L unrefined	5.8±0.1	74.0±0.2	18.5±0.0	1.7±0.1
FBP+L refined *	5.3±1.0	74.8±0.8	18.3±0.2	1.5±0.1

* The fully bleached, AA and KL pretreated pulp handsheets (FBP, FBP+A, and FBP+L, respectively) were refined for 90 min in a Hollander refiner. In the component fit analysis, carbon atoms are classified into four groups (named as C-C, C-O, O-C-O, and O-C=O) Depending on the number of bonds (0, 1, 2, or 3) to oxygen neighbors. standard deviation is included.

The KL in the extracted, unrefined FBP+L handsheet was seen as an increase in the non-cellulosic C-C component in high resolution XPS C 1s data when compared to the FBP handsheet. It corresponded to a 5% increase in the surface lignin content. This observation was in good agreement with UVRR spectra (Fig. 2) and SEM data (Fig. 6). The difference in results between the XPS analysis and the bulk chemical composition (Table 2) was most probably due to different sampling depths, which suggested that KL was distributed only on the topmost surface.

In the case of the unrefined FBP+A handsheet, the non-cellulosic C-C levels were unaffected by the AA pretreatment of pulp, as surface composition remained identical to that of the FBP handsheet being in good agreement with the UVRR data (Fig. 2).

Quite interestingly, the experimental scatter in the C-C content increased significantly upon refining. This was seen in all unrefined *versus* refined sample handsheet pairs and was independent of the pretreatments. In addition, only the FBP handsheet exhibited C-C levels that were affected by refining. In the case of cellulosic materials, the variations in non-cellulosic C-C and the increase in this component are strongly related with variations in surface energy of the materials. In general, surface energy correlates with the amount of carbonaceous contamination needed to passivate the surface of the material (*e.g.*, upon exposure to ambient air). Furthermore, this surface energy induced passivation in UHV conditions has been observed for cellulosic materials (Johansson *et al.* 2011), even for wood (Johansson *et al.* 2012).

Effect of Pretreatments on Strength Properties of Handsheets

To estimate the effect of AA and KL pretreatments on the mechanical properties of the pulp handsheets, the tensile strengths were measured before and after refining and thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) (Fig. 3). The handsheet density, grammage, and caliper values for the pulp handsheets are provided in the Appendix (Supplementary Material) in Table S1.

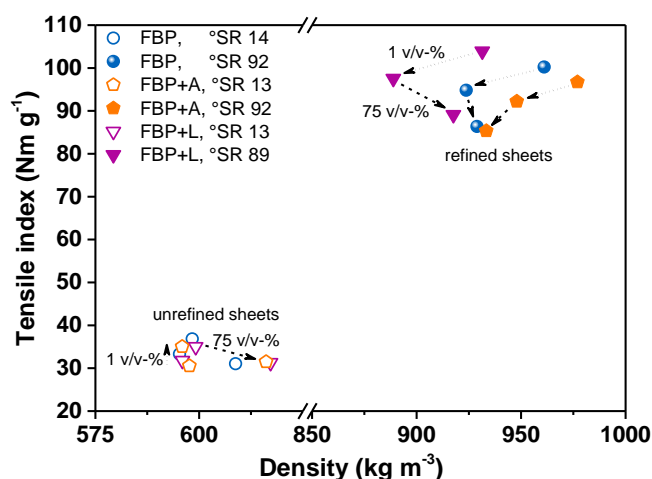


Fig. 3. Effect of the AA (FBP+A) and KL (FBP+L) pretreatments, refining and thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) on the tensile index of the handsheets. The pulps were refined for 90 min in a Hollander refiner. (Table S2 in the appendix represents the same data with standard deviation.)

Figure 3 shows that although the pulps had similar strength properties prior to refining, the tensile indices of the FBP+L handsheets improved marginally more than the reference handsheets (FBP) upon refining. A modest strength improvement was also observed when the precipitated kraft lignin was adsorbed on the surface of fibers (Maximova *et al.* 2001). Furthermore, in a microfluidization study of high yield pulp, the mechanoradical scavenging capacity of lignin was suggested to improve the strength properties of nanopaper (Ferrer *et al.* 2012). Thus, it is possible that the KL acts as a radical scavenger in intensive refining, retaining the DP of cellulose (Fig. 1) and pulp strength. In contrast to the KL pretreatment, the results in Fig. 3 demonstrate that the combination of

the AA pretreatment and refining notably impaired the strength of the pulp handsheets. The results are in line with the DP loss shown in Fig. 1.

The tensile strengths of the refined handsheets decreased more than the unrefined handsheets upon thermal treatments. This phenomenon can be explained in terms of the bonding of fibers. The loss in bonding that occurs upon heat treatment increases with increasing strength of the fiber network that develops during handsheet formation (Vainio and Paulapuro 2005). The thermal treatment in the water vapor atmosphere of 75% (v/v) resulted in a subsequent decrease in the tensile indices of the handsheets, which correlated positively with the decrease in degree of polymerization of the cellulose (Fig. 1).

The burst index measurement provided additional insight into the strength properties of the pulps. Notable differences were observed when the strength properties were estimated with the change in the burst indices of the thermal treatments of the refined FBP, FBP+A, and FBP+L handsheets. The change was evaluated by plotting the burst index values after the thermal treatments against to the initial values in Fig. 4.

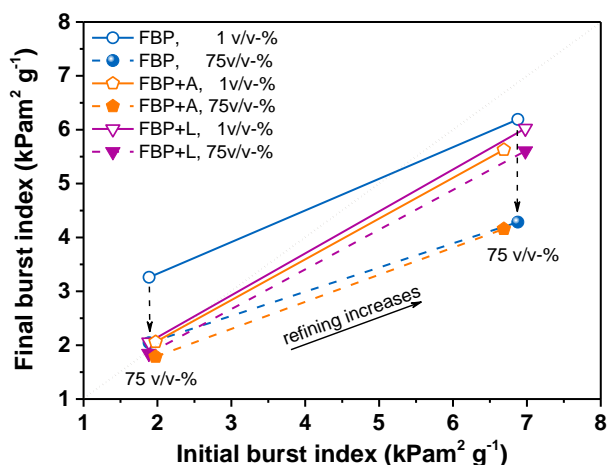


Fig. 4. Relationship between thermally treated (30 min, 225 °C, 1, and 75% (v/v)) and initial burst index for the fully bleached, AA (FBP+A) and KL (FBP+L) pretreated pulp handsheets before and after refining. The pulps were refined for 90 min in a Hollander refiner. (Table S2 in the appendix represents the same data with standard deviation.)

Figure 4 shows that the impregnation of pulp with KL prior to refining protected FBP+L handsheets against humid heat induced strength loss. The thermal treatments in the presence of water vapor (75% (v/v)) diminished the final burst indices of the refined FBP+A and FBP handsheets by 26% and 31%, respectively. The reductions were clearly higher than the 7% strength loss of the refined FBP+L handsheets. The positive effect of lignin on the strength stability has been reported after the heat treatments of oxygen delignified and unbleached pulps (Vänskä *et al.* 2014, 2015).

Surprisingly, Fig. 4 only exemplified an increase in the burst index of the unrefined FBP handsheets after the dry thermal treatment (1% (v/v)). Comparable improved strength values as a result of heat impact have been reported also previously (Vainio and Paulapuro 2007; Vänskä and Vuorinen 2015; Vänskä *et al.* 2015). This strength development is explained with the crosslinking and the hornification of fibers upon temperature increase (Kato and Cameron 1999; Pönni *et al.* 2012).

Thermal Yellowing

Color coordinates have been introduced to quantify the discoloration caused by the thermal degradation of fibers (Chen *et al.* 2012). Figure 5 shows the L^* and b^* parameters of the pulp handsheets before and after thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) upon refining.

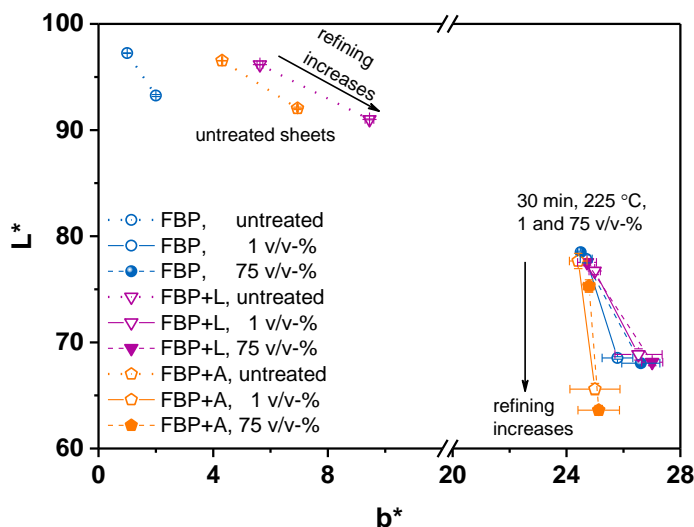


Fig. 5. Effect of the AA (FBP+A) and KL (FBP+L) pretreatments, refining, and thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) on the L^* and b^* parameters of the handsheets. Error bars show standard deviation. The pulps were refined for 90 min in a Hollander refiner.

Refining decreased the L^* value and increased the b^* value (*i.e.*, reduced the brightness and intensified the yellow color) in all pulp handsheets, while both AA and KL pretreatments enhanced the yellow color of the handsheets (Fig. 5). The intensified color of the FBP+L handsheets is consistent with the chromophores of lignin, while the auto-oxidation of ascorbic acid is most probably responsible for the color of the FBP+A handsheets (Pan *et al.* 1996). The discoloration of the FBP+A and FBP+L handsheets was more pronounced (61% and 68%) than for the FBP handsheets (53%) upon refining. The mechanically generated chromophores in the FBP+A may result from the oxidation of AA, as is explained in the DP of cellulose results in Fig. 1. The notable brightness loss and intensified yellow color of the refined FBP+L handsheets, however, may be attributed to the oxidation of phenoxyl radicals to colored compounds, similar to known lignin reactions that occur during the photo-oxidation of pulps (Schmidt and Heitner 1991; Li and Ragauskas 2000; Fagerlund *et al.* 2003; Chen *et al.* 2012).

After the thermal treatments, the refined pulp handsheets exhibited a more distinct brightness loss than the unrefined handsheets. The DP of cellulose has been shown to correlate positively with the brightness loss of the pulp (Vänskä and Vuorinen 2015). Furthermore, Fig. 5 confirmed that the refined FBP+A handsheets with the distinctively diminished DP of cellulose were more susceptible to heat induced brightness loss than the FBP and FBP+L handsheets.

The total color difference, ΔE^* , (Table 4) demonstrated how this value of the pulp handsheets is intensified with the AA pretreatment, refining, and water vapor present in the thermal treatment.

Table 4. Effect of the AA and KL Pretreatments, Refining, and Thermal treatments (30 min, 225 °C, 1 and 75% (v/v)) on the Total Color Difference, ΔE^* , of the Pulp Handsheets (\pm Standard Deviation)

Pulp	1% (v/v)	75% (v/v)
Unrefined FBP	28.6 \pm 0.1	28.0 \pm 0.1
Refined FBP *	32.3 \pm 0.4	33.2 \pm 0.3
Unrefined FBP+A	27.9 \pm 0.3	29.9 \pm 0.3
Refined FBP+A *	32.9 \pm 0.3	34.6 \pm 0.2
Unrefined FBP+L	27.8 \pm 0.2	27.0 \pm 0.0
Refined FBP+L *	28.7 \pm 0.2	29.6 \pm 0.1

* The fully bleached, AA and KL pretreated pulp handsheets (FBP, FBP+A, and FBP+L, respectively) were refined for 90 min in a Hollander refiner

Table 4 shows that the FBP+L handsheets were the most resistant towards thermal discoloration, whereas the ΔE^* was enhanced for the FBP+A handsheets. Overall, the color coordinates of the handsheets coincide systemically with the tensile strength (Fig. 3) and the depolymerization of cellulose (Fig. 1) results and with previous findings where the thermal stability of pulp has been shown to relate to the depolymerization of carbohydrates (Huang *et al.* 2014; Vänskä *et al.* 2014; Vänskä and Vuorinen 2015; Vänskä *et al.* 2015). Although the differences between the handsheets were modest, the results were significant when considering that the concentration of AA and KL in the pulp suspensions were approximately 0.08% during refining.

Scanning Electron Microscopy Imaging

Although the brown color of the KL pretreated pulp suspension indicated the presence of added lignin, the chemical composition (Table 2) and brightness (Fig. 5) of the prepared FBP+L handsheets were close to the reference FBP handsheets. The scanning electron microscopy (SEM) image of the FBP+L handsheet surface was recorded to verify the existence of KL on the pulp fibers (Fig. 6).

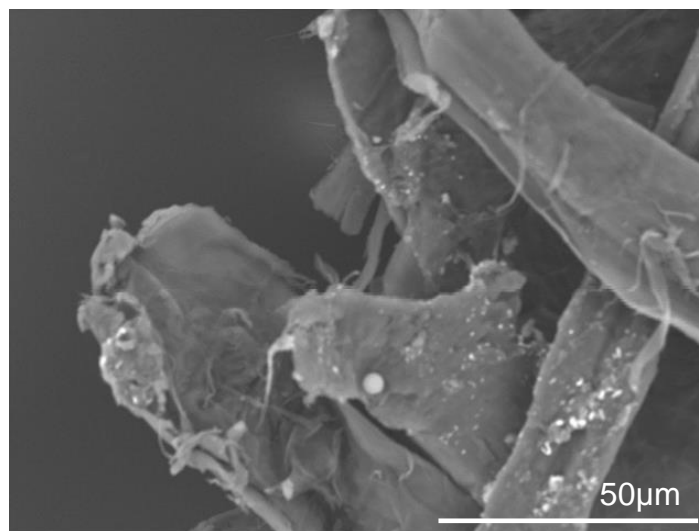


Fig. 6. The SEM image of the KL pretreated pulp (FBP+L) handsheet after the thermal treatment (30 min, 225 °C, 75% (v/v)). The FBP+L was refined for 90 min in a Hollander refiner.

Although KL was washed away during handsheet formation, Fig. 6 indicates that the increase in the non-cellulosic C-C component on the surface of the FBP+L handsheets (Table 3) was related to the adsorbed KL. Furthermore, KL appeared in the SEM images as distinct depositions on the surface of the thermally treated FBP+L fibers. Similar lignin aggregates on the surfaces of bleached fibers were not previously observed with SEM (Vänskä and Vuorinen 2015). In particular, Maximova *et al.* (2001) also found granules on the fiber surface after adsorption of lignin onto cellulose fibers.

At present, it is difficult to make clear statement on the relevance of the findings with regard to the radical scavenger activity of AA or KL in pulp refining. It is obvious, however, that the increased thermal durability (the reduced burst index loss and total color difference) of the KL pretreated pulp handsheets opens up completely new possibilities for the industrial utilization of KL. Further work is needed to demonstrate the potential of the KL pretreatment in radical scavenger applications.

CONCLUSIONS

1. The tensile and burst indices of the FBP+A handsheets were below the values of the reference handsheets before and after refining and thermal treatments (30 min, 225 °C, in water vapor atmospheres of 1 and 75% (v/v)). In addition, the AA pretreatment of the pulp reduced the brightness and increased the total color difference of the handsheets after the thermal treatments. This was attributed to the depolymerization of cellulose, as demonstrated by the viscosity measurements.
2. The tensile index of the FBP+L handsheets improved slightly more than the reference handsheets upon refining. Furthermore, the FBP+L handsheets showed resistance against the burst index deterioration upon the hot humid treatment. In addition, the total color difference of the FBP+L handsheets was lower when compared to the reference handsheets. KL was suggested to protect the pulp against carbohydrate degradation upon refining.
3. UVRR and XPS results indicated notable changes in the chemical characteristics of the refined pulp fiber surfaces.
4. Although the differences in the results between the handsheets were moderate, the results were systemically in line with previous findings, where the DP of cellulose is closely connected with the thermal stability of pulp.

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APPENDIX

Supplementary Material

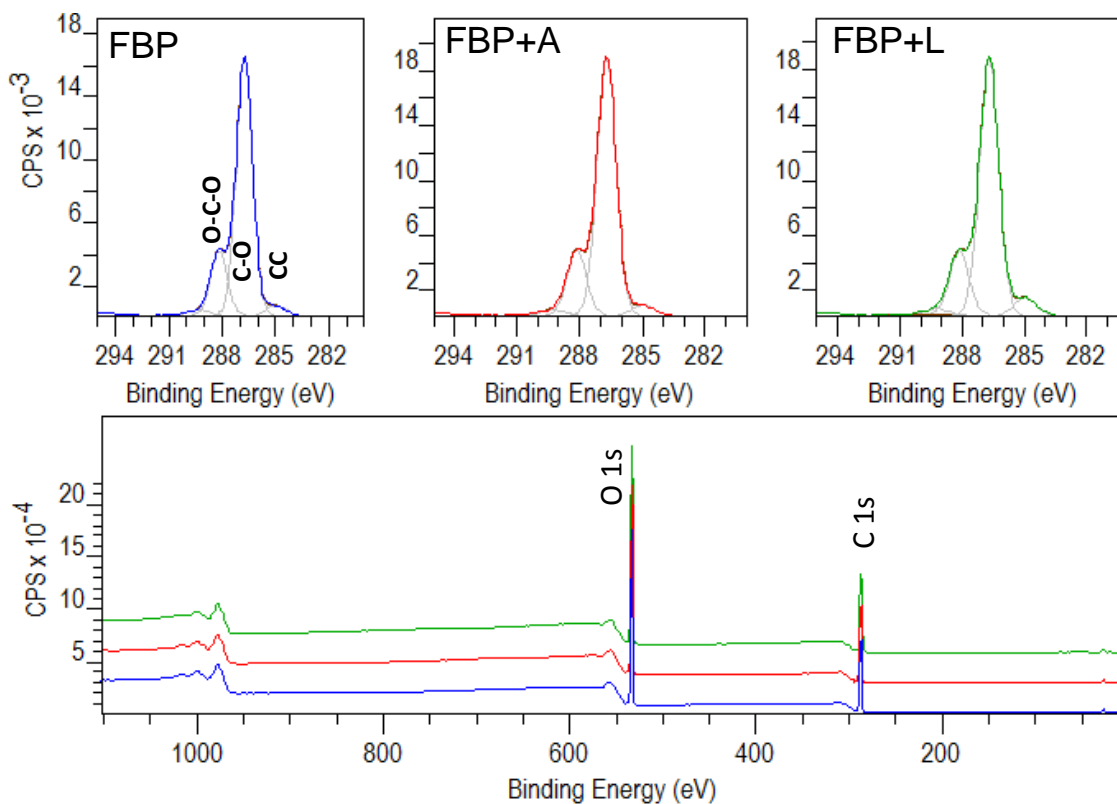


Fig. S1. Effect of the AA and KL pretreatments on unrefined pulp C 1s spectra. (a) FBP = fully bleached, (b) FBP+A = AA impregnated, and (c) FBP+L = KL impregnated sheets. The heights of the spectra were normalized relative to the signal intensity of the C-O component. (d) XPS survey on unrefined FBP, FBP+A, and FBP+L sheets.

Table S1. Effect of the AA and KL Pretreatments, Refining, and Thermal treatments (30 min, 225 °C, 1 and 75 v/v-%) on the Density and Thickness (\pm Standard Deviation) and the Average Basis Weight of the Sheets

Pulp	Density (kg m ⁻³)	Basis weight (g m ⁻²)	Thickness (μ m)
Unrefined FBP, initial	609 \pm 15	65.0	106.8 \pm 1.3
Unrefined FBP, 1 v/v-%	598 \pm 7	62.9	105.1 \pm 0.6
Unrefined FBP, 75 v/v-%	595 \pm 8	62.3	104.7 \pm 0.7
Refined FBP *, untreated	961 \pm 16	64.6	67.2 \pm 0.5
Refined FBP *, 1 v/v-%	924 \pm 6	62.7	67.9 \pm 0.2
Refined FBP *, 75 v/v-%	929 \pm 12	62.6	67.4 \pm 0.4
Unrefined FBP+A, initial	616 \pm 13	64.5	104.6 \pm 1.1
Unrefined FBP+A, 1 v/v-%	596 \pm 5	61.9	103.8 \pm 0.5
Unrefined FBP+A, 75 v/v-%	598 \pm 8	62.7	105.0 \pm 0.7
Refined FBP+A *, initial	977 \pm 13	66.8	68.3 \pm 0.4
Refined FBP+A *, 1 v/v-%	948 \pm 8	64.5	68.1 \pm 0.3
Refined FBP+A *, 75 v/v-%	933 \pm 10	65.2	69.8 \pm 0.4
Unrefined FBP+L, initial	617 \pm 24	65.4	106.0 \pm 2.1
Unrefined FBP+L, 1 v/v-%	599 \pm 11	63.5	106.1 \pm 1.0
Unrefined FBP+L, 75 v/v-%	596 \pm 12	63.7	106.9 \pm 1.1
Refined FBP+L *, initial	931 \pm 27	64.5	69.2 \pm 1.0
Refined FBP+L *, 1 v/v-%	889 \pm 17	63.6	71.5 \pm 0.7
Refined FBP+L , 75 v/v-%	918 \pm 5	63.3	69.0 \pm 0.2

* The fully bleached, AA and KL pretreated pulp sheets (FBP, FBP+A, and FBP+L, respectively) were refined for 90 min in a Hollander refiner.

Table S2. Effect of the AA and KL Pretreatments, Refining, and Thermal treatments (30 min, 225 °C, 1 and 75 v/v-%) on the Tensile and Burst Strengths (\pm Standard Deviation)

Pulp	Unrefined FBP *	Refined FBP *	Unrefined FBP+A *	Refined FBP+A *	Unrefined FBP+L *	Refined FBP+L *
Tens. Str. (Nm g ⁻¹) initial	31.1 \pm 2.0	100.2 \pm 2.6	31.5 \pm 0.8	96.7 \pm 4.7	31.3 \pm 1.0	103.9 \pm 6.5
1 v/v-%	36.8 \pm 1.7	94.8 \pm 3.3	35.0 \pm 1.8	92.2 \pm 3.3	35.0 \pm 1.5	97.6 \pm 3.4
75 v/v-%	33.3 \pm 0.9	86.4 \pm 7.9	30.5 \pm 1.3	85.3 \pm 3.4	31.8 \pm 1.2	89.1 \pm 2.8
Burst Str. (kPam ² g ⁻¹) initial	1.89 \pm 0.15	6.88 \pm 0.20	1.98 \pm 0.04	6.69 \pm 0.66	1.88 \pm 0.11	6.98 \pm 0.67
1 v/v-%	3.26 \pm 0.73	6.19 \pm 0.37	2.06 \pm 0.10	5.63 \pm 0.38	2.06 \pm 0.13	6.02 \pm 0.79
75 v/v-%	2.04 \pm 0.06	4.29 \pm 0.73	1.79 \pm 0.11	4.16 \pm 0.50	1.85 \pm 0.12	5.60 \pm 0.15

* The fully bleached, AA and KL pretreated pulp sheets (FBP, FBP+A, and FBP+L, respectively) were refined for 90 min in a Hollander refiner.