Fractionation of pulp and precipitated CaCO_3 -pulp composites: effects on sheet properties of selective CaCO_3 precipitation onto fiber size fractions

Teija Laukala · Kaj Backfolk · Isto Heiskanen

Received: 22 December 2020 / Accepted: 29 March 2021 / Published online: 11 May 2021
© The Author(s) 2021

Abstract CaCO_3 -pulp composite was prepared via precipitation of calcium hydroxide in the presence of pulp. In order to investigate the precipitation selectivity and mechanism, the substrate pulps and the obtained composites were fractionated (R30, R100, R200, R400 and a sedimented fraction that passed the 400 mesh wire) using a Bauer-McNett unit. The main fractionation criterion was therefore fiber length. The pulp used was CTMP (chemithermomechanical pulp), yielding a precipitated calcium carbonate-chemithermomechanical pulp (PCC-CTMP) composite with a targeted PCC-to-CTMP ratio of 1:1. The PCC consisted primarily of nano-sized primary particles which formed aggregates and clusters on the fibers. When the fiber morphology, zeta potential and surface charge density of the fractions were determined, a correlation was found between the surface charge density of the

CTMP and the ash content of the corresponding PCC-CTMP fractions. This supports the hypothesis that the precipitation on the CTMP fiber is driven by the charge interparticle interaction. The use of refined CTMP furnishes and fractionation of the PCC-CTMP furnishes demonstrates that PCC is preferably fixed on fines and fibrils since it appears at a higher content in the fines fractions. Fiber activation via fiber split, removal of primary wall and surface defibrillation enhanced the affinity of the PCC for the fibrils. The laboratory handsheets prepared from the material demonstrated the importance of controlling the substrate fiber properties for the mineral-fiber composite, e.g. via refining, as differences between the refining levels and fractions were found to lead to differences in both optical properties and bonding.

T. Laukala (✉)
Lappeenranta-Lahti University of Technology Packaging
technology of LUT School of Energy Systems,
P.O. Box 20, 53850 Lappeenranta, Finland
e-mail: teija.laukala@lut.fi

K. Backfolk · I. Heiskanen
Stora Enso OyjResearch Center Imatra, 55800 Imatra,
Finland

Graphic abstract

Keywords PCC · Precipitated calcium carbonate · CTMP · Improved filler · Composite filler · In-situ precipitation

Introduction

Calcium carbonate, CaCO_3 , is a commonly used filler or pigment in many industrial applications including ceramics, composites, paints, plastics and paper. While the effects of typical fillers and filling mechanisms on paper properties are fairly well understood and widely discussed in the literature, e.g. by Hubbe and Gill (2016), work on different filler dosing concepts and modified fillers is still in progress and requires more attention. In a review paper by Shen et al. (2009), different approaches for filler modification were explored and discussed, for example the use of inorganic substances to improve acid tolerance, the use of organic polymers to enhance filler-fiber bonding, and filler modification with cellulose and cellulose derivatives. The traditional way of adding fillers has its limitations, and alternative concepts such as in-situ precipitation onto fibers or in-line precipitation have therefore recently gained interest.

One approach where CaCO_3 is used as a filler is through in-situ precipitation (IS-precipitation), i.e. the synthesis and precipitation of calcium carbonate (PCC) in the presence of the cellulosic fiber, where the conditions of precipitation can be controlled and adjusted so that the PCC is precipitates directly onto cellulosic material (Rantanen 2016; Silenius 2002; Subramanian 2008) or into the lumen and cell wall

pores (Ciobanu et al. 2010; Fortuna et al. 2003). Mechanisms have been proposed to explain the PCC attachment onto the cellulose, but results and theories are controversial and there is still a lack of understanding of the fixation and adhesion mechanism. Subramanian (2008) suggested that the precipitation proceeds via an amorphous calcium carbonate (ACC) precursor which forms line-like aggregates on the cellulosic particles due to inter-particle interactions (due to polarization of the ACC particles), and is subsequently precipitated as calcite. Silenius (2002), on the other hand, suggested a heterogeneous nucleation based on classical crystallization theory. The crystallization on cellulose has been associated with the functional groups capable of binding metal ions (including Ca^{2+}), which is thought to lead to subcritical nuclei being formed on the cellulosic substrate, and subsequent nucleation (Dalas et al. 2000).

Silenius (2002) pointed out that the PCC precipitates mainly on the cellulosic fines due to the large surface area of the fines in comparison to that of the larger fibers. ‘Fines’ is usually defined as the material that passes the 200 mesh wire of Bauer McNett classifier (Heinemann and Vehniäinen 2009). Silenius’ (2002) result has been supported by Seo et al. (2017). Wood pulp fines also contain more carboxyl groups, metal ions and negative charges than the larger fibers (Odabas et al. 2016). This suggests that the preferential precipitation of PCC onto fines may be partially due to the charged, metal-binding groups. The importance of functional groups has also been observed with synthetic polymers. For example, Lakshminarayanan et al. (2003) precipitated PCC in-situ onto both untreated and chemically treated

synthetic polyamide fibers (Nylon 66 and Kevlar 29) and reported that the nucleation density was greater on the treated fibers, confirming the importance of charged sites. On the other hand, recent findings have demonstrated that PCC can also be precipitated on essentially uncharged fibers such as bacterial nanocellulose (Stoica-Guzun et al. 2012) or polyvinyl alcohol fiber (Park et al. 2017).

The formation of the PCC-fiber composite makes it possible to create a novel platform of engineered fillers which may provide new features for the papermaking process and end products. The surface morphology and chemistry of the fibers are altered by the mineral precipitation process, which can be used to enhance the material property space and to control optical properties, fiber-fiber contacts and bonding in sheets. The effects on sheet properties have often been contradictory when filling is done using IS-precipitated CaCO_3 . For example, sheet opacity has been reported to increase by Ciobanu et al. (2010), and to decrease by Klunness et al. (2000) and Kumar et al. (2009). The brightness has been reported to increase by Mohamadzadeh-Saghavaz et al. (2014) and to decrease by Klunness et al. (2000). Similarly, the tensile index has been reported to increase by Silenius (2002) and to decrease by Mohamadzadeh-Saghavaz et al. (2014).

One possible reason for the contradictory findings and statements is the use of different raw materials. A thorough review of the role of fiber source and particularly of the dependence on size fractions and fiber size in the precipitation mechanism and nucleation is lacking. Also identically performed IS-precipitation has been found to result in different PCC-fiber properties depending on the fiber source (Klunness et al. 2000).

In general, the presence of fines increases inter-fiber bonding in sheets. Fines affect many strength properties and especially the tensile strength (Odabas et al. 2016), although the strength-enhancing effect is greater with kraft fines than with mechanical fines (Retulainen et al. 1998). Light scattering, important for optical development of sheets, is instead increased by the presence of mechanical fines, while kraft fines tend to reduce it (Odabas et al. 2016). This is explained by the non-bonded surface of the mechanical fines (Leskelä 1998). The assumed preferential precipitation of PCC onto fines can be expected to alter the properties of the fines fraction more than those of the

coarser fiber fractions. The preferential precipitation might reduce the strength-enhancing properties of the fines fraction, although the optical properties would be positively affected.

In the present work, PCC was precipitated onto refined and unrefined chemithermomechanical pulp (CTMP) in order to study the role of CTMP composition and the precipitation of PCC onto the CTMP fines. The CTMP pulp, at three different refining levels, was then used for in-situ PCC precipitation and for making PCC-CTMP composite filler. The PCC-CTMP composite fillers were subsequently fractionated in order to gain a further understanding of the selectivity and precipitation efficiency of PCC onto each fraction. The effect of the different PCC-CTMP fractions on sheet properties were evaluated. The CTMP fiber was chosen because of its broad fiber size distribution and sufficiently high fines content, while primary wall parts still attached to some of the fibers.

Materials and methods

The CTMP was provided by Stora Enso (Kaukopää mill Imatra, Finland) as air dry sheets, which were disintegrated and refined using a Valley beater (SCAN-C 25:96). The Schopper Riegler freeness values (SCAN C 19:65) of the pulps were 23 (0 min refined), 42 (30 min refined) and 58° SR (60 min refined). The fiber length distributions of the CTMP materials are shown in Fig. 1. The calcium hydroxide ($\text{Ca}(\text{OH})_2$) was prepared from calcium oxide (CaO , Honeywell reagent, purity > 96 %).

Sample preparation

PCC-CTMP preparation

The three grades of PCC-CTMP were prepared by beating the pulp to three different levels. Each grade was prepared by reacting $\text{Ca}(\text{OH})_2$ and carbon dioxide (CO_2 (AGA, purity $\geq 99.8\%$)) in the presence of CTMP fibers in a 10 l open batch reactor. The reactor height was 50.6 cm and inner diameter 16.2 cm. The reactor was equipped with a gas outlet at the bottom and a stirrer with three impellers, 8.4 cm Roushton which was the lowest and two 8.5 cm pitched blade

Fig. 1 Fiber length distributions of CTMP: 0 min refined (23° SR), 30 min refined (42° SR) and 60 min refiner (58° SR). The values given are weighted with respect to fiber length

impellers. The impellers were placed 16 cm distance from each other.

The batch size was 9.5 l and the fiber consistency 1.3 wt% before precipitation. For each batch, the depletion of $\text{Ca}(\text{OH})_2$ was determined by the decrease in pH. At the beginning of the reaction, the temperature was ca. 20 °C, but it was allowed to change freely during the exothermic precipitation process. The CO_2 feed was 3 l/min and the target $\text{Ca}(\text{OH})_2$ dose (before precipitation) was 1.0 wt%, corresponding to 50 wt% CaCO_3 filler (ash) content assuming 100 % conversion.

The $\text{Ca}(\text{OH})_2$ used was prepared from CaO. Slaking was carried out for 4 h. The CaO-to- H_2O ratio used was 1:9. The initial temperature was 40 °C, but the temperature was allowed to change freely.

Pulp fractionation

The pulps (CTMPs and PCC-CTMPs) were fractionated using a Bauer-McNett classifier according to the SCAN-M 6:96 standard, with the exception of the dosed fiber weight. In case of PCC-CTMP, 20 g of solids (CTMP and PCC combined, containing approximately 10 g of CTMP), were used in the fractionation. In the case of the CTMP, the amount was equal to that used for the corresponding PCC-CTMP, i.e. close

to 10 g. The wires used during fractionation were 30, 100 and 200 of the ASTM series (nominal openings 595, 149 and 75 μm , respectively) and 400 mesh wire with a measured opening of 25 μm . The fractions were labelled to indicate residuals. For example R30 refers to fraction retained by 30 mesh wire. The scheme of experiments is shown in Fig. 2.

A minimum of seven fractionations were carried out for each pulp. Five were done to collect fractions in separate vessels for further use, and two to weigh the fractions and measure their ash. To do so the fractions were collected on ashless filter paper (Macherey-Nagel MN 640 m) and dried in an oven at 105 °C prior the ash content determination. TAPPI standards T 211 om-02 and T 413 om-11 were used in conjunction to determine the ash content.

Handsheet preparation

Handsheets were prepared according to the SCAN C 26:99 standard with the exception of the drying (drum, surface temperature ca. 60 °C) and the use of an auxiliary wire (90 gsm polyester satin, thread width approximately 300 μm). The auxiliary wire was placed on the sheet mould wire and removed after wet-pressing.

Analytical procedures

Fiber analysis

The CTMPs, PCC-CTMPs and fractions were analyzed using the L&W Fiber Tester (Lorentzen and Wettre, Kista, Sweden) using a dilution of approximately 0.1 g fibers in 100 ml of water. Fiber length, fiber width, shape factor, the amount of fines and the kink index were determined and recorded as length-weighted averages.

The ash and CaCO_3 contents of the samples were measured according to TAPPI standards T 211 om-02 and T 413 om-11 in conjunction.

Zeta potential

The zeta potentials of the pulps and fractions were measured using the streaming potential method (Mütek SZP-06, BTG Instruments GmbH, Herrsching, German). The conductivity of the samples was increased to 0.30 ± 0.01 mS/cm with 0.1 M NaCl

Fig. 2 Scheme of experiments. In the fractionation, the values refer to wire meshes used (ASTM series). The R30, R100, R200, and R400 fractions were collected from the wires and vessels

after the fractionation. An additional sedimentation phase was added after the fractionation, and this yielded the ‘pass’ fraction. The bold text indicates the samples taken for further analysis

solution at least 18 h before the measurements were made.

Some of the coarsest fractions could not be measured according to the recommended procedure due to the poor water retention of the fiber cake and resulting water overflow. A filter paper (Macherey-Nagel MN 616) was therefore used, as instructed in the manual. Use of the filter paper was however found to affect the absolute zeta potential value.

Surface charge density (cationic-demand titration)

The charge density of the pulps and fractions was measured using a cationic-demand titration procedure (PCD 02, BTG Müttek GmbH and Mettler DL25, GWB for titrant dosing). Titration was done as back titration as recommended by the manufacturer, although the amount of sample was modified.

The amount of fiber slurry containing approximately 0.2 g of fiber was filtered on a polycarbonate membrane (GE Water & Process technologies, 3.0 μ m) and rinsed into a decanter using deionized water to obtain a 5.0 g sample. The amount of poly(diallyldimethylammonium chloride) (PDADMAC, 1.0 mN, $M = 107\,000$ g/mol, BTG) solution added was 20 g. Fibers were removed from the residual PDADMAC by centrifugation (6400 g). Titration was carried out using polyethene sodium sulfonate (PES-Na, 1.0 mN and $M = 19\,100$ g/mol, BTG). After the titration, the fiber weight was determined by drying the fiber overnight at 105 °C. The results are given as averages of three or four measurements.

Scanning electron microscopy

The PCC-CTMP samples were characterized by scanning electron microscopy (SEM) using a Hitachi SU3500 equipped with a wolfram filament and backscatter electron (BSE) detector to capture micrographs of the samples. Composition (COMP) mode was used in order to obtain good contrast between PCC and the cellulosic fiber; the PCC particles or PCC rich areas therefore show lighter than areas free from PCC. The imaging was done on non-coated samples using the variable pressure (VP-SEM) mode at 60 Pa, 15 kV acceleration voltage and a working distance of 10 mm. These images are labeled with the text VP-SEM. The coated samples (sputter with an Au/Pd target) were imaged using secondary electron imaging (labeled SEM in the images), an acceleration voltage 15 kV and a working distance of 10 or 15 mm.

Handsheet testing

The handsheets were conditioned (23 °C and 50 % RH) and tested according to the SCAN standards SCAN P6:75 (grammage), SCAN P 7:96 (density and thickness), and SCAN P 38:80 (tensile index, tensile stiffness, and elastic modulus). The tensile and tensile stiffness indices were additionally calculated using a fiber-weight-based index, i.e. the ash weight was subtracted from the grammage used in the calculation. When the fiber-weight-based index is discussed, this is indicated in the text.

Brightness and opacity were measured using Elrepho (L&W) according to standards ISO 2470-1

(brightness) and ISO 9416 (light scattering coefficient (s_r), light absorption coefficient (k_r) and calculated opacity for 65 g/m² sheet), with the exception of measured samples (4 test pieces instead of 10).

Results

Fractionation of CTMP and PCC-CTMP

The different CTMP and PCC-CTMP furnishes were fractionated and characterized as shown in Table 1. With increasing refining, the fines content increased in both CTMP and PCC-CTMP. In the case of the PCC-CTMP, the ‘pass’ fraction corresponded to 40–50 % of the total dry material of the sample, which was significantly greater than for the CTMP. The ‘pass’ fraction was mainly PCC, as indicated by the high ash

content (80–85 wt% of all the ‘pass’ fraction samples). Most (84–89 wt%) of the total PCC was found to pass the finest 400 mesh wire.

When the cumulative residual was determined, excluding the fraction passing the 400 mesh wire (see Fig. 3), precipitation was found to affect the distribution: the fractions of smaller fiber sizes were emphasized. This was especially obvious when the fibers were refined. This was associated mainly with the weight of PCC in the finer fiber fractions, which reduced the relative weight of the less PCC-rich fractions (see Fig. 4), and to a lesser degree with the increasing tendency of material to pass the wires.

Figure 4 shows the distribution of total ash between the PCC-CTMP fractions and the ash content in each fraction. Most of the total ash that did not pass the 400 mesh wire was found in R100 (0 min refined sample) or R200 (30 and 60 min refined samples), but the ash

Table 1 Proportions of unfractionated pulps and pulp fractions as mean values with 95% confidence intervals. The amount of CaCO₃ was calculated based on the 525 °C and 900 °C ash content measurements, i.e. the approximate percentage of ash that was CaCO₃. Values are also given for CTMP, although the samples contained no added CaCO₃

	CTMP			PCC-CTMP		
	0 min	30 min	60 min	0 min	30 min	60 min
<i>Distribution in fractionation (wt%)</i>						
R30	20.4 ± 2.6	12.2 ± 0.9	7.5 ± 0.4	8.6 ± 1.5	4.9 ± 0.5	3 ± 0.4
R100	50.4 ± 2.3	50.9 ± 2.0	50.8 ± 1.1	30.6 ± 5.6	16.3 ± 2.4	16.3 ± 3.9
R200	17.9 ± 1.3	23.2 ± 2.0	26.9 ± 1.9	14.4 ± 1.4	28.9 ± 2.1	25.7 ± 2.8
R400	4.6 ± 0.2	5.4 ± 0.2	6.3 ± 0.7	4.6 ± 0.2	6.1 ± 0.9	5.7 ± 0.6
Pass	6.7 ± 1.2	8.2 ± 0.8	8.4 ± 0.5	41.8 ± 7.1	43.9 ± 3.3	49.3 ± 1.9
<i>Ash 525 ± 25 °C (%)</i>						
R30	1.2 ± 0.0	1.2 ± 0.2	1.3 ± 0.1	6.4 ± 0.9	8.7 ± 1.1	7.9 ± 2.3
R100	1.1 ± 0.1	1.1 ± 0.0	1.1 ± 0.0	8.1 ± 0.9	8.5 ± 1.5	8.7 ± 3.6
R200	1.3 ± 0.1	1.2 ± 0.1	1.2 ± 0.3	15.0 ± 1.4	11.2 ± 2.1	11.4 ± 4.5
R400	1.8 ± 1.1	1.9 ± 0.4	1.7 ± 0.3	42.2 ± 3	29.4 ± 2.9	29.0 ± 7.7
Pass				89 ± 0.1	86.3 ± 0.4	84.0 ± 0.4
Not fract	1.0 ± 0.0			47.9 ± 0.7	47.3 ± 0.2	48.5 ± 0.6
<i>Ash 900 ± 25 °C (%)</i>						
R30	0.8 ± 0.0	0.8 ± 0.2	0.9 ± 0.1	3.8 ± 0.5	5.1 ± 0.6	4.7 ± 1.2
R100	0.8 ± 0.2	0.8 ± 0.1	0.7 ± 0.0	4.8 ± 0.5	5 ± 0.7	5.1 ± 2.1
R200	0.9 ± 0.0	0.9 ± 0.1	0.8 ± 0.2	8.6 ± 0.9	6.5 ± 1.2	6.6 ± 2.5
R400	1.4 ± 0.9	1.5 ± 0.6	1.3 ± 0.2	24 ± 0.0	17 ± 1.8	16.8 ± 4.3
Pass				50.2 ± 0.1	48.7 ± 0.1	47.4 ± 0.2
<i>CaCO₃ (% of ash)</i>						
R30	69.9	75.9	68.2	92.3	93.8	91.6
R100	66.5	66.1	70.4	94.0	94.2	92.5
R200	63.8	63.0	62.7	96.7	95.5	96.0
R400	49.3	55.2	60.4	98.1	96.3	96.0
Pass				99.1	99.0	99.3

Fig. 3 Cumulative residuals on the wires, calculated by weight. The ‘pass’ fraction has been excluded to facilitate the comparison

Fig. 4 Ash distribution in the fiber fractions. The bars (indicated on the left-hand ordinate, “Of tot. ash in composite”) show the percentage of ash in the fractions of the unrefined and refined PCC-CTMP fillers after fractionation. The lines (indicated on the right-hand ordinate, “Ash content of fraction”) show the ash content in each fraction

content of the fraction increased with increasing mesh number. The ash contents of the samples refined for 30 and 60 min were essentially identical, although the 30 min sample fractions had a slightly higher percentage of total ash. This was explained by slightly better retention of ash in non-pass fractions in 30 min refined sample, and the slightly higher total ash of the 60 min refined sample.

Fiber analysis

The average fiber length, fiber width, shape factor, amount of fines and kink index are shown in Table 2. Refining of the unfractionated CTMP reduced the fiber length, fiber width and kink index, but increased the shape factor and amount of fines. Similar changes were detected for the PCC-CTMP, although the change in fiber width was negligible.

Comparison of the unfractionated CTMP and PCC-CTMP showed that the fiber length was unaffected by precipitation process of PCC. The fiber width, shape factor and amount of fines increased, but the kink index decreased. The changes caused by precipitation in width and shape factor were however very small: the maximum change detected for these values was 6.4 % increase in width.

The differences between the unfractionated PCC and PCC-CTMP were similar to those observed between the fractions. The fiber length in each fraction decreased slightly with refining, but no differences were seen between the CTMP and PCC-CTMP fractions. The main difference was in the fines content of the fractions. The CTMP fractions had more fines than the PCC-CTMP fractions, although the fines content of the unfractionated PCC-CTMP was larger than that of the CTMP.

The fiber length, fiber width and shape factor distributions of the fractions were essentially unaffected by the precipitation process, as the fines were not included in the distributions. This is illustrated in Figs. 5 and 6, which show the length and width distributions, respectively, in fractions of samples refined for 30 min.

Table 2 Physical fiber properties. Shape refers to shape factor. The amount of fines is given as a percentage of non-fines material. The values given are weighted with respect to fiber length

Sample	Length (mm)	Width (μm)	Shape (%)	Fines (%)	Kink index
CTMP					
0 min					
R30	2.65	42.8	91.2	0.6	0.19
R100	1.65	41.1	91.8	0.8	0.36
R200	1.00	36.8	91.6	11.3	0.48
R400	0.50	38.7	90.8	212.2	0.52
Not fract	1.49	39.3	90.8	10.9	0.46
30 min					
R30	2.52	44.1	93.0	0.5	0.24
R100	1.48	40.9	92.9	1.5	0.26
R200	0.95	37.1	92.4	12.2	0.33
R400	0.57	32.3	91.8	211.1	0.39
Not fract	1.26	38.2	91.0	14.5	0.33
60 min					
R30	2.40	44.1	96.6	0.4	0.10
R100	1.34	40.8	92.9	1.0	0.19
R200	0.87	37.2	92.6	11.9	0.17
R400	0.66	33.9	92.1	171.6	0.24
Not fract	1.15	38.2	91.1	15.3	0.30
0 min					
R30	2.73	43.8	92.3	0.7	0.12
R100	1.65	41.5	92.1	0.9	0.30
R200	1.06	37.8	91.8	9.3	0.38
R400	0.64	32.8	91.3	184.3	0.59
Pass	0.58	31.7	92.3	601.0	1.29
Not fract	1.50	40.4	91.1	13.7	0.38
PCC-CTMP					
30 min					
R30	2.63	45.3	93.1	0.3	0.08
R100	1.49	41.9	93.0	0.7	0.21
R200	0.94	37.8	92.6	10.0	0.31
R400	0.57	32.2	92.2	194.6	
Pass	0.77	30.6	92.6	617.6	0.50
Not fract	1.27	40.6	91.9	16.8	0.30
60 min					
R30	2.50	45.5	92.4	0.4	0.08
R100	1.33	42.0	92.9	0.8	0.21
R200	0.87	38.1	92.7	10.0	0.27
R400	0.51	31.5	91.9	270.5	
Pass	0.61	31.7	90.7	433.7	1.13
Not fract	1.12	40.3	92.2	17.0	0.25

Fig. 5 Fiber length frequency distributions for CTMP and CTMP-PCC refined for 30 min. Note the logarithmic x-axis

Fig. 6 Fiber width frequency distribution for CTMP and CTMP-PCC refined for 30 min. Note the logarithmic x-axis

Zeta potential and surface charge density

The zeta potential and surface charge density data are shown in Table 3; Fig. 7. Although the samples were either anionic (CTMP and most PCC-CTMP samples) or essentially non-charged (some of the PCC-CTMP samples), the unfractionated PCC-CTMPs showed positive zeta potentials. Refining of the CTMP increased the surface charge density but reduced the zeta potential, presumably due to the creation of more cellulose rich areas on the CTMP fiber surfaces (Hubbe 2006). This was observed particularly for the R30 CTMP samples. Increasing refining did not affect the surface charge of the R400 fractions in an obvious manner.

The charge development detected for CTMP is in good agreement with the literature. Sundberg and Holmbom (2004) reported that flake-like CTMP fines had a higher total charge than fibril-like fines, both of which had a total charge more than twice that of the CTMP fibers. Mosbye and Laine (2002) reported that the primary fines of mechanical pulp had a higher total charge than secondary fines, although the difference was greatly diminished by alkali treatment used to imitate the effect of bleaching. In our case the pulp was bleached.

Although the charge of PCC is commonly cationic due to an excess of positive calcium (Ca^{2+}) (Laine 2007), all fractions of PCC-CTMP, including the extremely PCC rich ‘pass’ fraction, had negative or essentially neutral surface charges. This may have been due to adsorbed anionic dissolved (and colloidal) material without significant incorporation of the materials into crystal as described by Jada and Verraes (2003) for a different polymer or the “cleaning effect” of the in-situ precipitation of PCC, in which dissolved (and perhaps colloidal) material is absorbed onto the PCC as reported by Matula et al. (2018).

The positive zeta potentials of unfractionated PCC-CTMP were probably an artifact caused by small, PCC-rich particles found on the ‘pass’ fraction of the unfractionated pulps, as they were poorly immobilized during the zeta potential measurement and were able to pass the wire and disturb the measurement. Another possible explanation was over-emphasizing of possibly cationic PCC residing on fiber surfaces of unfractionated samples due to the flow conditions and ion

Table 3 Zeta potential and surface charge mean values with 95% confidence limit. Note that R30 zeta potential absolute value was affected by the use of a filter paper

	CTMP			PCC-CTMP			Surface charge density ($\mu\text{ekv/g}$)	
	Zeta potential (mv)	pH	EC (mS/cm)	Zeta potential (mV)	pH	EC (mS/cm)	CTMP	PCC-CTMP
<i>0 min</i>								
R30							-5.8 ± 4.3	-1.2 ± 3.9
R100							-7.1 ± 2	-3.4 ± 5.2
R200	-52.2 ± 1	7.3	0.30	-50.3 ± 2.9	8.0	0.29	-9.7 ± 0.9	-3.8 ± 3.2
R400	-29.1 ± 0.6	7.5	0.29	-26.1 ± 0.6	8.0	0.29	-46.9 ± 2.4	-41 ± 2.2
Pass								-20.2 ± 2.5
Not fract	-64.9 ± 1.6	6.5	0.30	16.8 ± 0.1	8.1	0.30	-18 ± 0.6	-26 ± 1.6
<i>30 min</i>								
R30	-20.4 ± 4.4	7.3	0.3				-8.3 ± 3.1	-1.9 ± 5.2
R100	-47.4 ± 1.1	7.6	0.30	-63 ± 2.3	7.9	0.29	-8.2 ± 2.1	2.1 ± 6.4
R200	-48.8 ± 2.2	7.4	0.31	-54.6 ± 1.7	7.9	0.30	-11.3 ± 3.6	-5.2 ± 3
R400	-26.8 ± 0.6	7.4	0.30	-22.8 ± 0	7.9	0.28	-47.3 ± 1.7	-42.1 ± 1.2
Pass								-31.1 ± 4.1
Not fract	-55 ± 1.6	6.3	0.3	14.2 ± 1.7	8.5		-21.2 ± 2.7	-20.5 ± 1.2
<i>60 min</i>								
R30	-13.6 ± 1.1	7.7	0.29				-10.7 ± 4.2	-10.9 ± 4.3
R100	-47.3 ± 1.4	7.5	0.31	-60.8 ± 1.2	8.0	0.30	-12.1 ± 0.5	-9.7 ± 1.5
R200	-51.8 ± 1.6	7.5	0.30	-32.1 ± 0.8	8.0	0.30	-10.8 ± 2.7	-16.6 ± 1.7
R400	-26.8 ± 9.5	7.4	0.30	-23.7 ± 0.4		0.29	-45.9 ± 5.5	-57.6 ± 1.1
Pass								-38.2 ± 1.6
Not fract	-44.6 ± 1.7	6.7	0.30	12.4 ± 0.5	8.5	0.30	-27.8 ± 0.4	-15.5 ± 3.4

Fig. 7 Surface charge densities of the samples. C refers to CTMP and P-C to PCC-CTMP. The error bars represent 95 % confidence values. n/f = not fractionated

flux. In addition, the streaming potential method used in this study is affected by fiber pad compression (Hubbe 2006), and the fiber pad compression was visibly dependent on the fraction measured, which may explain why the zeta potential was closer to zero for R30 and R400 than for R100 and R200.

Scanning electron microscopy

Scanning electron microscopy of the fractionated PCC-CTMP samples further confirmed that the ash content increased with decreasing fiber size, see Fig. 8. The PCC was in the form of typically nano-sized roundish particles and their aggregates or clusters. No variation in PCC morphology or primary particle size was detected between the different fiber fractions, but the larger amount of PCC in the fines fraction suggested that the PCC nanoparticle aggregate size perhaps increased.

Fig. 8 SEM micrographs of fractionated PCC-CTMP samples. **a** (30 min R200): a band of outer fiber layers essentially free from PCC (indicated with the arrow), surrounded by more PCC rich areas. **b** (0 min R200): heavily fibrillated fiber with high

content of PCC and a more intact fiber with substantially no PCC. **c** (0 min ‘pass’ fraction): fibrils and fines extremely rich in PCC. Image **d** (60 min R200): split or cleaved fiber with PCC deposited in lumen and outer layer essentially free from PCC

The PCC was located mainly on fiber regions where the outer layer of the fibers had been removed (Fig. 8a) or where the fiber surface was damaged or subjected to fibrillation (Fig. 8b). The tendency of the PCC to attach to fibrils or to damaged regions of the fiber was clearly evident in the fractionated samples with the highest amount of fines, i.e. the R400 and in ‘pass’ fractions (Fig. 8c). Split fibers had enriched PCC deposits in the lumen, while the outer surface appeared to be essentially free from PCC (Fig. 8d). This type of finding was usually seen in R100 and R200, but occasionally also in R30.

When the fractions of PCC-CTMP were compared with the unfractionated PCC-CTMP (Fig. 9), it was evident that a larger portion of the fibers were substantially free from PCC in the fractionated pulps than in the unfractionated sample. Some of this difference could be explained by the hypothesis that the fines in the unfractionated pulp were attached or otherwise located on larger fibers (thus appearing a

part of them), and these objects containing more PCC were removed during fractioning. The surfaces of the larger CTMP fibers were however also affected by fractionation: some of the PCC residing on the fiber surface was removed during fractionation.

Handsheet properties

Physical properties

The physical properties of the handsheets are shown in Table 4 and in Figs. 10, 11, 12 and 13. The sheets had an average grammage of 68.6 g/m² (standard deviation 5.8 g/m²). The ash content of the sheets was assumed to be close to that of the pulp or fraction used in sheet preparation (Table 1), since the auxiliary wire improved mechanical retention.

The density of PCC-CTMP handsheets from unfractionated pulps was higher than that of CTMP handsheets free from PCC. The difference in density

Fig. 9 Unfractionated pulp (a) and fractionated pulp (b) R30. Both images were taken on PCC-CTMP refined for 60 min

was 16, 14 and 7 % for samples refined for 0, 30 and 60 min, respectively. The handsheet strength increased with decreasing fiber size and increasing pulp refining for both CTMP and PCC-CTMP. The coarse, stiff fibers, as in R30, are known to give high bulk and a highly porous sheet, but poorer bonding than the more flexible and conformable finer fibers (Retulainen et al. 1998). This result was, therefore, expected.

A more relevant comparison between CTMP and PCC-CTMP sheets reveals the effect of the PCC. The increase in density of the PCC-CTMP fraction sheets with increasing refining level was not as pronounced as that of the CTMP sheets. PCC-CTMP sheets from the 60 min refined pulp fractions had lower density than the corresponding CTMP sheets. This was associated with the debonding effect of nanosized particles and agglomerates of PCC on the fiber. The debonding effect is supported by the tensile index and tensile stiffness index results.

There was a good linear correlation between tensile index, elastic modulus, tensile stiffness and density for both CTMP and PCC-CTMP sheets made of fractions (Fig. 14). The slopes of the regression lines differed greatly for CTMP and PCC-CTMP sheets in the case of tensile index versus density (0.130 and 0.061, respectively) and tensile stiffness index versus density (0.015 and 0.010, respectively). The difference in slope was significantly less for elastic modulus versus density (0.0075 and 0.0062, respectively).

When the fiber-weight-based indices were calculated, the tensile index values of the fractionated PCC-CTMP and the corresponding CTMP sheets were similar, although the tensile index of the PCC-CTMP

sheets was lower than that of the CTMP sheets. Similarly, fiber-weight-based tensile stiffness index for PCC-CTMP was only slightly lower for R100 and R200. PCC-CTMP R400 sheets instead had a clearly higher tensile stiffness index than the corresponding CTMP R400 sheets.

Optical properties

Both the brightness (Fig. 15) and the opacity (Fig. 16) of the PCC-CTMP handsheets were greater than those of the CTMP sheets when unfractionated pulps were used. This was not, however, the case for the individual fractions. The opacity of all the fractions increased when PCC was added, but the brightness decreased for fractions R30, R100 and R200 sheets, and increased for R400 sheets.

The scattering coefficient (s_r) and absorption coefficient (k_r) (Table 5), showed that the PCC-CTMP fraction sheets had, on average, a slightly higher s_r and k_r than the CTMP sheets, except for the R400 fraction sheets. In other words, although the light scattering improved, the change in the opacity of the fractions was due to an increase in light absorption rather than due to an increase in light scattering. The increase in opacity and brightness of the unfractionated PCC-CTMP sheets over those of the unfractionated CTMP

Table 4 Physical properties of the handsheets. n/f = not fractionated pulp. n/d = not detected (in this case due to poor sheet strength). For the ash contents of the pulps, see Table 1.

	Grammage (g/m ²)		Thickness (μm)		Density [kg/m ³]		Tensile index [Nm/g]		Elastic modulus [MPa]		Tensile stiffness index [kNm/g]	
	CTMP	PCC-CTMP	CTMP	PCC-CTMP	CTMP	PCC-CTMP	CTMP	PCC-CTMP	CTMP	PCC-CTMP	CTMP	PCC-CTMP
<i>0 min</i>												
R30	73.0	69.5	382 ± 80	359 ± 26	192	194	n/d	n/d	n/d	n/d	n/d	n/d
R100	69.0	67.5	337 ± 36	333 ± 22	205	202	n/d	n/d	n/d	n/d	n/d	n/d
R200	68.0	68.0	254 ± 8	253 ± 12	267	268	8.1 ± 0.6	6.4 ± 0.5	0.38 ± 0.02	0.31 ± 0.02	1.4 ± 0.03	1.15 ± 0.10
R400	52.0	81.0	134 ± 16	179 ± 19	387	454	24.7 ± 1.6	11.8 ± 0.4	1.34 ± 0.04	1 ± 0.03	3.48 ± 0.11	2.21 ± 0.08
Pass		67.5	74 ± 7	74 ± 7		914						
n/f	67.0	68.0	275 ± 18	241 ± 30	243	282	10.7 ± 0.9	n/d	0.44 ± 0.03	n/d	1.81 ± 0.14	n/d
<i>30 min</i>												
R30	69.0	67.0	390 ± 28	366 ± 18	177	183	n/d	n/d	n/d	n/d	n/d	n/d
R100	71.0	67.0	329 ± 30	305 ± 31	216	220	5.5 ± 0.6	4.3 ± 0.1	0.2 ± 0.02	0.16 ± 0.02	0.91 ± 0.11	0.73 ± 0.03
R200	69.0	65.0	251 ± 12	250 ± 29	274	260	10.3 ± 0.4	7.7 ± 0.6	0.49 ± 0.02	0.39 ± 0.02	1.8 ± 0.06	1.49 ± 0.09
R400	73.0	81.5	171 ± 10	166 ± 15	427	492	29.5 ± 1.5	21.5 ± 1.1	1.61 ± 0.04	1.76 ± 0.08	3.77 ± 0.10	3.57 ± 0.17
Pass		67.5		68 ± 0		991						
n/f	65.5	65.0	249 ± 22	216 ± 17	263	300	18.9 ± 0.7	n/d	0.74 ± 0.04	n/d	2.81 ± 0.15	n/d
<i>60 min</i>												
R30	75.0	68.5	327 ± 50	321 ± 17	229	213	5.4 ± 0.3	5.7 ± 0.5	0.21 ± 0.01	0.21 ± 0.01	0.92 ± 0.05	0.96 ± 0.08
R100	70.5	66.5	286 ± 21	284 ± 22	246	234	7.1 ± 0.6	5.5 ± 0.4	0.33 ± 0.02	0.24 ± 0.01	1.34 ± 0.07	1.04 ± 0.06
R200	67.0	66.5	224 ± 14	237 ± 18	298	280	12 ± 1.4	8.2 ± 0.5	0.66 ± 0.05	0.46 ± 0.02	2.21 ± 0.17	1.65 ± 0.06
R400	61.0	79.0	139 ± 9	154 ± 13	441	512	34.7 ± 1.7	23 ± 0.7	1.92 ± 0.03	2.04 ± 0.05	4.36 ± 0.07	3.97 ± 0.09
Pass		69.0		68 ± 0		1043						
n/f	66.5	62.5	196 ± 11	172 ± 8	339	363	20.9 ± 2.5	n/d	1.08 ± 0.08	n/d	3.2 ± 0.24	n/d

Fig. 10 Densities of the CTMP and PCC-CTMP sheets. n/f = not fractionated

Fig. 11 Tensile index of CTMP and PCC-CTMP sheets. n/f = not fractionated. The tensile indexes of unfractionated PCC-CTMP sheets were below the test limit

sheets was therefore mainly due to the presence of the mineral-rich ‘pass’ fraction.

Discussion

Effect of CTMP refining on the in-situ precipitation of calcium carbonate

The current work confirms that mechanical refining changes the precipitation efficiency and thus the composition and properties of the PCC-fiber composite. The CTMP has a large particle size distribution in

Fig. 12 Tensile stiffness indexes of the CTMP and PCC-CTMP sheets. The category n/f refers to the sheets made using unfractionated pulp. Tensile stiffness indexes of unfractionated PCC-CTMP sheets were below test limit

Fig. 13 Elastic moduli of the CTMP and PCC-CTMP sheets. n/f = not fractionated. The elastic moduli of unfractionated PCC-CTMP sheets were below the test limit

which fines have physical and chemical properties different from those of the coarse fraction. Refining introduces changes, including fiber damage and removal of the fiber layer and the formation of debris.

Calcium carbonate precipitation onto the fibers can be affected by refining. PCC was found to be more prone to attach to the fiber parts where the outer layer (P1) had been removed or damaged, and SEM images showed that a prolonged refining and formation of higher content of split fibers means that PCC can be found on the inner lumen wall, despite the fact that the outer layers of CTMP fibers (primary wall and

Fig. 14 Tensile index versus sheet density of fractionated sheets. The lines show the linear regression

Fig. 15 Brightness (R457C) of the handsheets prepared using fractions of CTMP and CTMP-PCC. n/f indicates sheets made using unfractionated pulp

secondary wall S1) are known to be richer in charged species (such as lignin) than the inner layers of the fibers, which in turn are richer in less charged cellulose (Hubbe 2006). The study showed an approximately linear correlation between the ash content of the PCC-CTMP fractions and the anionic surface charge density of the corresponding CTMP fraction (R^2 of liner fit was 0.849, see Fig. 17).

Assuming that the metal-binding ability of the functional groups correlates with their charge, this is partly in conflict with the hypothesis that the functional metal-binding groups steer the precipitation onto the fibers. The situation is however more complex. The dominating interaction is stated to be

Fig. 16 Opacity of the handsheets prepared using fractions of CTMP and CTMP-PCC. n/f indicates sheets made using unfractionated pulp

the interaction with Ca^{2+} and the partial negative charge of the hydroxyl group (due to polarization) (Dalas et al. 2000), but the hydroxyl groups on the fibers require alkaline conditions to ionize (Sjostrom 1989) and contribute to the fiber surface charge. The fiber charge at neutral pH range is commonly attributed to carboxyl groups found e.g. in hemicelluloses instead of cellulose (Laine 2007; Sjostrom 1989), and CaCO_3 has been reported to precipitate onto surfaces via an ACC precursor that attaches onto the surface containing carboxyl groups (Stephens et al. 2011).

Lignin is known to form complexes with metals (Schmidt 2010) and has been reported to have a high affinity towards Ca^{2+} (Torre et al. 1992). The mechanism of metal uptake of lignin is however not well understood (Guo et al. 2008; Suhas et al. 2007). It has been linked with proton displacement (Christ et al. 2002; Guo et al. 2008) and carboxylic and phenolic sites, of which phenolic groups are thought to be dominant (Guo et al. 2008). The hydroxyl groups of cellulose may undergo metal-ion facilitated deprotonation especially at high pH (Al-Sogair et al. 2011), whereas it has been reported that lignin exhibits the opposite behavior, i.e. a decreasing deprotonation with increasing pH (Christ et al. 2002). This could explain why cellulose was “more effective than its charge” in initiating PCC precipitation under the conditions used in our work, especially if the charges are compared at neutral pH.

Another possible reason for the increase in ash content with increasing beating and increasing surface

Table 5 Optical properties of CTMP and PCC-CTMP handsheets

	R457C	s_r (m ² /kg)	k_r (m ² /kg)	Opacity (YC/2)
CTMP				
0 min				
R30	50.0	22.42	1.92	81.3
R100	53.3	27.11	1.82	84.0
R200	54.4	37.63	2.34	90.4
R400	55.7	69.69	4.18	97.9
Not fract	64.7	35.71	1.09	84.8
30 min				
R30	51.2	23.22	1.86	81.6
R100	53.3	26.85	1.84	83.9
R200	55.1	35.51	2.18	89.2
R400	55.5	64.78	4.01	97.5
Not fract	63.0	40.94	1.49	88.7
60 min				
R30	49.8	23.24	1.98	82.1
R100	53.2	27.54	1.90	84.6
R200	55.2	34.80	2.10	88.7
R400	56.1	59.83	3.60	96.7
Not fract	65.8	39.54	1.17	86.8
PCC-CTMP				
0 min				
R30	43.8	22.47	2.63	84.2
R100	46.9	28.95	2.81	88.4
R200	50.7	36.91	2.92	91.7
R400	58.8	78.23	4.13	98.3
Pass	75.7	60.70	1.11	91.8
Not fract	65.8	47.86	1.48	90.6
30 min				
R30	43.9	24.15	2.86	86.1
R100	47.5	29.28	2.79	88.5
R200	50.4	36.39	2.94	91.5
R400	57.1	74.73	4.37	98.3
Pass	74.5	60.25	1.29	92.4
Not fract	68.9	52.03	1.33	91.0
60 min				
R30	43.0	23.51	2.95	85.9
R100	47.1	28.35	2.78	88.1
R200	50.0	34.68	2.86	90.8
R400	57.9	79.36	4.51	98.5
Pass	70.7	47.24	1.39	90.1
Not fract	69.0	54.70	1.41	91.8

charge density was the increase in surface area and fiber damage (resulting in high energy sites). It can be argued that the surface created in refining has, for the

most part, a charge similar to that of pre-existing surface because the newly created surface has a chemical composition similar to that of the pre-

Fig. 17 Ash content of PCC-CTMP fractions plotted against the surface charge of the corresponding CTMP fraction. The error bars represent 95 % confidence values

existing surface. In this case the surface charge would be indicative of an approximately proportional increase in surface area, and the observed correlation with the surface charge density could indicate a correlation with surface area. The changes in the surface area alone do not, however, explain why PCC appeared to discriminate against the areas with intact primary wall, and it does not explain the obvious difference in fiber coverage by PCC between fines and larger fibers.

It is tempting to think that the correlation between ash content and surface charge supports a precipitation mechanism similar to that described by Subramanian (2008), i.e. that the precursor of PCC aggregates on the cellulosic particles due to electrostatic interactions, and that it adheres and subsequently crystallizes as CaCO_3 . The precursor was expected to be cationic due to an excess of Ca^{2+} in compared to the CO_3^{2-} during precipitation. The “charge neutralization by CaCO_3 precursor” concept may be partially supported by the data, as the PCC-CTMP R30 and R100 fractions refined for 0 and 30 min had essentially no anionic surface charge and that of R200 was also extremely low. On the other hand, the highly anionic surface charge of R400 and the ‘pass’ fraction, although the ‘pass’ fraction had a high mineral content, do not fully support the simple “charge neutralization by CaCO_3 precursor” mechanism.

The surface charge of a pulp commonly depends on the production process (Laine 2007). Therefore, the

relationship between the surface charge or the surface concentration of a functional groups and precipitated filler could be useful for controlling the formation of PCC-fiber composite material, if such a correlation were universally established. It was shown that the fiber surface and morphology plays a role in PCC precipitation, and that this affects the homogeneity of the PCC-fiber composite, although the precipitation was carried out in a simplified system free from many substances, such as cationic polymers and inorganic salts such as sulphates at present in paper mill waters (Laine 2007). Some of these substances may be designed to alter fiber surfaces (such as cationic polymers) and some, for example sulphonates (Tang et al. 2012), may affect the precipitation of PCC. While the concentration of a single substance in PCC-fiber composite preparation may be below the concentration it alone would significantly affect the precipitation and steering of particles onto the fiber, the net effect of different substances is difficult to predict.

Papermaking potential of PCC-CTMP: influence on fiber bonding and optical properties

As the fiber morphology remained essentially the same, the differences between the CTMP and PCC-CTMP sheets were associated with the presence of the mineral. The information regarding the role of different fractions may help to explain why the same precipitation process on different pulps may result in differences in the relative development of optical and strength properties, as was reported by Kumar et al. (2009) to happen.

The physical and optical properties of the CTMP and PCC-CTMP sheets made using the fractionated pulps suggested that the enrichment of PCC onto the desired fractions of the pulp (or onto the desired parts of the fiber) is important when tailoring the PCC-fiber composite. The differences observed between CTMP and CTMP-PCC sheets were primarily associated with differences in surface characteristics, i.e. mainly in light scattering but also in debonding as indicated by the tensile strength and density development of the sheets. The presence of a salt such as sodium or calcium chloride has been associated with changes in fiber swelling and tensile index (Fält and Wågberg 2003), but it is not known whether the PCC precipitation can alter fiber swelling. Another factor

affecting the bonding was that the PCC was precipitated in (split fiber) lumens and perhaps inside the fibrillated structures of the more well-fibrillated CTMP, which is expected to stiffen the fibers, to make them less conformable and less collapsible (Kumar et al. 2011). Such factors are desirable when high bulk is required, but they tend to have a negative effect on bonding.

There was significantly less debonding with the separate fractions than with the unfractionated PCC-CTMP. The large-fiber fractions retained their strength properties better than the small-fiber fractions. A comparison of the fiber-weight-based indices for PCC-CTMP and CTMP sheets showed only a slight decrease on strength for most fractions, and the tensile stiffness index of R400 even increased although filler is known to disturb the formation of a fiber network (Hubbe and Gill 2016). The conserved strength could depend on the distribution of PCC in the sheets (different perhaps to that of traditionally filled sheets, as reported by Silenius (2002)), or due to differences in segment activation compared with a typical sheet. The results suggest, however, that the fines fractions may be capable of containing a considerable amount of PCC without losing their bonding potential to a proportional degree.

Based on the SEM micrographs, most the PCC present was expected to form a PCC-CTMP composite, i.e. the yield of CTMP and $\text{Ca}(\text{OH})_2$ to PCC-CTMP was considered to be high. This suggests excellent retention during sheet-making, but this may not be so since the fines easily passed wires during fractionation.

Fines were expected to grow in size due to attachment of PCC. This may partially explain why the fines content increased during precipitation of PCC onto CTMP (i.e. they were better detected by the fiber analyzer), but the increase in size does not explain the increased tendency for the fines to pass the wires. We suggest that the loss of fines during fractionation was due to the precipitated PCC that reduced the tendency of the fines to attach onto other particles. Such result has been reported by Klunness et al. (1996): In their pilot trial, when using a PCC-fiber composite the total first pass retention was negatively affected, though first-pass retention of filler increased.

The PCC attached onto the fines appeared to prevent the fines from forming a gel-like, water-removal-resisting structure, which was observed on

the 400 mesh wire when the CTMP was fractionated. Reduced interparticle interactions can explain the increase in fines content during precipitation of PCC and the loss of fines during fractionation. This is in good agreement with the report that water removal from a MNFC-containing furnish is increased when PCC-fiber composite is created on the MNFC (Rantanen et al. 2015), although the increase in the amount of mobile fines is expected to decrease the water removal from the sheet (Hubbe and Heitmann 2007). Since the PCC was found to be attached mainly onto the fines, which increases the light scattering of mechanical pulp (Leskelä 1998), the increase in s_r was probably also low for the fines fraction.

Therefore, assuming that PCC is enriched on the fibrils of externally fibrillated fibers similarly than it attaches onto fines and damaged CTMP fibers, a carefully executed refining of the pulp prior to precipitation phase could be beneficial for pulp intended for PCC-fiber composite preparation. By controlling external fibrillation it could be possible to tailor PCC-fiber composites, for example by steering the precipitation onto larger fiber fractions by the use of external fibrillation. The use of selected fractions in pulp blends could also be of interest, although fractionation as such may not be the most alluring industrial approach.

Conclusions

Fractionation of the PCC-CTMP composite showed that the ash content increased with decreasing fraction size. The PCC was attached well onto the fiber, as shown by its tendency to remain in the samples and by SEM micrographs in case of the ‘pass’ fraction.

The reason for the preferred precipitation onto fines is unclear, but a correlation was found between the anionic surface charge density of the CTMP fraction and the ash content of the PCC-CTMP fraction. SEM micrograph data suggests that the PCC prefers to precipitate to the areas typically associated a lower charge than the primary wall. This may, however, be explained by chemical changes such as metal-ion facilitated deprotonation in cellulose due the higher pH. The correlation is therefore thought to support the suggestion that the interparticle (fiber-ACC) interactions, perhaps partially originating from cationic-

anionic interactions, steer the ACC onto the cellulosic fibers, onto which it subsequently precipitates as PCC.

The PCC-CTMP handsheets based on the coarser fiber fractions were more prone for brightness loss, probably due to a combined effect alkali yellowing and less enhanced light scattering due to lower PCC content, whereas sheets comprising higher content of the fine fractions provided positive effects especially on light scattering. The fines also contained significant amount of PCC without proportional loss in fiber-weight based tensile index, suggesting that the substrate fiber properties can greatly affect the PCC-fiber composite and its effects on paper. These findings demonstrate the importance of controlling the substrate fiber properties e.g. by ensuring that the pulp contains the different fiber fractions in desirable proportion, or by favorable external fibrillation of larger fibers. The findings also suggest that careful, target-oriented refining of the fiber is an important pre-treatment when attempting to control the properties of PCC-fiber composite material.

Acknowledgments Stora Enso Oyj is acknowledged for financial support of the project. Dr Anthony Bristow is thanked for linguistic revision of the work.

Funding Open access funding provided by LUT University (previously Lappeenranta University of Technology (LUT)). This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Al-Sogair F, Operschall BP, Sigel A, Sigel H, Schnabl J, Sigel RKO (2011) Probing the metal-ion-binding strength of the hydroxyl group. *Chem Rev* 111:4964–5003. <https://doi.org/10.1021/cr100415s>
- Christ RH, Martin JR, Christ DR (2002) Heavy metal uptake by lignin: comparison of biotic ligand models with an ion exchange process. *Environ Sci Technol* 36:1485–1491. <https://doi.org/10.1021/es011136f>
- Ciobanu M, Bobu E, Ciolacu F (2010) In-situ cellulose fibres loading with calcium carbonate precipitated by different methods. *Cellul Chem Technol* 44(9):379–387
- Dalas E, Klepetsanis PG, Koutsoukos PG (2000) Calcium carbonate deposition on cellulose. *J Colloid Interf Sci* 224:56–62. <https://doi.org/10.1006/jcis.1999.6670>
- Fält S, Wågberg L (2003) Influence of electrolytes on the swelling and strength of kraft-liner pulps. *Nord Pulp Pap Res J* 18(1):69–73. <https://doi.org/10.3183/npprj-2003-18-01-p069-073>
- Fortuna ME, Harja M, Bucur D, Cimpeanu SM (2013) Obtaining and utilizing cellulose fibers with in-situ loading as an additive for printing paper. *Materials* 6:4532–4544. <https://doi.org/10.3390/ma6104532>
- Guo X, Zhang S, Shan X (2008) Adsorption of metal ions on lignin. *J Hazard Mater* 151:134–142.
- Heinemann S, Vehniäinen A, The character and properties of mechanical pulps, in 'Papermaking chemistry' 2nd ed, Papermaking science and technology vol. 5, Lönnberg B. (ed), 2009, p. 458–514
- Hubbe MA (2006) Sensing the electrokinetic potential of cellulosic fiber surfaces. *BioResources* 1(1):116–119
- Hubbe MA, Gill RA (2016) Fillers for papermaking: a review of their properties, usage practices, and their mechanistic role. *BioResources* 11(1):2886–2963
- Hubbe MA, Heitmann JA (2007) Review of factors affecting the release of water from cellulosic fibers during paper manufacture. *BioResources* 2(3):500–533
- Jada A, Verraes A (2003) Preparation and microelectrophoresis characterisation of calcium carbonate particles in the presence of anionic polyelectrolyte. *Colloid Surf A* 2019:7–15. [https://doi.org/10.1016/S0927-7757\(03\)00010-4](https://doi.org/10.1016/S0927-7757(03)00010-4)
- Klungness JH, Sykes MS, Tan F, Abubakr S, Eisenwasser JD (1996) Effect of fiber loading on paper properties. *Tappi J* 79(3):297–301. <https://doi.org/10.1177/1687814016664258>
- Klungness J, Ahmed A, Ross-Sutherland N, AbuBakr S (2000) Lightweight, high-opacity paper by fiber loading: filler comparison. *Nord Pulp Pap Res J* 15(5):345–350. <https://doi.org/10.3183/npprj-2000-15-05-p345-350>
- Krogerus B (2007) Papermaking additives. In: Alén R (ed) Papermaking chemistry, 2nd edn. Gummerus Oy, Jyväskylä, pp 56–121
- Kumar P, Gautam S, Kumar V, Singh S (2009) Enhancement of optical properties of bagasse pulp by in-situ filler precipitation. *BioResources* 4(4):1635–1646
- Kumar P, Negi YS, Singh SP (2011) Filler loading in the lumen or/and cell wall of fibers - a literature review. *BioResources* 6(3):526–546

- Laine J (2007) General aspects of papermaking chemistry. In: Alén R (ed) Papermaking chemistry, 2nd edn. Gummerus oy, Jyväskylä, pp 28–53
- Lakshminarayanan R, Valiyaveetil S, Luan Loy G (2003) Selective nucleation of calcium carbonate polymorphs: role of surface functionalization and poly(vinyl alcohol) additive. *Cryst Growth Des* 3(6):953–958. <https://doi.org/10.1021/cg034022j>
- Leskelä M (1998) Optical properties. In: Niskanen K (ed) Paper physics. Gummerus Oy, Jyväskylä, pp 117–137
- Matula J, Räsänen J, Tahkola K (2018) In-line PCC technology cleans up circulation water from dissolved materials, metals and bio based microorganisms resulting to clean process and high runnability. In: PaperCon 2018. Charlotte, North Carolina, April 15–18
- Mohamadzadeh-Saghavaz K, Resalati H, Ghasemian A (2014) Cellulose-precipitated calcium carbonate composites and their effect on paper properties. *Chem pap* 68(6):774–778. <https://doi.org/10.2478/s11696-013-0513-7>
- Mosbye J, Laine J (2002) The charge and chemical composition of fines in mechanical pulp. *Nord Pulp Pap Res J* 17(3):352–356. <https://doi.org/10.3183/npprj-2002-17-03-p352-356>
- Odabas N, Henniges U, Potthast A, Rosenau T (2016) Cellulosic fines: properties and effects. *Prog Mater Sci* 83:574–594. <https://doi.org/10.1016/j.pmatsci.2016.07.006>
- Park Y, Rawat P, Ford E (2017) Role of Polymerized Micelles on the Calcium Carbonate Mineralization of Nanofibers. *Ind Eng Chem Res* 56:8241–8250. <https://doi.org/10.1021/acs.iecr.7b00902>
- Rantanen J (2016) The manufacturing potential of micro and nanofibrillated cellulose composite papers Ph.D. Dissertation (Tech.), Aalto University
- Rantanen J, Dimic-Misic K, Kuusisto J, Maloney TC (2015) The effect of micro and nanofibrillated cellulose water uptake on high filler content composite paper properties and furnish dewatering. *Cellulose* 22:4003–4015. <https://doi.org/10.1007/s10570-015-0777-x>
- Retulainen E, Niskanen K, Nilsen N (1998) Fibers and bonds. In: Niskanen K (ed) Paper physics. Gummerus Oy, Jyväskylä, pp 55–83
- Schmidt JA (2010) Electronic spectroscopy of lignins. In: Heither C, Dimmel DR, Schmidt JA (eds) Lignin and lignans: advances in chemistry. CRC Press, Miami, pp 49–102
- Seo BS, Ahn JH, Lee HL (2017) Upgrading waste paper by in-situ calcium carbonate formation. *J Clean Prod* 155(1):212–217. <https://doi.org/10.1016/j.jclepro.2016.09.003>
- Shen J, Song Z, Qian X, Liu W (2009) Modification of paper-making grade fillers: a brief review. *BioResources* 4(3):1190–1209
- Silenius P (2002) Improving the combinations of critical properties and process parameters of printing and writing papers and paperboards by new paper-filling methods. Dissertation PhD (Tech.), Helsinki University of Technology
- Sjostrom E (1989) The origin of charge on cellulosic fibers. *Nord. Pulp Paper Res J* 4(2):90–93. <https://doi.org/10.3183/npprj-1989-04-02-p090-093>
- Stephens CJ, Kimy Y-Y, Evans SD, Meldrum FC, Christenson HK (2011) Early stages of crystallization of calcium carbonate revealed in picoliter droplets. *J Am Chem Soc* 133:5210–5213. <https://doi.org/10.1021/ja200309m>
- Stoica-Guzun A, Stroescu M, Jinga S, Jipa I, Dobre T, Dobre L (2012) Ultrasound influence upon calcium carbonate precipitation on bacterial cellulose membranes. *Ultrason Sonochem* 19:909–915. <https://doi.org/10.1016/j.ultsonch.2011.12.002>
- Subramanian R (2008) Engineering fine paper by utilising the structural elements of the raw materials. Ph.D. Dissertation (Tech.), Helsinki University of Technology
- Suhas, Carrott PJM, Ribeiro Carrott MML (2007) Lignin – from natural adsorbent to activated carbon: a review. *Biore-source Technol* 98:2301–2312. <https://doi.org/10.1016/j.biortech.2006.08.008>
- Sundberg A, Holmbom B (2004) Fines in spruce TMP, BTMP and CTMP - chemical composition and sorption of man-nans, Nord. Pulp Pap Res J 19(2):176–182. <https://doi.org/10.3183/npprj-2004-19-02-p176-182>
- Tang Y, Zhang F, Cao Z, Jing W, Chen Y (2012) Crystallization of CaCO₃ in the presence of sulfate and additives: experimental and molecular dynamics simulation studies. *J Colloid Interf Sci* 337(1):430–437. <https://doi.org/10.1016/j.jcis.2012.02.069>
- Torre M, Rodrigues AR, Saura-Calixto F (1992) Study of the interactions of calcium Ions with lignin, cellulose, and pectin. *J Aric Food Chem* 40:1762–1766. <https://doi.org/10.1021/jf00022a007>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.