

# The Effect of Carbonation Conditions on the Properties of Carbohydrate-Calcium Carbonate Hybrid Pigments

Jonna E. Kuusisto\* and Thad C. Maloney

The influence of two polysaccharides, native corn starch and carboxymethyl cellulose (CMC), on the precipitation of calcium carbonate was examined by utilizing two different carbonation processes. In a batch process, carbon dioxide gas was fed through calcium hydroxide slurry at pH 11.5 to 12.0. The reaction was complete when the pH had been decreased to 7. In a fed-batch reaction, the carbon dioxide was dissolved in water while calcium hydroxide was pumped into the water, maintaining a constant pH of  $6.0 \pm 0.5$ . Scanning electron microscopy, particle size analysis, and specific surface area analysis were used to characterize the structure of the precipitated calcium carbonate (PCC) pigments. In application testing, the impact of modified pigments on paper properties was examined. The results showed that carbohydrates can significantly affect the crystallization of calcium carbonate, but the influence depends on the precipitation conditions and the type and concentration of the carbohydrate added. The starch-modified PCC, produced by the fed-batch reaction, improved the mechanical properties of the paper, whereas CMC-modified PCC yielded paper with good surface and optical performance but weakened strength properties.

*Keywords:* PCC; Starch; CMC; Co-precipitation; Carbonation; Composite pigment; Paper properties

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## INTRODUCTION

Most paper grades are composed primarily of cellulosic fibers and mineral pigments. The fiber fraction is the main load-bearing part of the structure and is responsible for the strength properties of the sheet, whereas the pigment fraction imparts other useful properties, such as light scattering, smoothness, and printability, to the sheet. Bulk pigments are typically cheaper than cellulose fibers and thus improve the cost structure of paper manufacture. Paper manufacturers are interested in increasing the pigment content of paper beyond current limitations without the deterioration of various paper properties (*e.g.*, runnability, stiffness, surface strength, and offset dusting).

To some extent, filled paper is a composite of cellulose fibers and mineral pigments, with other structural additives such as starch playing smaller roles. In modern papermaking processes, the pigment filler is added to sheet in the wet end and stochastically incorporated into the paper structure. Thus, pigment partially resides at fiber interstices and weakens fiber-fiber bonds, decreasing stiffness and tensile strength. The current approach of integrating pigments and other additives into paper could be improved. In the present work, new routes for integrating the primary building blocks of paper (fiber, pigment, and polymeric additives) into higher-performing and potential new fiber products are explored.

One of the most widely used pigments in papermaking is calcium carbonate ( $\text{CaCO}_3$ ), which is formed either by natural precipitation (ground calcium carbonate, GCC)

or produced synthetically (precipitated calcium carbonate, PCC). Calcium carbonate is an inorganic mineral occurring in three anhydrous crystalline polymorphs (calcite, aragonite, and vaterite). The most thermodynamically stable form is calcite, which can exhibit *e.g.* scalenohedral, rhombohedral, or prismatic morphology. Metastable aragonite crystallizes at high pressure and often has an acicular morphology, but the aragonitic structure is usually stable only at relatively low temperatures and can be readily converted to calcite under other conditions. Vaterite is the least thermodynamically stable of the anhydrous polymorphs and transforms rapidly to calcite or aragonite in aqueous solutions (Mann 2001; Husband 2009)

Crystallization of CaCO<sub>3</sub> from solution is a two-step process consisting of nucleation and crystal growth (Myerson and Ginde 2002). Because it can be crystallized in a variety of morphologies, the properties of the CaCO<sub>3</sub> particles, such as their size and size distribution, as well as their surface area and morphology can be tailored to control the physical and chemical properties of paper. Specific morphologies of CaCO<sub>3</sub> particles are produced *via* controlled synthesis. In conventional carbonation processes, PCC is produced as follows: the first stage is the lime slaking process in which calcium hydroxide (Ca(OH)<sub>2</sub>) is formed by reacting calcium oxide (lime) with water according to the reaction:



The slaked lime is then carbonated with carbon dioxide (CO<sub>2</sub>) gas to form PCC:



The crystallization of CaCO<sub>3</sub> is a complicated phenomenon, and the properties of the precipitated particles are determined by numerous process variables such as the initial reaction temperature, pH, ionic strength of the solution, and CO<sub>2</sub> flow rate. In addition, various organic additives (*e.g.*, polysaccharides or proteins) can be used to influence the crystallization process and modify the properties of the precipitated particles. Controlled nucleation and growth of inorganic crystals is believed to result from specific molecular interactions at inorganic-organic interfaces (Mann and Archibald 1993). Interfacial molecular recognition between calcium carbonate and polysaccharides includes geometric matching (epitaxis) as well as electrostatic and stereochemical complementarity. Whilst the polysaccharides can affect the nucleation and growth of calcium carbonate, the nucleation and growth of the calcium carbonate crystals also have an influence on the polysaccharides (Yang *et al.* 2003).

Paper manufacturers and pigment and chemical suppliers are well aware that new pathways for integrating raw materials and building sheet architecture can add value. For example, several companies have developed processes to preflocculate the filler (normally 1- to 5- $\mu\text{m}$  particle size) into aggregates in the range of 20- to 40- $\mu\text{m}$ . The larger aggregates have a lower outer surface area and thus interfere with fiber bonding to a lower extent than normal filler pigment. In some cases (Siitonen and Putnam 2014; Torvinen *et al.* 2014), strengthening polymers or nanocellulose are incorporated into the flocs to improve bonding properties. Filler flocculation technologies have been demonstrated to improve the cost structure of paper and are employed in a number of paper mills today.

To increase the strength of paper, modification of pigments with polysaccharides has also been widely studied in recent years. Starch is the most common dry strength

additive used in paper manufacturing because of its relatively low price and its ability to form hydrogen bonds, which results from the large number of hydroxyl groups it has in its structure (Yoon and Deng 2006a). Carboxymethyl cellulose (CMC), a water-soluble, carboxylated derivative of cellulose, is also a strength agent used in papermaking, but its relatively high price limits its use.

Zhao *et al.* (2005) reported that improvements in the tensile and tear strength as well as in the folding endurance of paper were achieved by coating precipitated calcium carbonate (PCC) with swollen starch gel. By cooking starch at high solids content in the presence of PCC, they were able to add 12% of unmodified starch to PCC. However, the procedure of filler coating consisted of several steps including mixing, dewatering, cooking, grinding, and breaking up the coated particles. Yan *et al.* (2005) formed starch-coated clay particles, which were dried and ground prior to their use in paper, and were able to increase tensile strength of paper significantly already at low starch contents (2.5 wt% of filler). Their technique was further developed by Zhao *et al.* (2008) to make it suitable for large-scale production *via* spray-drying the starch-coated clay. To prevent accumulation of soluble starch in whitewater when using such a large amount of starch, Yoon and Deng (2006a,b) prepared starch-clay composites by precipitating starch with a fatty acid or ammonium sulfate in the presence of pigment. When incorporated into the paper, its physical properties, especially its bonding strength, were improved. Shen *et al.* (2010) managed to encapsulate PCC with CMC using alum and markedly increased the retention of PCC without negative effects on paper strength.

Whereas the focus of the preceding techniques have been on surface modifications of pigment such as coating or encapsulation, Håkansson (2007) and Saastamoinen *et al.* (2013) developed true composite structures by precipitating PCC in the presence of polysaccharides such as starch, carboxymethyl cellulose, and nanocellulose. Håkansson (2007) added polysaccharides either to the lime prior to the slaking or into the suspension of calcium hydroxide prior to the precipitation. In their research, Saastamoinen *et al.* (2013) continued precipitation until pH decreased to acidic and carbonate ion solution was formed *i.e.* calcium carbonate was dissolved. Polysaccharide was then added to the carbonate ion solution and carbonate salt was precipitated from the slurry into the polysaccharide. Both reported improved strength properties, which would enable papermakers to increase the amount of pigment in paper.

The present work considers two routes for incorporating polysaccharides into pigment and potentially building particles with improved bonding and other properties. The work is focused on synthesizing precipitated calcium carbonate (PCC) with hydrogen bonding polymers incorporated into the mineral structure. This could yield a route for building mineral pigments and pigment aggregates which have hydrogen bonding capability and could improve the strength performance of paper. The inherent flexibility and control of the PCC plant could be exploited to yield stable particles with desirable, unique morphologies.

In this work, methods by which the PCC process could be used in two different variations (batch and fed-batch process) and with two different carbohydrates (native corn starch and CMC) to synthesize inorganic/organic hybrid pigments were explored. The goal was to examine the pigment and paper properties and to understand the feasibility and limitations of combining both starch and CMC into the PCC particles to enhance pigment performance.

## EXPERIMENTAL

### Materials

Lime was provided by Lhoist, Ltd. (La Mède, France). Two different polysaccharides, starch and CMC, were used to modify precipitated calcium carbonate. Native corn starch was obtained from Roquette, Ltd. (Lestrem, France), and technical grade CMC (Calexis L-H1) with degree of substitution between 0.45 and 0.65 was provided by CP Kelco Oy (Äänekoski, Finland). Bleached pine and birch kraft pulps were provided by Stora Enso, Varkaus mill (Finland). A two-component retention aid system consisting of cationic polyacrylamide (Fennopol K3400R) and anionic micropolymer (Fennosil EO742) obtained from Kemira, Ltd. (Espoo, Finland) was applied during handsheet preparation. Deionized water was used in all experiments.

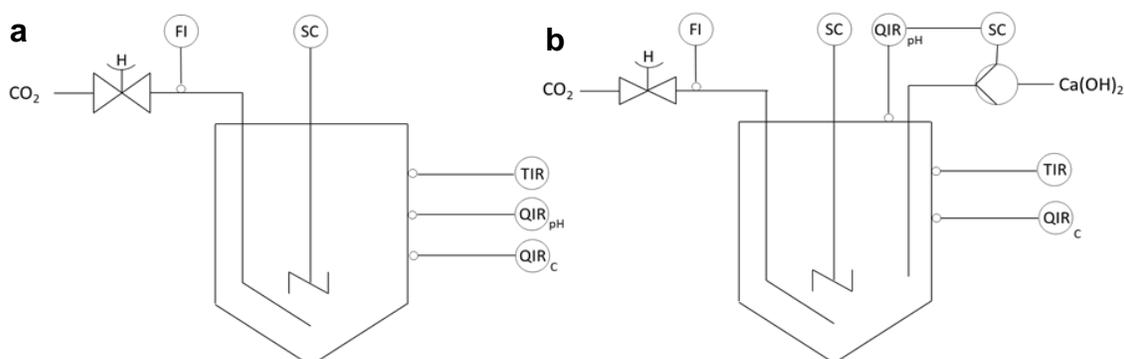
### Methods

#### *Precipitation of CaCO<sub>3</sub> composite pigments*

Precipitated calcium carbonate preparation began with the lime slaking process. Lime and water were mixed with a high-shear mixer for 10 min to form Ca(OH)<sub>2</sub> (slaked lime). The initial water temperature was 50 °C, and the lime-to-water ratio was 1:5. After slaking, the Ca(OH)<sub>2</sub> slurry was screened to remove impurities. Polysaccharides were dissolved prior to their use. Starch was dissolved by heating the starch suspension (3 wt. %) at 95 °C for 30 min. Carboxymethyl cellulose was dissolved by mixing with water at room temperature for 1 h.

Precipitations were performed in a laboratory-scale reactor equipped with a high-shear impeller mixer, a CO<sub>2</sub> gas feed system with a rotameter, thermoelement casings, and pH, conductivity, and temperature sensors. The volume of the cylindrical reactor was 5 dm<sup>3</sup>. Two variations of the PCC process, batch and fed-batch, were used for precipitation. The reactor set-up for both processes is illustrated in Fig. 1. In the batch precipitation process, Ca(OH)<sub>2</sub> slurry was adequately mixed with polysaccharide solution inside the reactor before precipitation began. As a reference experiment, calcium carbonate was precipitated in the absence of polysaccharides. The initial pH of the slurry was 11.5 to 12.0. The flow rate of CO<sub>2</sub> was 2.3 dm<sup>3</sup>/min, and the rotational speed of the stirrer was 800 rpm. The total volume of the batch was 2.5 dm<sup>3</sup>. Conductivity and pH were continuously monitored, and the completion of the reaction brought about abrupt, consecutive decreases in conductivity and pH. The reaction was finished when the solution pH decreased to 7. The PCC slurry was then screened to remove impurities.

The fed-batch process was started by bubbling 1 dm<sup>3</sup> of water with CO<sub>2</sub> to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which caused the pH in the reactor to decrease to 5.5±0.5. The polysaccharide solution was then added into the reactor and adequately mixed. Calcium hydroxide (Ca(OH)<sub>2</sub>) was slowly fed into the reactor at a flow rate adjusted to maintain the pH of solution at 6.0±0.5. The same batch volume, CO<sub>2</sub> flow rate, and mixing rate were applied as in batch precipitation. At first, batch precipitations were performed in the presence of various concentrations of starch (0 to 5 wt.% of Ca(OH)<sub>2</sub>) at 50 °C, and the properties of the resulting composite pigments were analyzed. In subsequent experiments, the concentration of starch or CMC was kept constant (2 wt.% of Ca(OH)<sub>2</sub>) and both batch and fed-batch processes were applied at different temperatures. The initial temperatures were 50 and 70 °C in the batch precipitations and 20 and 50 °C in the fed-batch precipitations. In all experiments, the concentration of Ca(OH)<sub>2</sub> was 7.4%, which should yield 10% PCC after carbonation.



**Fig. 1.** Reactor set-up for the (a) batch and (b) fed-batch processes. In the batch process, the total volume of the  $\text{Ca}(\text{OH})_2$  slurry was placed inside the reactor before  $\text{CO}_2$  feed began, whereas in the fed-batch process,  $\text{CO}_2$  was dissolved in water inside the reactor and  $\text{Ca}(\text{OH})_2$  was pumped into the water at a flow rate adjusted to maintain a constant pH.

#### Characterization of composite pigments

The volume median particle size (later referred to as the average particle size),  $d(0.5)$ , and the size distribution (the span) were measured with a particle size analyzer (PSA; Malvern Instruments, Mastersizer 2000; UK) which uses a laser diffraction technique to measure the size of the particles. A single, narrow mode of analysis and a refractive index of 1.572 (calcite) with an adsorption index of 0.1 were chosen. Ultrasound was applied in the measurements. The span was calculated using the following equation,

$$\text{Span} = \frac{d(0.9) - d(0.1)}{d(0.5)} \quad (3)$$

where  $d(0.9)$ ,  $d(0.5)$ , and  $d(0.1)$  are the particle diameters at which 90, 50, and 10% of the volume distributions are below these values, respectively.

The specific surface area (SSA) was determined *via* the multi-point Brunauer-Emmett-Teller (BET) method (Brunauer *et al.* 1938) with a Micromeritics Tristar II 3020 (USA) using nitrogen gas as an adsorbate. Before measurements, the samples were dried at 150 °C for 60 min. The morphology of the precipitated particles was analyzed by scanning electron microscopy (SEM) using a JEOL JSM-7500FA (Japan) and a Zeiss Sigma VP (Germany). Prior to imaging, dried samples were mounted on adhesive tape and coated with a thin layer of gold. An accelerating voltage of 3 kV was applied during imaging.

The sorption of polysaccharides onto PCC was analyzed with a TOC-V<sub>CPH/CPN</sub> (Shimadzu, Japan) by measuring the amount of total organic carbon (TOC) in the supernatant after centrifuging the composite sample for 10 min at 3000 rpm. More information about this method can be found in the work of Ghosh (2013). In this paper, the term “sorption” refers to polymer that is either fully or partially incorporated into the crystal lattice or absorbed onto the crystal surface.

#### Paper sheet preparation and characterization

Dried birch and pine pulps were soaked in water for 10 min prior to refining. Pulps were refined with a Voith Paper Laboratory Refiner LR 40 (Germany). Softwood pulp was refined with 1.5 J/m specific edge load and 111 kWh/t net specific energy. The

corresponding values for hardwood refining were 0.5 J/m and 47 kWh/t. Refining time was 15 min. Softwood and hardwood pulps were refined to Schopper-Riegler numbers ( $^{\circ}\text{SR}$ ) 24 and 25, respectively.

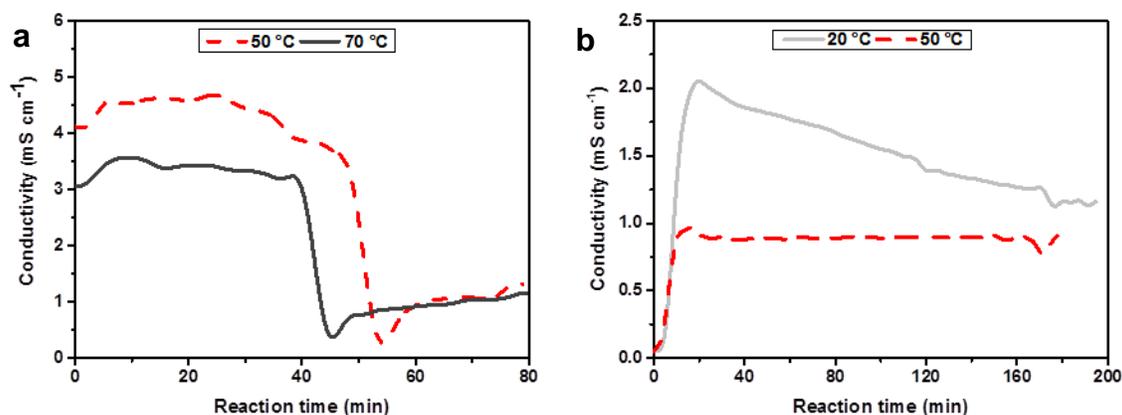
Paper sheets were prepared in a laboratory sheet mold according to standard ISO 5269-1 (2005), with following modifications: 80 g/m<sup>2</sup> sheets were prepared, sheets were pressed at 490 kPa for 4 min, and sheets were dried in a drum dryer at 65 °C for 2 h. A mixture of softwood and hardwood pulps (30/70) and a two-component retention aid system with cationic (300 g/t) and anionic (400 g/t) components were applied during sheet preparation. Sheets were conditioned according to ISO standard 187 (1990). Reference sheets, which contained unmodified PCC, were prepared at PCC contents of 20 and 30% and the results were normalized to 25% PCC. The sheets containing modified PCC were prepared only at 25% PCC content. The PCC content of the sheets was measured according to the standard ISO 1762 (2001). The physical properties of the paper sheets were tested according to the following standards: density and bulk ISO 534 (2005), internal bond strength T 569 pm-00 (2000), tensile strength ISO 1924-2 (1994), brightness ISO 2470 (1999), opacity ISO 2471 (2008), and Parker Print-Surf (PPS) roughness ISO 8791-4 (1992).

## RESULTS AND DISCUSSION

### Reaction Conditions

The conductivity progress curves during the batch and fed-batch precipitations are presented in Fig. 2. Because of the high concentration of  $\text{Ca}(\text{OH})_2$  in the batch process, the test points were obtained at the supersaturation point of  $\text{Ca}^{2+}$ , so these conductivities (Fig. 2a) were higher than in the fed-batch reactions (Fig. 2b). Because the conductivity is affected by the concentration of dissolved electrolytes in the solution and the dissolution of  $\text{Ca}(\text{OH})_2$  and  $\text{CO}_2$  is greater at lower temperatures, lower precipitation temperatures resulted in higher conductivities.

Because it is neutral in nature, starch had no notable effect on conductivity, whereas the addition of anionic CMC increased the conductivity during both batch and fed-batch reactions. These results are not shown.

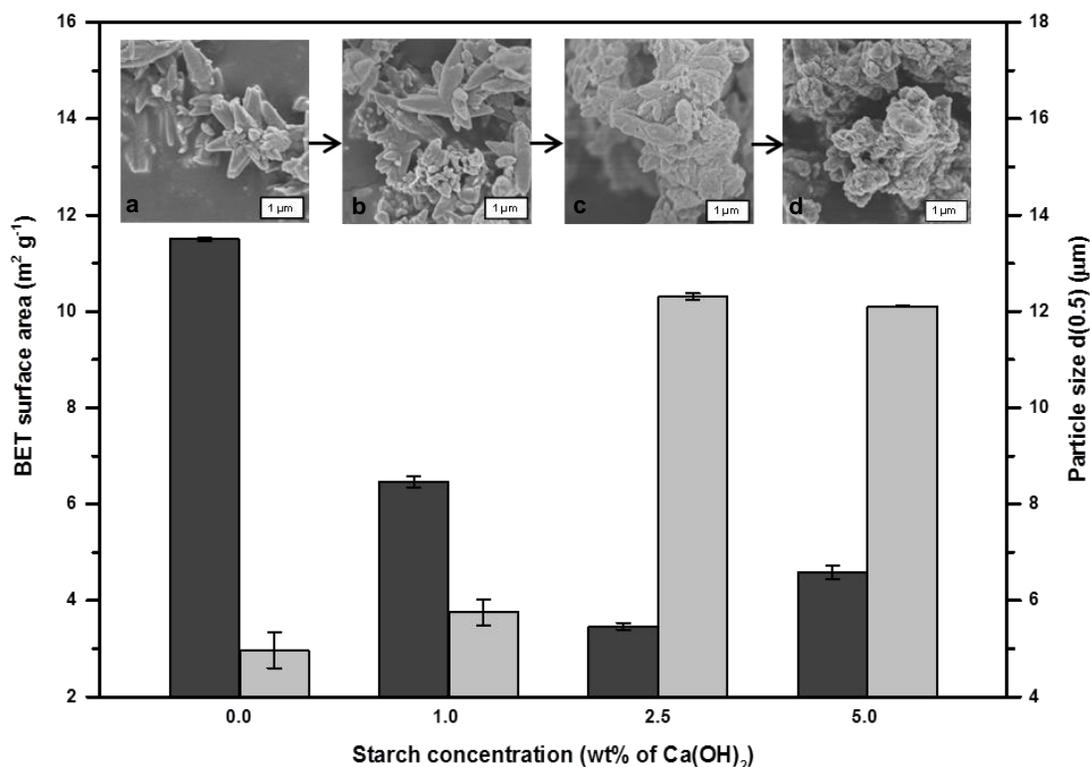


**Fig. 2.** Conductivity progress curves during (a) batch precipitation reaction and (b) fed-batch precipitation reaction performed at different temperatures in the absence of polysaccharides. The initial  $\text{Ca}(\text{OH})_2$  concentration of the batch reactions and the total  $\text{Ca}(\text{OH})_2$  concentrations of the fed-batch reactions were 7.4%.

## Properties of the Composite Pigments

### *Effect of polysaccharide concentration*

The effect of starch on the batch precipitation of  $\text{CaCO}_3$  at various starch concentrations was studied. As illustrated in Fig. 3, reference PCC crystals (starch concentration 0.0 wt% of  $\text{Ca}(\text{OH})_2$ ) had a scalenohedral morphology, characteristic of calcite. Scalenohedral morphology is known (Jung *et al.* 2000; García-Carmona *et al.* 2003; Ukrainczyk *et al.* 2007; Jung *et al.* 2010) to result from excess of  $\text{Ca}^{2+}$  ions (*i.e.*, a high  $[\text{Ca}]_{\text{tot}}/[\text{CO}_3]_{\text{tot}}$  ratio) during precipitation at elevated temperatures, similar to the conditions of batch precipitation. The lowest concentration of starch present in the precipitation preserved the scalenohedral structure of the crystals, but the average particle size increased slightly and SSA decreased. As the concentration of starch was increased to 2.5 wt.% of  $\text{Ca}(\text{OH})_2$ , the morphology of the PCC changed, the size of the particles doubled, and the SSA decreased to one-third of the initial value. Increasing the starch concentration further had no significant effect on either the size or the SSA of the particles. Increased particle size might, to a large degree, be attributed to the particle aggregation caused by starch. The reduced SSA indicates the disappearance of the scalenohedral morphology.



**Fig. 3.** Morphology (SEM-images), BET surface area (■), and average particle size (□) of the composite pigments precipitated in the presence of various concentrations of starch: (a) 0.0, (b) 1.0, (c) 2.5, and (d) 5.0 wt.% of  $\text{Ca}(\text{OH})_2$ . Capped error bars represent the standard deviation of the measured values. Batch precipitation was conducted at 50 °C and the  $\text{Ca}(\text{OH})_2$  concentration was 7.4%.

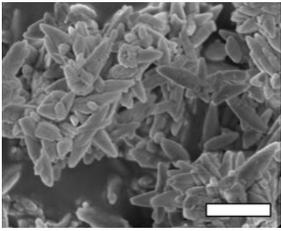
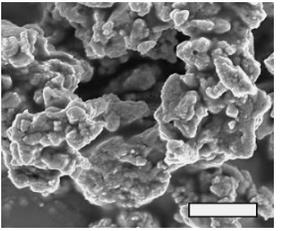
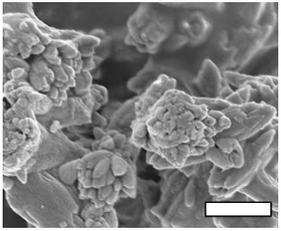
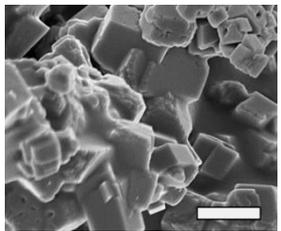
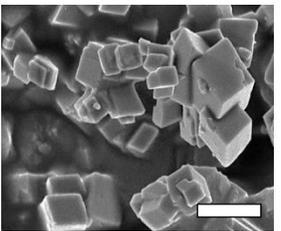
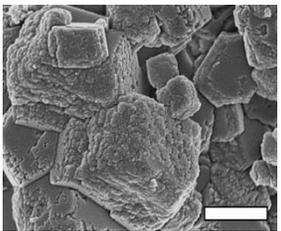
The observed change in morphology can be ascribed to the adsorption of starch onto the crystal surfaces of calcite when using high enough starch concentrations (Kontrec *et al.* 2008). Yang *et al.* (2003) proposed an underlying mechanism. There is an excellent geometric match between the secondary structure of starch and the crystal lattice of calcium

carbonate. The spatial arrangement of hydroxyl groups in the secondary structure of starch is ordered, and  $\text{Ca}^{2+}$  ions combine with these hydroxyl groups. The crystal nucleus is then formed when  $\text{CO}_3^{2-}$  ions aggregate around the  $\text{Ca}^{2+}$  ions. Although the exact mechanism is unknown, it is clear that the presence of starch in sufficient quantities interrupts crystal growth and distorts the scalenohedral morphology.

#### *Effect of polysaccharide type and precipitation process*

The effect of starch and CMC on the batch and fed-batch precipitation of  $\text{CaCO}_3$  was examined. The concentration of polysaccharide was 2 wt.% of  $\text{Ca}(\text{OH})_2$ , which corresponds to 1.5 wt.% of PCC. Starch and CMC were found to have different effects on the morphology of the precipitated particles depending on the precipitation process. As previously illustrated in Fig. 3, the scalenohedral morphology of PCC produced by the batch process was lost in the presence of higher concentrations of starch, whereas CMC forced the crystals into a rosette structure (Table 1). During fed-batch precipitation, the ratio of total dissolved calcium-to-carbonate species ( $[\text{Ca}]_{\text{tot}}/[\text{CO}_3]_{\text{tot}}$ ) was low, and cuboid particles were produced. Unlike in batch precipitation, the morphology of the particles was not affected by starch. On the contrary, CMC modified the morphology of the particles. Presumably because of electrostatic interaction between  $\text{Ca}^{2+}$  ions and the carboxyl groups of CMC, the edges and acute corners of the particles were eroded and smooth surfaces became rough, consistent with the findings of Liang *et al.* (2004).

**Table 1.** Morphology of the Reference, Starch-modified, and CMC-modified PCC Particles Produced by the Batch and Fed-batch Precipitation Processes\*

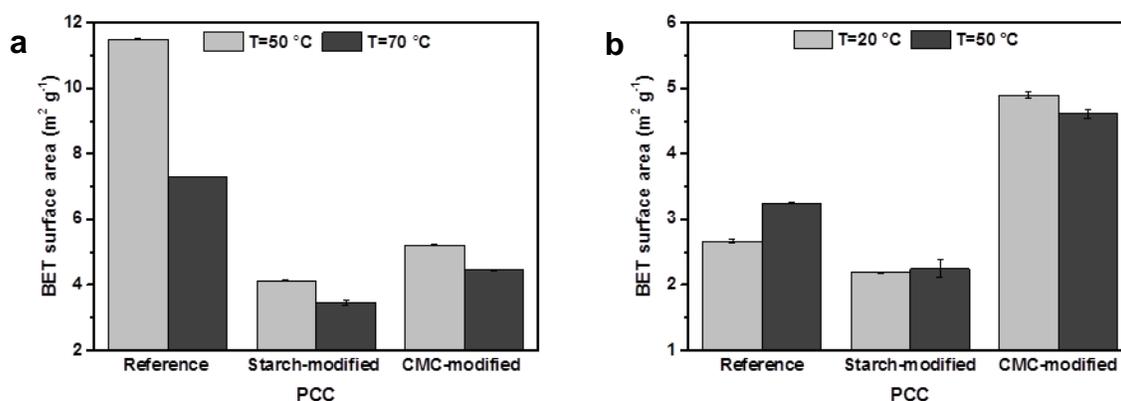
Precipitation process	PCC		
	Reference	Starch-modified	CMC-modified
Batch			
Fed-batch			

\* Conditions: 50 °C, polysaccharide concentration of 2 wt.% of  $\text{Ca}(\text{OH})_2$ , and total  $\text{Ca}(\text{OH})_2$  concentration of 7.4%. The scale bar in the SEM images corresponds to 1  $\mu\text{m}$ .

Figure 4 illustrates the impact of starch and CMC on the SSA of PCC produced at various temperatures *via* batch and fed-batch processes. The addition of polysaccharides into the batch precipitation (Fig. 4a) caused an abrupt decrease in the SSA of the particles.

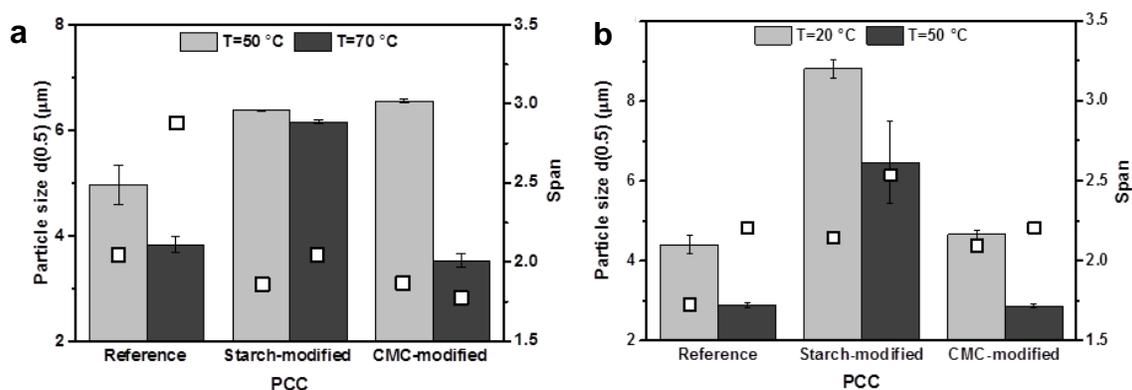
When precipitation was conducted at higher temperature, the SSA of the particles produced was smaller, especially in the absence of polysaccharides. These results are in agreement with the findings by Yang *et al.* (2010) and with a model developed by Ukrainczyk *et al.* (2007) which predicts increasing specific surface area with decreasing temperature and increasing conductivity.

Figure 4b shows the SSA of the particles produced by fed-batch precipitation. Reference PCC particles had a cuboidal shape and much lower SSA than the scalenohedral PCC produced *via* batch precipitation. Unlike the batch process, the SSA of the particles was only slightly diminished by starch during fed-batch precipitation. However, the addition of CMC increased the SSA of particles, presumably because of surface roughening. Unlike in the batch process, temperature had no prominent effect on the SSA of the particles.



**Fig. 4.** BET surface area of reference, starch-modified, and CMC-modified PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide concentration was 2 wt.% of Ca(OH)<sub>2</sub>. Capped error bars represent the standard deviation of the measured values.

The average particle sizes and spans are presented in Fig. 5. Higher initial precipitation temperature generally resulted in smaller particle size, as reported by other authors (Wen *et al.* 2003; Cheng *et al.* 2004).



**Fig. 5.** Average particle size (columns) and span (□) of the reference, starch-modified, and CMC-modified PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide concentration was 2 wt.% of Ca(OH)<sub>2</sub>. Capped error bars represent the standard deviation of the measured values.

The addition of starch into the batch process increased the average particle size regardless of the precipitation temperature. Similar behavior was seen when CMC was added to the low-temperature batch process. However, when the higher precipitation temperature was used in the presence of CMC, the particle size remained unaffected. The spans were slightly smaller when polysaccharides were added to the precipitation.

Starch highly aggregated the particles during the fed-batch precipitation, but CMC had no prominent influence on the size of the particles. Also the size distributions were broadened in the presence of starch, whereas CMC increased the span only at low-temperature fed-batch process.

The interactions between minerals and polysaccharides have been widely studied. When natural polysaccharides such as starch or cellulose are used, they are thought to bond to minerals *via* hydrogen bonds (Liu *et al.* 2000; Laskowski *et al.* 2007). However, if functional groups are introduced into the polysaccharide structure, they can form chemical bonds with minerals. For instance, Volkert *et al.* (2004) reported that introduction of carboxyl groups into the starch markedly improved its calcium-binding capacity. In addition, the interaction of polysaccharides with minerals has been reported to be strongly dependent on pH (Liu *et al.* 2000). For example, with metal-hydroxides, the maximum adsorption is often found to occur near the mineral's isoelectric point (at the pH at which the zeta potential is zero).

The sorption of starch and CMC to PCC is illustrated in Table 2. Under alkaline conditions (batch process), the sorption of CMC onto PCC was much higher than that of starch. This may be because of the strong interaction between the carboxyl groups of anionic CMC and calcium ions. When the slightly acidic precipitation process (fed-batch) was used, both polysaccharides were almost completely sorbed onto the calcium carbonate. There may be several reasons for the increased interaction between the polysaccharides and PCC during the acidic process because acidic crystallization is very different from the conventional alkaline process. In the fed-batch process, crystallization took place very rapidly when Ca(OH)<sub>2</sub> was fed into the reactor. It can also be considered a heterogeneous nucleation process, in which the polysaccharide acts as a nucleation site and PCC precipitates onto it. In addition, the pH during the crystallization was close to neutral and the ionic strength of solution was much smaller than that during the alkaline precipitation.

**Table 2.** Sorption of Starch and CMC to PCC during Batch and Fed-batch Processes\*

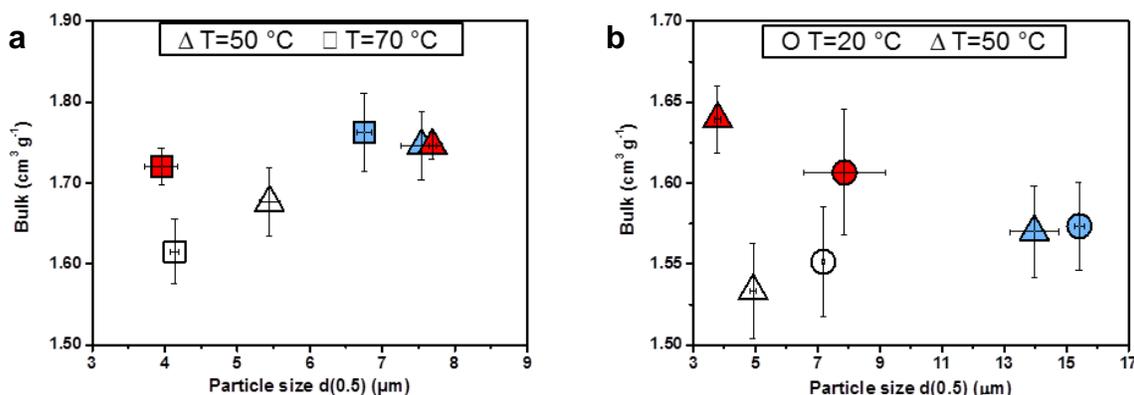
Process	Initial T (°C)	Sorbed polysaccharide (%)	
		Starch	CMC
Batch	50	50.2	89.4
Batch	70	66.4	90.1
Fed-batch	20	96.9	95.3
Fed-batch	50	96.9	96.9

\* Conditions: Polysaccharide concentration of 2 wt.% of Ca(OH)<sub>2</sub> and total Ca(OH)<sub>2</sub> concentration of 7.4%

## Paper Properties

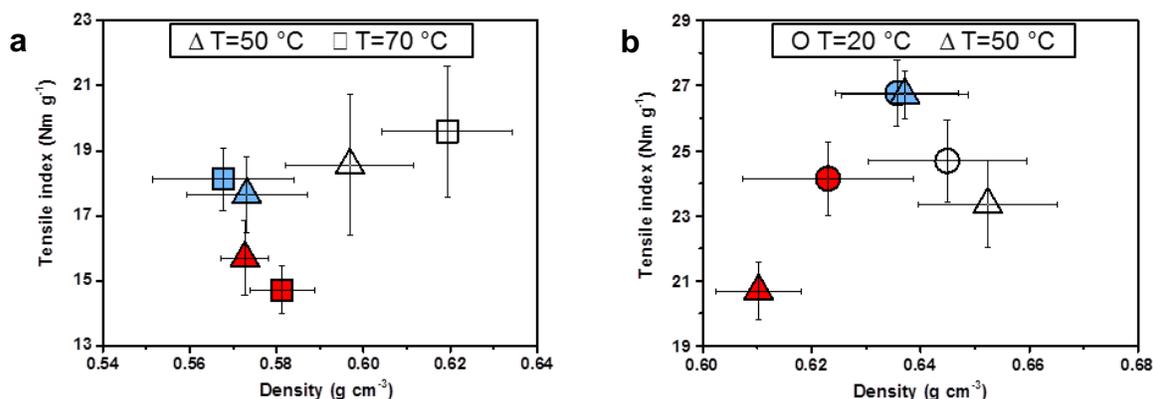
The paper properties at 25% PCC and with polysaccharide addition of 1.5 % of the amount of PCC were determined. This means that, following the complete absorption of the polysaccharide, the corresponding content in the handsheet would be 0.37%. As illustrated in Fig. 6, the addition of polysaccharides to batch precipitation resulted in greater

bulk attributed to the increased particle size and its distribution (Velho 2002). When starch was added to the fed-batch process, the particles were extremely large but the improvement in bulk was only moderate. Fed-batch precipitation in the presence of CMC resulted in higher bulk regardless of the small particle size. Batch precipitation of particles generally resulted in higher bulk derived from the lower packing ability of particles with scalenohedral shapes.



**Fig. 6.** Bulk of handsheets with 25% reference (white), starch-modified (light blue), and CMC-modified (red) PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide addition was 2 wt.% of Ca(OH)<sub>2</sub>. Capped error bars represent the standard deviation of the measured values.

The mechanical properties of the paper sheets, including the tensile strength (Fig. 7) and the internal bond strength (Fig. 8), increased when pigments produced by fed-batch precipitation were applied to the sheets. Several researchers, such as Fairchild (1992), Gill (1988), Kajanto (2008), Li *et al.* (2002), and Velho (2002), have reported that pigments or pigment blends with high surface area, small particle size, and narrow particle size distribution are more detrimental to paper strength, which is in agreement with the results of the present study.

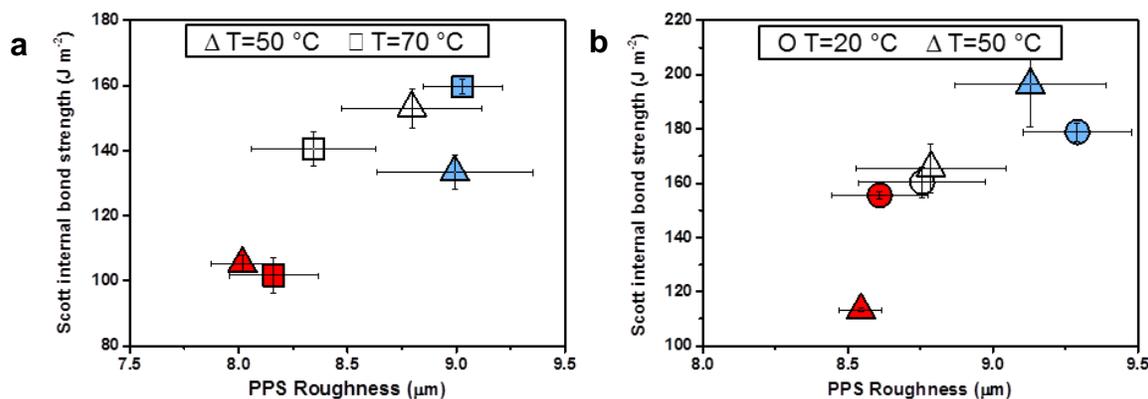


**Fig. 7.** Tensile index vs. density of the handsheets with 25% reference (white), starch-modified (light blue), and CMC-modified (red) PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide addition was 2 wt.% of Ca(OH)<sub>2</sub>. Capped error bars represent the standard deviation of the measured values.

The addition of CMC to PCC precipitation decreased the strength properties of the paper, but the effect of starch was different. When starch was added to batch precipitation,

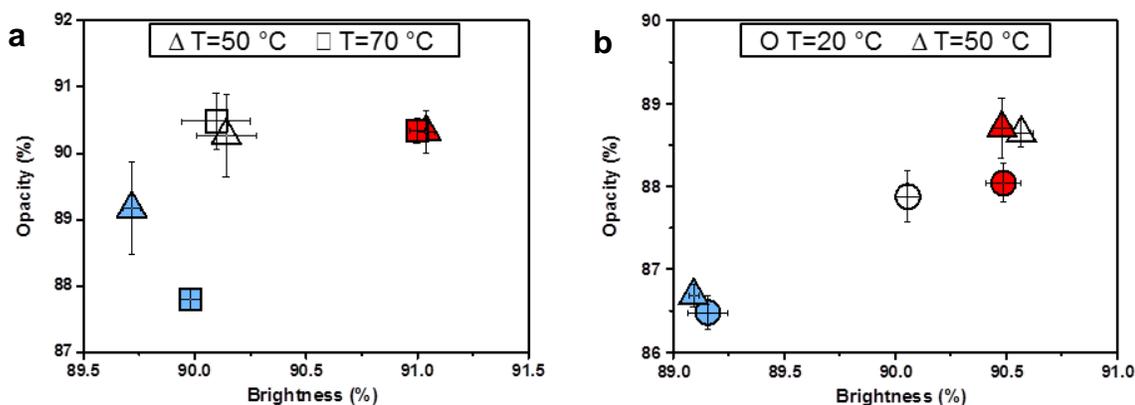
there was no significant change in paper strength. However, in the fed-batch process, a considerable benefit was achieved by the addition of starch. Other mechanical properties, such as the bending stiffness and elastic modulus, were positively affected (results not shown). The influence of the fed-batch-precipitated, hybrid pigments on paper strength can be attributed to the particle properties. Starch-PCC particles had low SSA and substantial particle size whereas CMC-PCC particles had larger SSA but relatively small particle size.

The addition of CMC into the precipitation reaction decreased the roughness of the paper, as illustrated in Fig. 8. On the contrary, starch had a negative impact on the roughness of the paper. The use of batch-produced pigments resulted in smoother paper, but the difference when using fed-batch pigments was rather small.



**Fig. 8.** Scott internal bond strength vs. PPS roughness of the hand sheets with 25% reference (white), starch-modified (light blue), and CMC-modified (red) PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide addition was 2 wt.% of  $\text{Ca}(\text{OH})_2$ . Capped error bars represent the standard deviation of the measured values.

The optical properties of the paper sheets are presented in Fig. 9. The pigments produced by batch precipitation resulted in better optical properties because of the scalenohedral morphology and greater SSA of these pigments.



**Fig. 9.** Opacity vs. brightness of the handsheets with 25% reference (white), starch-modified (light blue), and CMC-modified (red) PCC particles produced by (a) batch and (b) fed-batch precipitation processes at different initial temperatures. The polysaccharide addition was 2 wt.% of  $\text{Ca}(\text{OH})_2$ . Capped error bars represent the standard deviation of the measured values.

Generally, finer particles with narrow particle size distributions are known to be more beneficial to optical performance (Velho 2002). To achieve maximum light scattering, particles must be within the optimal size range, which is around half the wavelength of visible light for spherical pigments (Pauler 2008). The starch-modified PCC particles with large particle sizes negatively influenced the brightness and opacity of paper, whereas the introduction of CMC to the precipitation process helped maintain the opacity and even slightly improved the brightness of the paper.

The goal of the present work was to fabricate hybrid pigments with hydrogen bonding capability to improve the strength performance of paper. In this study, the pigment and paper properties for the samples produced when the carbohydrate is applied as a dissolved additive were analyzed. A much wider range of polymers and conditions than what were reported in this article were studied. Generally speaking, the dissolved polymeric additives tend to cause the pigments to aggregate, and the morphology to distort and become more heterogeneous. Although some paper properties were improved with the polymeric additive, this happened at the expense of other properties. Furthermore, the strength increase from the addition of hydrogen bonding polymers was only small to modest. This suggests that the hybrid pigments reported here do not have significant hydrogen bonding capability. Much of the polymer is likely buried inside the crystal, and the increased strength effects can be ascribed to aggregation and changes in pigment morphology.

The ongoing work is focused on developing more efficient routes for introducing hydrogen bonding capability to inorganic pigments while simultaneously enhancing morphological structure.

## CONCLUSIONS

1. The extent of PCC modification was mainly dependent on the added polysaccharide and its concentration. Starch and CMC modified the size, surface area, and morphology of PCC particles differently depending on the precipitation process (batch or fed-batch) and temperature.
2. The replacement of PCC with composite pigments impacted various paper properties. The use of CMC in precipitation yielded good optical and surface properties and improved bulk, but strength properties were negatively affected. On the other hand, starch impaired the optical and surface properties, but the strength properties were improved when the fed-batch process was utilized in the precipitation of starch-modified PCC.
3. The two different precipitation processes produced particles with totally different properties and had a remarkable impact on paper properties. When the batch process was applied, better bulk, optical, and surface properties were achieved, whereas fed-batch precipitation yielded paper with better mechanical performance. The initial precipitation temperature had no systematic effect on paper properties.
4. The overall target of the present study was to build hybrid pigments with unique properties such as bonding capability. Even though interesting pigment structures were produced, their impact on paper properties was insignificant.

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