PRECIPITATED CALCIUM CARBONATE (PCC) – CELLULOSE COMPOSITE FILLERS; EFFECT OF PCC PARTICLE STRUCTURE ON THE PRODUCTION AND PROPERTIES OF UNCOATED FINE PAPER

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This work examines the precipitation of PCC – pulp composite fillers with varying crystal habits and their effects on the papermaking properties of printing and writing paper. Colloidal (c-PCC), rhombohedral (r-PCC), and scalenohedral types (s-PCC) of composite PCCs were produced and compared with commercial reference PCCs. Scanning electron microscopy showed the c-PCC to be a high-surface-area nano-structured PCC. The rhombohedral composite was formed in clusters like a spider-web structure. Under similar experimental conditions, composite PCC was formed as individual ellipsoidal crystals and some of the particles had malformed structure, in contrast to the structured reference s-PCC. The co-precipitation and the structure of PCC significantly influence the forming, consolidation, and properties of paper, as well as its performance in printing.

Composite c-PCC showed the highest retention during forming. At higher filler contents, dewatering was reduced significantly with handsheets containing s- and r-PCC composite fillers. Colloidal composite handsheets showed the lowest tensile index and internal bond strength, while the rhombohedral composite gave the highest z-directional bond strength. Compared with the traditional reference samples containing commercial PCCs, paper with s- and r-composites had significantly higher density but similar light scattering ability. Addition of fibrillar fines to fine paper increased print rub fastness significantly in both laser and inkjet printed samples.

Keywords: Composite filler, Calcium carbonate filler, PCC morphology, Fine paper, Uncoated wood free paper, Scanning electron microscopy (SEM), Retention, Dewatering, Fine paper properties, Rubfastness

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INTRODUCTION

Comparing the market prices of filler and pulp fibers, the advantage of replacing fibers with pigment is evident, and hence, fillers are an important component in practically all printing and writing papers. Pigment properties are important in determining the effects of filler on the properties of paper and paperboard (Bown 1997; Fairchild 1992). In printing and writing papers, precipitated calcium carbonate (PCC) is being increasingly used to reduce raw material costs and basis weight of paper while maintaining thickness, or to customize the products by improving some critical paper

properties. On the other hand, the progressive addition of PCC in paper is limited by its negative effects on the bond strength and bending stiffness of paper (Holik 2006). Several methods have been proposed to increase the filler content in paper (Middleton et al.1985; Allan et al. 1998; Klungness et al. 1993). Composite fillers, formed by the in-situ precipitation of PCC in a suspension of cellulosic fibrils, have been shown to improve the performance of PCC and to allow increased amounts of filler in paper (Silenius 2002; Subramanian et al. 2005). However, the effects of the crystal habit of composite PCC on the properties of printing and writing paper have not been examined in detail in these studies.

In the present work, cellulosic fines were produced with a Masuko refiner (Kang et al. 2004). Three different composite PCCs — colloidal, rhombohedral and scalenohedral — were precipitated in-situ with pulp fines. Similar experimental conditions were employed for the production of composite and reference PCC fillers. The effects of adding composite PCCs on the properties and quality of fine paper were compared with the effects of reference PCCs. Handsheets were printed using HP LaserJet ("LaserJet" is a trademark of HP) and Epson ink-jet printers to compare the effects on toner adhesion and absorption, using reference and composite fillers, the inks being used as a probe material rather than defining printability in this case.

EXPERIMENTAL

Preparation of Composite Fillers

ECF bleached unrefined never dried pine pulp obtained from a mill, in Finland, was ground in a Masuko refiner to produce fines. Bauer-McNett analysis of the fines showed that 92% of the fines passed through a 200-mesh screen. The consistency of the fines-PCC composite was in the range of 0.085% to 0.1%. Equivalent amounts of calcium hydroxide suspension was added to the fines suspension in order to obtain a 2:1 PCC-fines mixture, which was carbonated to crystallize PCCs with colloidal, rhombohedral, and scalenohedral structures.

PCC morphology was controlled through crystallization of intermediary phases as described by Yamada and Hara. Colloidal PCC was thus obtained through amorphous calcium carbonate (ACC) (Yamada and Hara 1985_a).

$$Ca(OH)_2 \rightarrow ACC \rightarrow \text{Colloidal PCC} \quad (1)$$

It is believed that the ACC is transformed into colloidal PCC through a spinodal decomposition reaction of the ACC. Rhombohedral PCC was obtained through amorphous calcium carbonate (ACC) and basic calcium carbonate (BCC) (Yamada & Hara, 1985_b).

$$Ca(OH)_2 \rightarrow ACC \rightarrow BCC \rightarrow \text{Rhombohedral PCC} \quad (2)$$

Scalenohedral PCC was precipitated directly from $Ca(OH)_2$ (Yamada & Hara, 1985_c; Meuronen Jari, 1997). The progress of the reaction was monitored by conductivity

measurement, as shown in Fig. 1 for the production of 2:1 colloidal composite filler. The reaction was terminated when the conductivity suddenly dropped and approached 0 S/m, as shown in Fig.1.

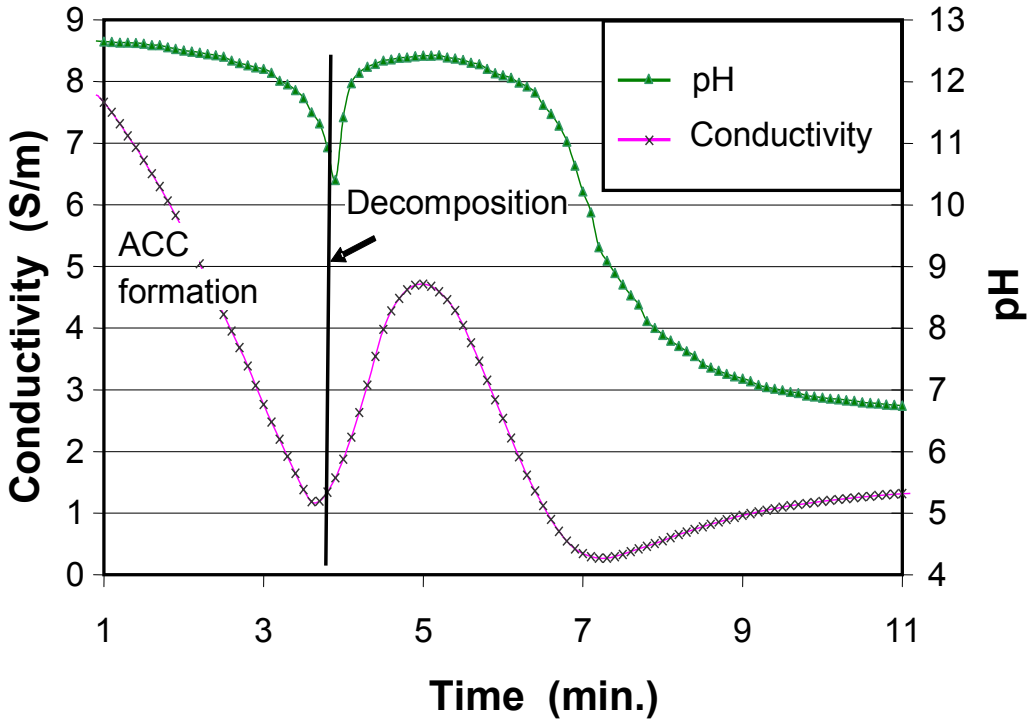

Fig. 1. Parameters observed during the crystallization of composite calcium carbonate filler with colloidal morphology

Sheet Forming and Testing

Refined pine softwood (23º SR) and birch hardwood pulp (18º SR) in a 30:70 ratio were used as the base furnish. Cationic acrylamide copolymer (C-PAM, 250g/t paper) was used as the retention aid in forming handsheets. The polymer solution was mixed in the handsheet mould, by air mixing, for 20 seconds. No other additives were used. Reference fillers, provided by J.M. Huber, produced under similar conditions as composite PCCs were used in the reference experiments.

Handsheets (80g/m^2) were produced in a standard handsheet mould with addition of retention aid, according to the ISO standard (ISO 5269-1). The samples were pressed twice in a Material Testing System (MTS) press at a pressure of 3.3 Mpa for 0.02 seconds with two blotting papers on each side. The handsheets were dried under standard conditions in a drum drier (ISO 5269-1). The first-pass retention was calculated as a percentage of the PCC retained in the handsheets to the total amount present in the stock suspension. In case of composite fillers, the total filler was measured from the whole composite sample, by ashing at 550^{o}C, and used to compute the amount of filler added to the base furnish. The handsheets were tested according to ISO standards. Internal bond strength was measured according to TAPPI T569 pm-00 standard method.

The PCC attached to the fibers was separated from them by oxidizing the cellulosic fibers for 2 hours in atmospheric air at low temperature (300ºC), followed by oxidation for 1 hour at 500°C.

The specific surface area of the PCC attached to the fibers was determined with the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The measurement was carried out with a Micromeritics Gemini 2375. The particle size distribution was determined by sedimentation of the ash residue with a Sedigraph 5100.

The method of ashing was used to assess the primary particle size distribution properties of the filler. The functionality of the filler, especially when combined with fibre, will additionally depend on the structures formed, including agglomerates and/or composites. Interpretation of the role of particle size in this case needs to be viewed in close relation with the microscopic analysis of composite particle structures. From the log-normal graph of the particle size vs. cumulative mass percentage we determine the median particle size (MPS), which represents the equal division of the mass of all particles present in the suspension. The particle size "75/25 ratio" was calculated from the Sedigraph as the measured value of the pigment particle size measured in microns at the 75 percentile divided by the particle size measured in microns at the 25 percentile. The 75/25 ratio is a measure of the breadth of the particle size distribution, and lower and higher values of 75/25 slope indicate that the particle size distributions are narrower and broader, respectively.

It is our experience (Maloney et al. 2005) that the slow ashing preserves the particle size of the PCC. Therefore, Sedigraph particle size results can be directly compared with particle sizes measured in the conventional way on standard fillers, while BET values should be treated with more care, preferably only by comparing the data obtained from slowly ashed samples.

Absorption and Structural Properties of the Handsheets

The handsheets were printed by HP LaserJet (4350dtn) and inkjet (Epson stylus C44UX) printers. The density and gloss were measured using Viptronic 4-794 and Vipgloss-I (4 -778), respectively. Printing ink rub resistance was tested with a PATRA print rub tester, using VTT test method 4716-94, with 2696g weight and 200 disc revolutions.

RESULTS AND DISCUSSION

Scanning Electron Microscopic (SEM) Study of the Composite Precipitated Calcium Carbonates

The colloidal calcium carbonates were seen to consist of precipitated nano-crystals aggregated into ellipsoidal shapes, as shown in Fig. 2. The precipitation occurred at random sites, mostly on the end of fibrils and, hence, the fibrils were partially covered with calcium carbonate fillers. The particle size of colloidal PCCs was less than 100nm.

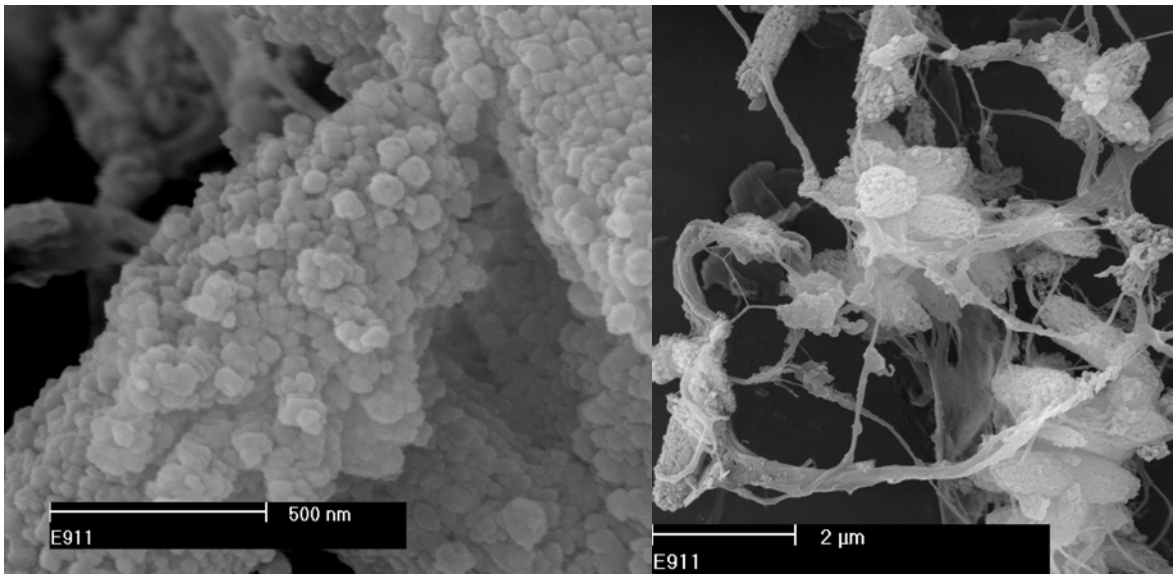

Fig. 2. Colloidal precipitated calcium carbonate composite

The rhombohedral PCCs were found in clusters, forming a pearl necklace structure with the fibrils, as shown in Fig. 3. Some fibrils covered PCC particle surfaces. In addition, films of microfibrils covering PCC surfaces were seen in the micrographs. The particle size of rhombohedral PCCs was below 2µm.

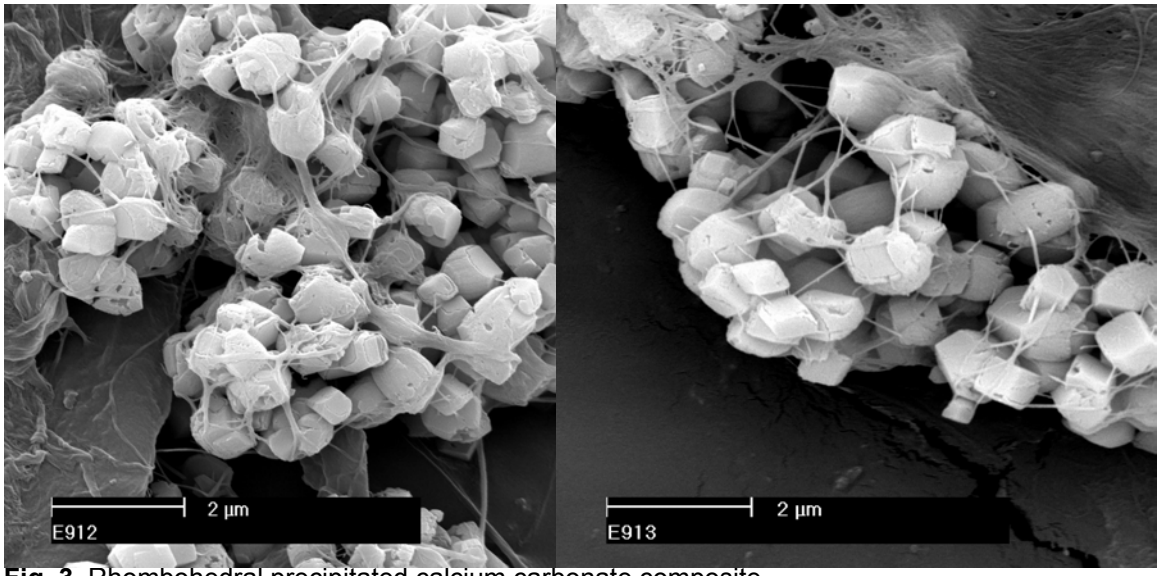

Fig. 3. Rhombohedral precipitated calcium carbonate composite

Alince has described that the light scattering ability of a pigment is a function of its refractive index and size (Alince, 1986), and in the case of agglomerates, also the particle spacing. Unbonded fibre surfaces contribute to light scattering due to debonding and their micrometre dimensions (Alince et.al. 1985). The SEM picture, Fig. 3, shows that the fibril width connecting the PCCs was below 200nm, and hence, may not contribute to light scattering, in contrast to the unbonded fibre surfaces.

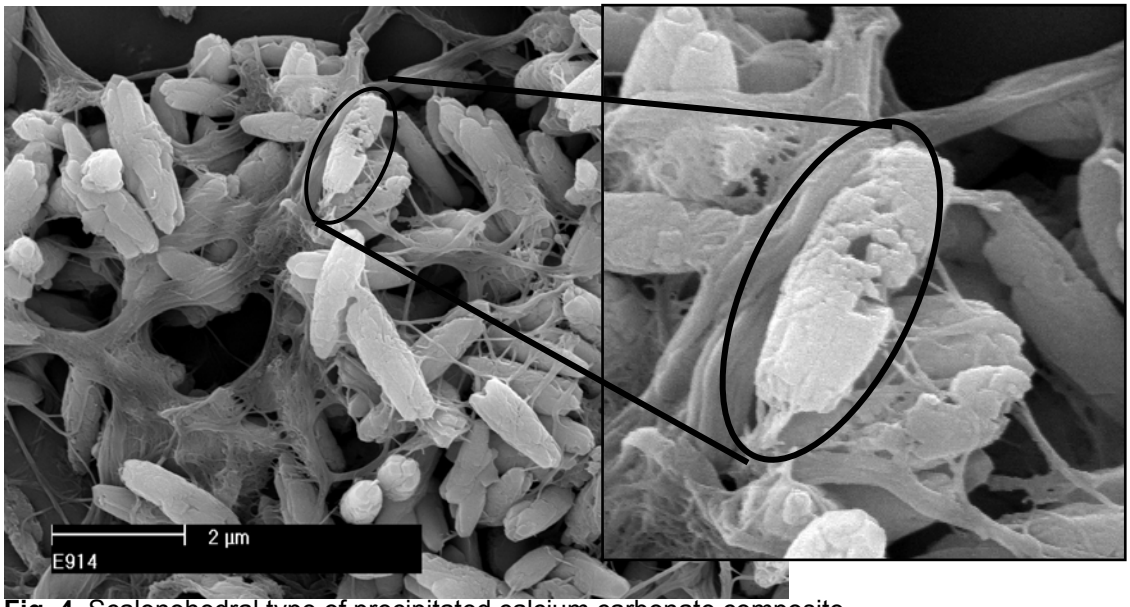

Fig. 4. Scalenohedral type of precipitated calcium carbonate composite

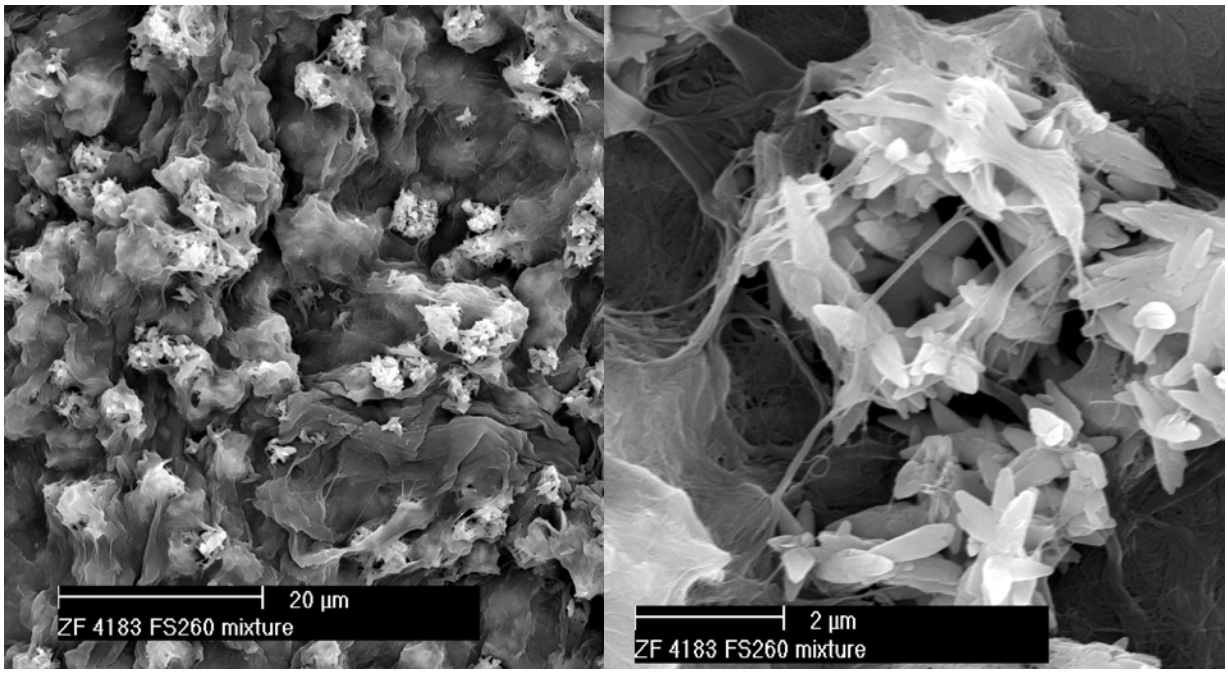

Fig. 5. Reference scalenohedral PCC mixed with cellulosic fines

The structure of the scalenohedral type of composite PCC formed under the experimental conditions was similar to that of the reference scalenohedral PCC, as shown in Fig. 4. Due to low solids and the presence of fines in the suspension, the precipitate appeared to have ellipsoidal form and was not structured, in contrast to the structured reference s-PCC. The presence of fibrils appeared to disrupt and inhibit the growth by covering the particle surfaces, as shown by the dark voids in the picture. Therefore, the particle size of these precipitates was lower, compared to the reference commercial PCC.

The precipitates were intertwined in a network structure. The fines surface coverage was higher with s-PCC composite than with other morphologies.

Fig. 5 illustrates mixing of fines and reference filler. It is seen that the filler was embedded into the fines network and partially covered by the fibrils. The filler was structured with a mean particle size of 2µm. It is to be noted that, during mixing, the PCC penetrated into the fibril network and prevented the collapse of the fibrils.

Filler Characteristics

The properties of the precipitated composites are compared with those of their respective reference PCC in Table I. The particle size distribution of the composite and reference particles was steep, as shown by the 75/25 ratio, with the exception of colloidal PCC. The measured surface areas of the reference fillers were larger than those of the composite PCCs. As stated above, this may, however, be a consequence of the preparation procedure. The colloidal PCCs had the largest surface area, as measured with the nitrogen absorption technique, among the various crystal habits in both composite and reference fillers. Also, at the same particle size, colloidal composite and reference fillers showed significant difference in their surface areas. Colloidal PCCs may thus be described as small aggregates of nano-sized crystals, a description that is also supported by the SEM investigation. The PCCs in fine and coarse rhombohedral composites did not differ significantly in size characteristics, in comparison to the reference rhombohedral PCCs.

Table 1 Characteristics of Composite and Reference PCC Filler

Type of filler	BET surface area (m^2/g)	Median particle size (µm)	75/25 ratio
composite c-PCC	12.02	1.42	3.0
composite fine r-PCC	3.91	1.31	1.75
composite coarse r-PCC	3.36	1.73	1.82
composite s- PCC	3.87	1.35	1.78
reference c-PCC	20.76	1.32	2.74
reference fine r-PCC	9.1	0.97	2.65
reference coarse r-PCC	4.32	2.29	2.16
reference s-PCC	5.81	2.19	1.74

Retention and Dewatering

The first-pass retention of the different types of filler is shown in Fig. 6. PCC-fibrillar fines composite filler gave higher retention than reference PCC, due to the higher flocculation index of fines with C-PAM retention aid (Solberg 2003). It was observed that the colloidal composite filler showed the highest first-pass retention, which is probably due to the PCC morphology (Fig. 2) and agglomeration. It has been shown that the retention of particles increases with increase in particle size, aggregated pigments, platy type filler, and coarse particles (Bown 1996).

On the other hand, the retention of reference PCCs decreased significantly with increased addition of filler. The mixture of reference filler and fines had a higher retention than reference filler, but lower than the composites. Mixing of filler with fines trapped the filler into the fines network (Fig. 5), resulting in higher retention than with addition of reference filler by itself.

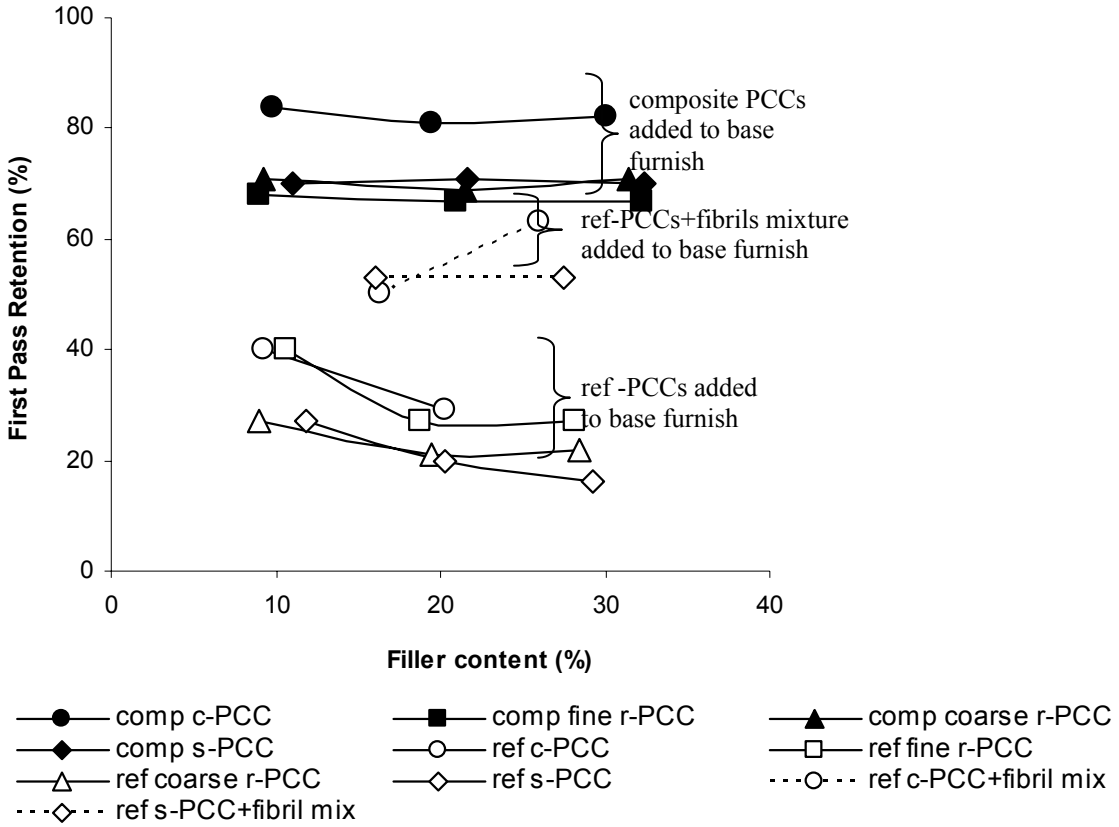

Fig. 6. First-pass retention of composite PCCs, ref-PCC's and ref-PCCs+fines mixture. Abbreviations: comp = composite; ref = reference; c= colloidal PCC; r = rhombohedral PCC; s=scalenohedral PCC; mix = mixture

Dewatering of the handsheets with various fillers after the first press is illustrated in Fig. 7. It is seen that the reference PCC gave the highest dry solids with increasing filler fraction in the paper. Mixing of fines with PCC significantly reduced the dry solids of handsheets after pressing. Among the reference fillers, structured s-PCC showed lower dry solids because of the water retention in the pores of the particles.

Among the composites, at lower handsheet filler content the colloidal composite showed the lowest dry solids, probably due to the homogeneous distribution of fillers leading to poor drainage. At higher filler contents, the drainage of colloidal fillers increased due to the expansion of the network structure. The expansion of the structure was confirmed by the increased bulk shown by the colloidal composite filled handsheets. At high filler contents, greater than 20%, the drainage of s- and r-PCC composite samples decreased significantly, probably due to the higher amount of film-forming fines in the structure.

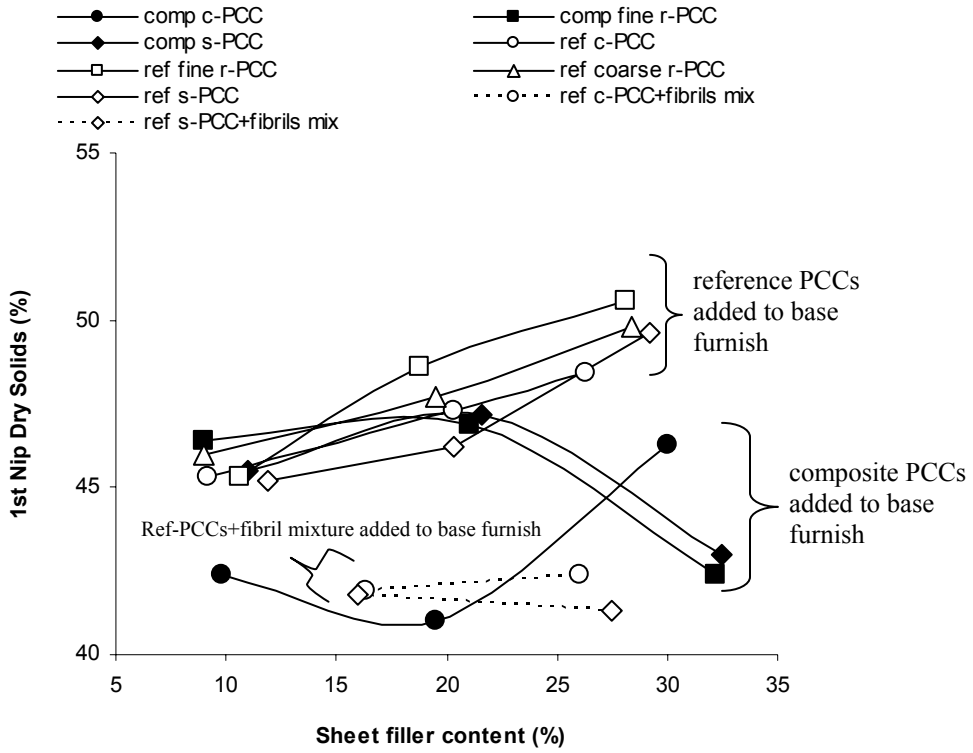

Fig. 7. Dewatering of composite fillers, reference PCCs and PCC-fines mixture handsheets at first press nip. For abbreviations, refer to Fig. 6

Paper Properties

The effect of addition of fines, in the form of composites or as a mixture of reference filler and fines, on the structural properties of paper is shown in Fig. 8. In contrast to reference PCC, a composite filler containing kraft fines enhances Campbell's forces, and thus aids in forming a dense network structure (Retulainen 1997). Among the reference fillers, addition of s-PCC caused a significant increase in the air permeability and a decrease in density. Addition of colloidal PCC resulted in a minimal increase in the air permeability of paper.

Addition of fines improved bending stiffness, as shown in Fig. 8, due to stronger bonding (Xu et al. 2005_b) and improved sheet consolidation (Seth, R.S., 2003). Mixing of fines and reference PCC gave the highest bending stiffness resistance. Reference r- and c-PCC gave the lowest bending stiffness, which decreased with increased addition of filler.

Comparing the internal bond strength and tensile index of various morphologies of PCC (Fig. 9), composites were found to give higher tensile strength than the reference fillers. These results correlate with earlier research findings (Xu et al. 2005_a) showing that fines contribute to strength by acting as a sealent-glue that increases the bonding area in filled paper. Among composites, at all filler contents, colloidal PCC and rhombohedral PCCs added to paper showed minimum and maximum internal bond strength respectively. Colloidal PCC composite gives reduced tensile strength at low filler contents.

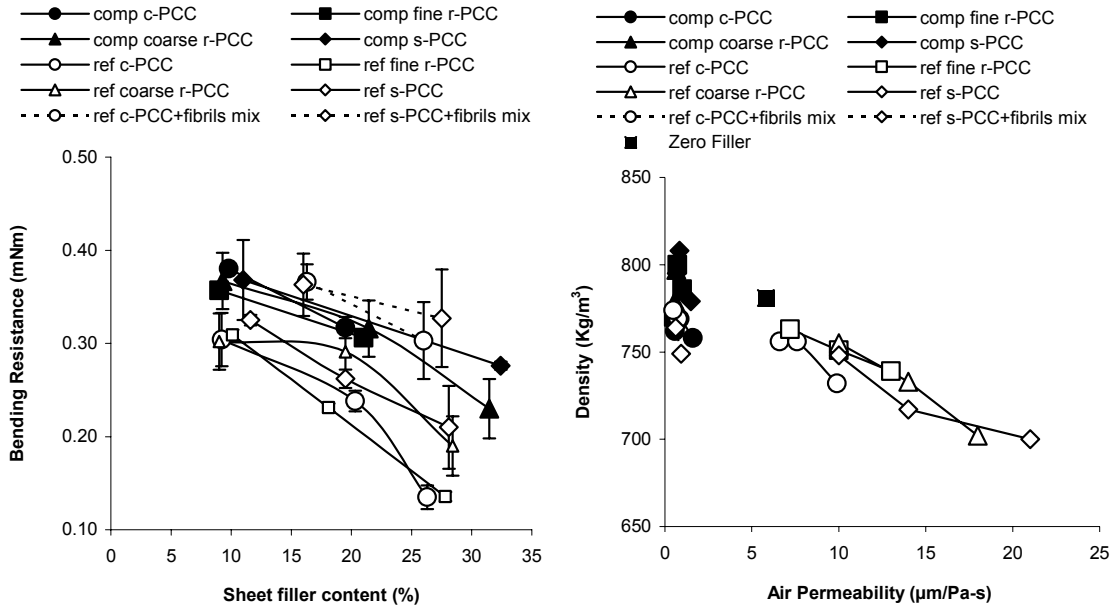

Fig. 8. Impact of PCC filler loading, as a function of PCC particle morphology, on the structural properties of paper. For abbreviations, refer to Fig. 6

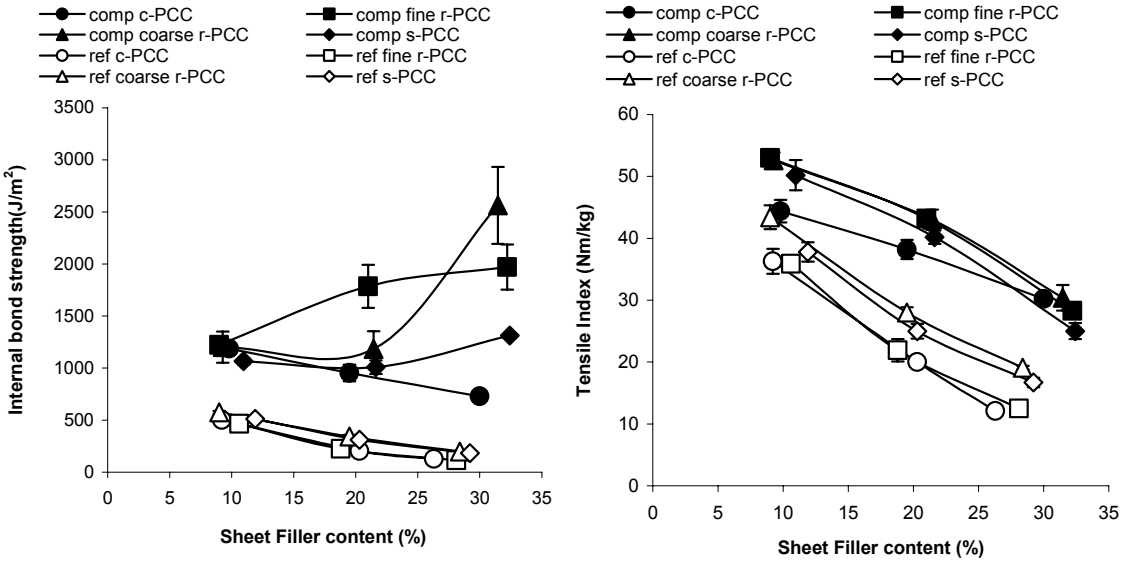

Fig. 9. Comparison of the strength properties of handsheets as a function of filler amount for composite and reference PCC filler with three different morphologies. For abbreviations, refer to Fig. 6

According to Fig. 10, increased addition of filler enhanced the light scattering of paper when using reference and composite fillers. Silenius (2002) has noted that the light scattering of composite fillers depends upon the particle size of the precipitated calcium carbonate particles. In our results we found that in-situ precipitation can lead to lowering

of surface area and particle size of the composite particles. Also, the dimensions of the fibrillar fines used in the co-precipitation of composites had a significant impact on the light scattering of the composite handsheets. As explained earlier (Fig. 3), less than 200 nanometer sized dimensions of the fibrils might not contribute to the light scattering, in contrast to the micrometer sized fiber dimensions. Thus, we found that the light scattering was similar for composite and reference filler added paper, in contrast to earlier experiments (Subramanian, et al. 2005).

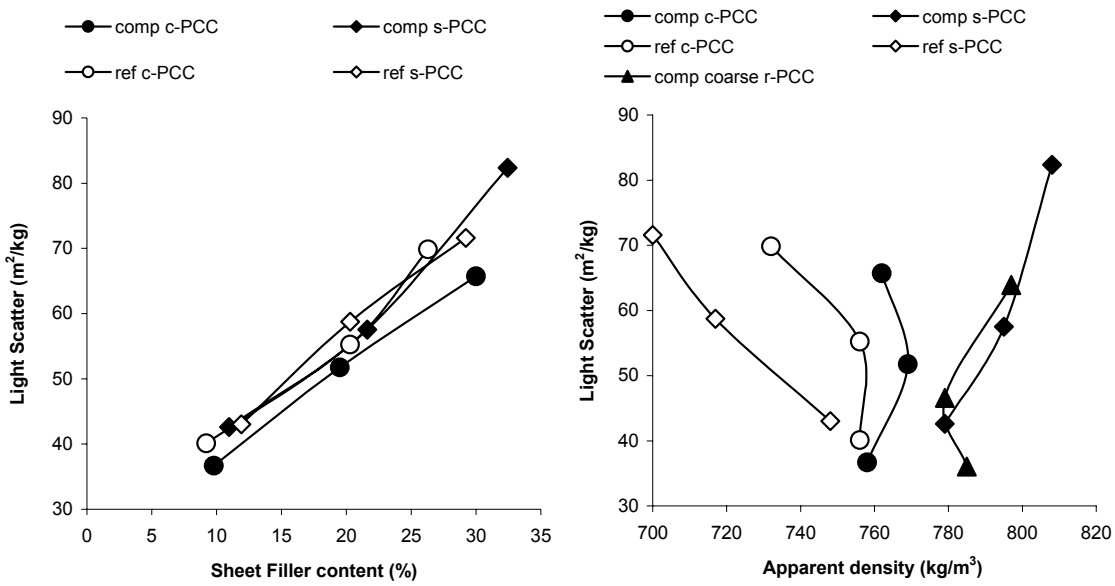

Fig. 10. Impact of PCC particle morphology on the light scattering properties of composite and reference PCC filled handsheets. For abbreviations, refer to Fig. 6

However, even with increased density, addition of composite filler to sheets imparted light scattering similar to that of reference fillers. This is due to the higher number of optical pores generated in the PCC-composites network structure, as shown in Fig. 4. The number of optical pores has a direct impact on the light scattering property of paper (Alince et al. 2002).

Print Rub Fastness

HP LaserJet and Epson ink-jet printed samples had an average density of 1.5, and an average gloss of 3 and 2 respectively. The suitability of these uncalendered and unsized handsheets for print analysis, per se, is not the aim of the exercise. However, the relative changes of absorption (ink jet) and of toner adhesion (laser printing) are of relevance in understanding the role of the different filler types. The whiteness of the rub-off samples is shown in Fig. 11, where the whiteness of a contact sheet is quoted, i.e. decreasing whiteness indicates high intensity of rub-off from the printed samples onto the contact sheet.

Addition of fibrillar fines, in the form of a composite or in a mixture of PCC and fines, was seen to enhance the rub resistance of the printed samples. This effect was more pronounced at higher filler contents.

Addition of fines increased sheet density of handsheets formed with composites and reference PCC-fibril mixtures. On the other hand, as shown in Figs. 3, 4, and 5, mixing of fines or in-situ PCC precipitation created network structures consisting of higher numbers of fine pores in the handsheets. Lowering of pore size, and thereby increasing the capillarity and adsorbing surface area had a positive effect on print rub resistance (Gane et al. 2006). Coarser colloidal PCC agglomerates added to handsheets resulted in lower print rub fastness with a significantly higher negative slope.

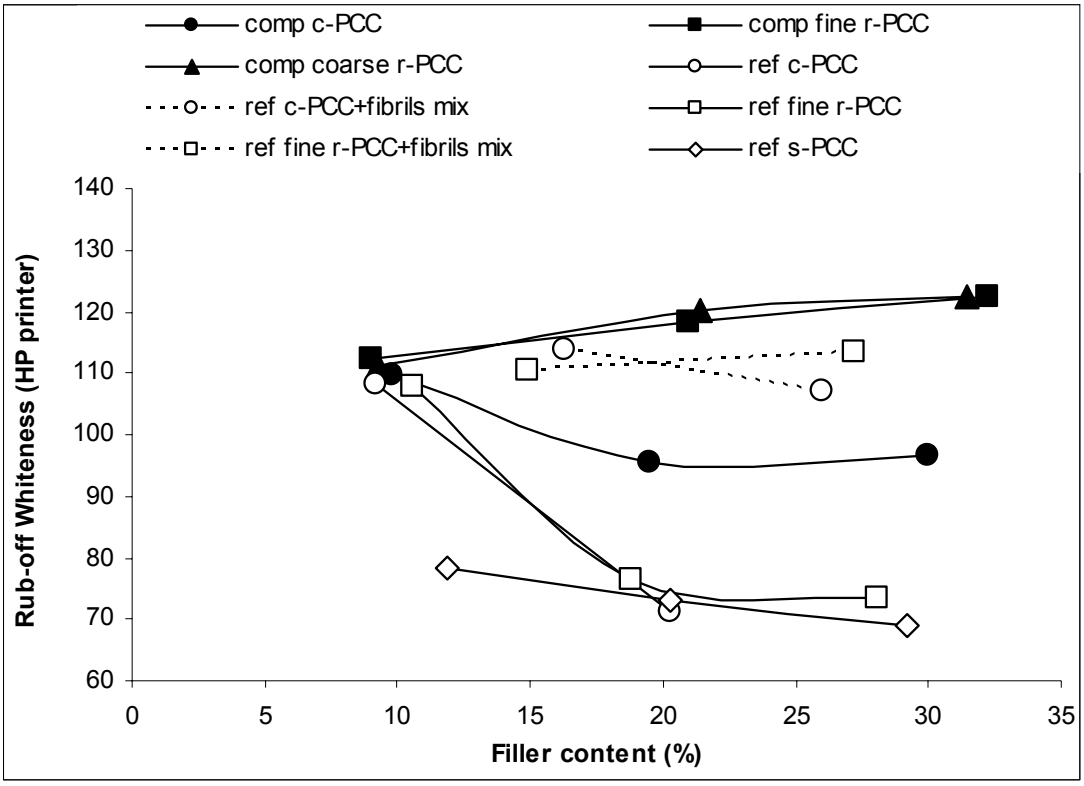

Fig. 11. Rub fastness, measured as the whiteness of copy paper rubbing surface, of HP laser-jet printed handsheets formed with the addition of composite filler, reference PCC's, and a PCC-fines mixture. For abbreviations, refer to Fig. 6

Similar trends were observed with inkjet printed samples. With inkjet printing, due to the lower strength of the base paper, the surface of the reference sample was completely scuffed below 100 revolutions.

CONCLUSIONS

1. In this work colloidal, rhombohedral, and scalenohedral types of PCC composites were precipitated. The characteristics of composite PCCs and their influence on the papermaking properties of printing and writing papers were determined.

2. The results showed that colloidal PCC consisted of nano PCC crystals agglomerated into an ellipsoidal shape on the surface of cellulose fibrils. Rhombohedral PCC and scalenohedral types of PCC formed a spider network with the fibrils. In the production of scalenohedral PCC crystals we found that particles had ellipsoidal shape and some of the particles had malformed structure.

3. First-pass retention was highest for colloidal PCC. At high filler contents, film-forming fibrillar fines increased the moisture content of wet pressed handsheets. Mixing of filler with fines results in higher retention compared to the mineral filler added alone due to the trapping of filler into the fines network.

4. Among composites, at all filler contents, colloidal PCC and rhombohedral PCCs added to paper showed minimum and maximum internal bond strength, respectively. At constant light scattering, handsheets that had been prepared with s- and r-composite PCC showed significantly higher density in contrast to the reference.

5. Print rub fastness increased with increased amounts of fibrillar fines in the handsheets.

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