Preferred citation: R. Gaudreault, N. Di Cesare, T.G.M. van de Ven and D.A. Weitz. The structure and strength of flocs of precipitated calcium carbonate induced by various polymers used in papermaking. In Advances in Pulp and Paper Research, Oxford 2009, *Trans. of the XIVth Fund. Res. Symp. Oxford, 2009*, (S.J. l'Anson, ed.), pp 1193–1219, FRC, Manchester, 2018. DOI: 10.15376/ftc.2009.2.1193.

# THE STRUCTURE AND STRENGTH OF FLOCS OF PRECIPITATED CALCIUM CARBONATE INDUCED BY VARIOUS POLYMERS USED IN PAPERMAKING

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## ABSTRACT

When the percentage of filler is increased in paper, the optical properties are improved and the production cost lowered. However, fillers weaken paper strength by decreasing the fibre-fibre bonded area. Little is known about the optimum filler floc size or filler floc properties to allow developing optimum paper characteristics. Consequently, the floc structure and strength of precipitated calcium carbonate (PCC) aggregates was studied using various polymers (flocculants and dry strength agents): by static light scattering/diffraction (SLS), real time fluorescent video imaging, image analysis, photometric dispersion analysis (PDA) and scanning electron microscopy (SEM).

It was found that PEO/cofactor induced PCC aggregates were weaker at high shear and far more irreversible than those induced by the partially hydrolysed polyvinyl formamide copolymerised with acrylic acid (PVFA/NaAA) or C-starch. Flocs produced at low polymer dosages were smaller and weaker than those produced at higher dosages. The number of discrete PCC particles in aggregates was measured using real time fluorescent video imaging combined with image analysis.

# INTRODUCTION

The rate of change in the pulp and paper industry is gradually increasing, and additives other than cellulose fibre have become essential components in the papermaking process. Fillers make up the most significant portion of these products. Typical filler addition levels range from 3% to 30% [1]. While most filler are naturally occurring minerals, others are manufactured, using chemical processes. The most common are [1]: kaolin clay, calcium carbonate, titanium dioxide, talc, silica, and silicate. These fillers are generally divided into two categories: 1) mineral fillers that are cheaper than fibre (regular and delaminated clays, ground calcium carbonates (GCC), precipitated calcium carbonates (PCC) and talc), and 2) specialty fillers that are more expensive than fibre, and are used for more specific purposes (titanium dioxide, precipitated silica, silicates, as well as structured clays) [1]. PCC is produced in scalenohedral, rhombohedral, and needle shaped or aragonite structures, with scalenohedral PCC being the most widely used in the wet end of papermaking. Aragonite can be produced in different ways and interestingly by changing the sequence of addition in the Kraft caustisizing process [2]. Recent work by Pouget et al. [3] showed that the initial stages of templatecontrolled CaCO<sub>3</sub> formation starts with pre-nucleation clusters with dimensions of 0.6 to 1.1 nm (step 0). Aggregation of theses clusters in solution leads to the nucleation of amorphous calcium carbonate (ACC) nanoparticles with a size distribution centered around 30 nm (step 1). Association of these particles with the template surface initiates the growth of ACC (step 2), using the nanoparticles in their neighbourhood as feedstock. Next crystallization starts, resulting in the formation of poorly crystalline particles (step 3). Randomly oriented nanocrystalline domains are formed inside the otherwise amorphous particles (step 4). In the last steps, the orientation that is stabilized through the interaction with the monolayer becomes dominant (step 5) and develops into a single crystal (step 6). This single crystal probably grows by the further addition and incorporation of ions and clusters from solution. Gebauer et al. [4] speculate that the release of water molecules from the hydration shell of ions provides a substantial entropy gain favouring pre-nucleation cluster formation. Piana *et al.* [5] are using metadynamics to explore the free energy surface for ion diffusion across the  $CaCO_3$  surface. Obviously, our work occurs at a much larger scale and is described later in this text.

Fillers can either be added in pulp prior to the headbox, or as a coating applied to the surface of the sheet once it is already formed. Although each type of filler has specific characteristics and fulfills particular functions, their role in the pulp and paper industry can be summarized as follows: 1) reduce production cost (fibre substitution); 2) improve optical properties (opacity, brightness); 3) improve printability; 4) improve sheet formation; 5) improve smoothness; 6) improve dimensional stability [1]. However, fillers may have negative effects: 1) reduce mechanical strength (interference with interfibre bonding); 2) abrasion (on wires, blades and printing plates); 3) impair retention (increase of retention aid dosage); 4) increase two-sidedness; 5) reduce stiffness; 6) increase dusting tendency; 7) increase the quantity of deposits in the paper machine system; and 8) require a more complex white water recirculation loop. Some fillers are more detrimental to paper strength than others. When compared at constant total area of filler per mass of paper, the burst strength follows the trend clay > talc > GCC [6, 7]. Similar strength effects were shown for GCC and PCC [8] whereas, at a subtler level, it seems that prismatic PCC is less detrimental to strength than scalenohedral PCC [9, 101.

Filler shape, aspect ratio, average particle size, size distribution, aggregate size, density, and specific surface area are critical parameters that detemine paper properties. The smallest fillers have the most detrimental effect on paper strength [11, 12], for a given filler type and a given dosage. Bown [13] studied sheet properties with 20% filler content using chalk and kaolin having particle sizes of 1 to 12 µm. He showed the effect of aggregating the kaolin to produce either a rigid, open structure (calcined kaolin) or a flexible, compressible structure (strongly flocculated kaolin) [13]. The size distribution within the sheet is unlikely to be the same as the original size distribution of the filler dispersion. Recent methods showed that the filler distribution in paper sheets is irregular in the z (thickness) direction [14–16]. This reflects the complex influences of paper machine design, operational conditions, drainage, wet end chemistry, etc. Beazley and Petereit [6] published the most widely quoted model for filler strength effects which employs the specific surface area as the only filler property. However, Li et al. [11] reported that their conclusion was valid only within a narrow range of filler types.

Literature [11, 17] suggests that fillers weaken paper by lowering the fibrefibre bonded area. One possibility is that filler particles act as flaws causing local areas of stress concentration, which initiate sheet failure [18]. Tanaka *et al.* [17] showed that the addition of potato starch improves the strength properties of non-filled sheets made solely from Kraft pulp, without changing the structure while beating or addition of filler changes their structure. Many authors have studied ways to introduce calcium carbonate fillers, and/or calcium carbonate composites, in pulp or paper and their effects on the optical and physical properties [19–30]. Several patents have been issued regarding the increase of calcium carbonate filler level in paper [31–37].

Fillers often form aggregates well before sheet consolidation, especially in the short circulation loop [38]. Filler aggregation has been studied from the perspective of aggregation prior to being injected in the pulp furnish [39], and to a much smaller extent within the papermaking process. Mill trials, using starch for PCC aggregation, and prior to the addition of PCC in papermaking pulp, has also helped to reduce linting and dusting [40]. Lindström and Floren [8] showed that the effect of cationic starch wet end addition on sheet consolidation is larger the smaller the filler particle size. Modgi *et al.* [40] showed that potato and tapioca starches were able to aggregate PCC in process water (PW) at  $50^{\circ}C$ . However, tapioca starch gave the highest rate of aggregation and aggregate size compared to potato starches [40].

How many of the fillers will persist in real papermaking conditions as aggregates, is still an open question. However, Figure 1 clearly shows that filler aggregates are present in fine paper. Figure 2 shows an undesirable situation where the filler particles, in a white top liner, are not uniformly distributed, which could negatively alter the optical properties of paper. However, this could favour the strength properties. Numerous SEM pictures were taken from different sampling points of a linerboard process (white top liner) and filler aggregates were observed all across the papermaking process, i.e. from the pulper to the end product. Interestingly, the size of the aggregates was increasing as the pulp samples were taken closer to the headbox. This can probably be explained by the flocculating agents added prior to the headbox and by the flocculation of the originally non-retained fillers, which can then be incorporated as aggregates in the sheet, which occurs in the short circulation loop [38, 41]. The challenge is to find the best compromise between the optical and strength properties of paper.

Macromolecules adsorbed onto colloidal particle surfaces may either stabilize or destabilize the dispersions. The behaviour will depend on the degree of surface coverage, molecular weight, charge density, type of polymer, and degree of dissolution. For partially covered surfaces, the already adsorbed polymer on a given particle may attach to the bare surface on another one forming a particle-particle bridge (bridging flocculation) [42–46]. The bridging flocculation mechanisms were extensively studied [42–51].

An important question is: how can aggregation be induced to give a



Figure 1. a) SEM pictures showing filler aggregates in fine paper grade made from recycled fibres. b) The picture on the right is an enlargement of a floc seen on the left.c) SEM and d) SEM/X-ray mapping of calcium in the filler aggregates.



Figure 2. SEM pictures showing filler aggregates in white top linerboard.

specific type of aggregate? The kinetics of the interactions probably plays a critical role in the type of aggregates that can be created. Polymer type, concentration and experimental conditions can be adjusted to create open or dense aggregates. Two distinct limiting regimes of irreversible colloid aggregation (without shear) have been identified: "Diffusion-Limited Colloid Aggregation" (DLCA) giving open aggregates and "Reaction-Limited Colloids Aggregation" (RLCA), giving dense aggregates [52-60]. Each one has its own characteristic dynamics and produces aggregates with different fractal dimensions  $(d_t)$  where the mass of aggregate scales as  $a^{d_t}$   $(M \approx a^{d_t})$ . Lin et al. [56-60] showed the universality of DLCA and RLCA. DLCA was studied by increasing the ionic strength of the system to ensure that the system is only limited by diffusion and not by electrostatic repulsion. RLCA is the opposite, in the sense that the colloids are aggregating at a slow rate due to the presence of electrostatic charges, or other interactions, thus giving dense aggregates. Lin et al. [56] used gold (a = 7.5 nm), silica (a = 3.5 nm) and polystyrene (a = 19 nm) to demonstrate the universality in colloid aggregation. They showed a striking similarity in the structure of the clusters of the different colloids in each regime: DCLA which covers rapid coagulation,  $d_f = 1.75$ , and RCLA resulting from slow coagulation,  $d_f = 2.1$  [56]. In terms of flocculation efficiency (a, W = 1/a) one would expect that low flocculation efficiency would result in denser aggregates, higher fractal dimension, whereas high flocculation efficiencies would give open aggregates i.e. lower fractal dimension. The above two phenomena are different from the aggregation of large PCC particles which is shear induced [61]. Nevertheless, they parallel each other in the sense that it might be possible to control the experimental conditions to obtain open or dense aggregates. In papermaking, both perikinetic (diffusion controlled) and orthokinetic (shear induced) interactions are present [62], although most PCC aggregation will be shear induced.

Yilmaz and Alemdar [63] developed a technique, based on steady state fluorescence measurements, to study the cluster-cluster aggregation and sedimentation kinetics of organoclay. They reported that pyranine was used as a fluoro-surfactant (bridging effect), and argued that the fluorescence intensity during the sedimentation process can be used to measure the fractal dimension of the aggregates as a function of organoclay concentration [63].

In our previous work [61], the kinetics of PCC aggregation was studied and compared with theoretical models. It was found that the flocculation efficiency depends on the PCC surface area that can participate in bridging (bridging surface area), i.e. the surface area associated with the most protruding surface asperities. This surface area is much smaller than the total surface area available for polymer adsorption. We proposed that the bridging surface area, which can form bonds between PCC particles or aggregates, should be used to study the kinetics of PCC aggregation, and not the total or projected surface area [61].

In this work we studied the properties of the final PCC flocs and correlate them with the type of polymer and with the flocculation kinetics studied earlier [61]. PCC aggregation was studied using static light scattering/diffraction (SLS), real time fluorescent video imaging (RTFVI), photometric dispersion analysis (PDA), image analysis, scanning electron microscopy (SEM) and light microscopy. Moreover, the reversibility and the strength of the aggregates, as well as the type of aggregates, were investigated.

## MATERIALS AND METHODS

#### Chemicals

#### Precipitated calcium carbonate (PCC)

Precipitated calcium carbonate, Albacar-HO from Mineral Technology inc., with a weak negative charge density of -1.3 meq/kg (ionic charge of the slurry: -272 µequiv/L), was used. The charge density was measured for a 20.9% suspension of PCC sampled from the satellite production plant, without dilution. pH of the PCC suspension was 9.0. Pure PCC is positively charged [64], as confirmed by molecular modelling calculations [65], but turns negative upon dilution by adsorbing impurities, even in distilled water, because of the small surface area of dilute PCC [64]. It also turns negative in process water. No dispersant was added to the PCC sampled from the satellite plant process water, resulting in slightly negative particles. The average particle size, measured by static light scattering/diffraction, is 4.4 µm (Figure 3). Measurements with and without ultrasound gave very similar PCC particle sizes.

Because these results were higher than measured by sedimentation (1.43  $\mu m$ ), SEM was performed to validate them. The SEM pictures were performed by taking one drop of stirred 20.9% PCC suspension, and diluted to 1/1000 to ensure discrete particles. Results showed the PCC particles to be irregular in shape, having lots of asperities, within the same size range as measured by SLS/diffraction (Figures 3 and 4). The experimental specific surface area (SSA), measured by nitrogen adsorption, was reported to be 13.95 ± 0.70 m<sup>2</sup>/g PCC by the supplier (2-year average).

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Figure 3. Particle size distribution of scalenohedral PCC measured by static light scattering/diffraction (SLS).



Figure 4. Typical SEM images of PCC particles in the original commercial 20.9% suspension.

## Polymers

The polymers used to flocculate PCC are in Table 1, together with their charge density and some other properties. For all commercial dry polymers, including PEO, fresh solutions were prepared the day of experiment. Starch was cooked at 95°C for 45 minutes at 2 % (w/w) solids. After the cooking time, the starch was diluted with water and kept warm (40–45°C) during the experimental work. All other polymers were dissolved using de-ionised water.

# Adsorption isotherm

The adsorption isotherms were measured to determine the maximum amount of polymer adsorbed on the slightly negative PCC [61]. Two different chemistries were evaluated using: (a) sodium salt of partially hydrolysed PVFA/ NaAA, an amphoteric polymer (Table 1, Figure 5), and (b) cationic potato starch, because it is commonly used in papermaking processes (Table 1).

Results showed that both chemistries yielded high affinity type adsorption isotherms, with a maximum amount of adsorbed polymer of:  $\Gamma_{max} \approx 7 \text{ mg/g}$  PCC [61]. The  $\Gamma_{max}$  of PVFA/NaAA on PCC was validated and found to be identical to that of an external laboratory, using photometric titration (UV-VIS spectrophotometer) methods (Ref: BASF, Germany).

Even though the chemistry differs, polyethyleneimine (PEI) has been shown to adsorb on GCC and PCC and adsorption isotherms after one hour of equilibration gave  $\Gamma_{max}$  in the range of 4–10 mg PEI/g of PCC, depending on the particle size, surface area, and electrophoretic mobility [66]. Our results are within their range.



**Figure 5.** Molecular structure of the sodium salt form of partially hydrolysed polyvinyl formamide copolymerised with acrylic acid (PVFA/NaAA).

## Particle size analyser (static light scattering/diffraction)

Particle size analyses were performed using a Malvern Mastersizer instrument equipped with a Hydro 2000S wet dispersion accessory (A). Static light

Table 1. Characteristics	of the chemical compound	IS	
Product	Commercial name	Charge density (equiv/kg dry)	Description
Cationic potato starch (C-starch)	EmCat C3 (AKP Canada Inc.)	+0.48	0.3% nitrogen
Poly(ethylene oxide) (PEO)	Oxicol (Ciba Specialty Chemicals)	Nonionic	Mw ≈ 6 MDa
Cofactor	Oxirez (Ciba Specialty Chemicals)	Anionic	Sulphone type resin
PVFA/NaAA	Catiofast PR 8236 (BASF)	Amphoteric -1.2 (pH 9.0)	Sodium salt of partially hydrolyzed polyvinyl formamide copolymerized with acrylic acid. $Mw \approx 0.6 \text{ MDa}$
Polyethylenimine (PEI)	Polysciences Inc.	+13.1 (pH 7.0) +5.5 (pH 9.0)	Mw ≈ 70 KDa

scattering/diffraction (SLS) uses the full Mie theory to calculate the particle size. A refractive index of 1.607 was used for PCC. Results for PCC and PCC/ polymer systems are an average of five measurements, with a stirring rate of 1925 rpm and no ultrasound.

## Photometric dispersion analyzer (PDA)

#### Aggregation

Changes in the state of PCC aggregation were monitored by a Photometric Dispersion Analyzer (PDA 2000 Rank Brothers, Cambridge, UK) [67, 68]. The PCC suspension was pumped from the outlet of a 1-L beaker through a transparent 3 mm diameter tubing into the photocell of the PDA, which monitors the fluctuations in intensity of transmitted light (Figure 6). The experimental apparatus has a recirculation loop to allow measurements of the flocculation and break-up kinetics.



Figure 6. Experimental set up for the photometric dispersion analysis (PDA) experiments. The shear in the suspension can be controlled in the beaker by stirring and in the tube by the peristaltic pump (flow rate).

The transmitted light intensity has two major components:  $\bar{v}$  which represents the average transmitted light intensity and a much smaller component  $(v_{rms})$  defined as the standard deviation around the mean signal. The  $v_{rms}$  increases considerably as particles aggregate, whereas the aggregation only slightly changes  $\bar{v}$ . Therefore a significant increase in the ratio (R) is a clear indication of particle aggregation, with R defined as:

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$$R = \frac{V_{rms}}{\overline{V}} \tag{1}$$

For dilute systems, R varies linearly with the square root of the concentration, and for polydisperse systems R is approximately linear with the particle radius, a [67, 68]:

$$R \cong CN^{1/2}a \tag{2}$$

where N is the number of particles per unit volume, and C a constant. As shown before [61], changes in R ( $\Delta$ R) correlate with changes in size ( $\Delta$ *a*) measured by static light scattering/diffraction. This technique is ideal to measure the break-up of aggregates and hence their floc strength.

#### Reversibility of aggregation

The 1000 ppm PCC suspension was flown through flexible 3 mm I.D. tubing at room temperature through the PDA. No salt was added. The flow rate was controlled using a peristaltic pump with a recirculation loop. The suspension was stirred at 300 rpm. The shear rate in the tubing was first increased from low to high and subsequently lowered from high to low. The first part of this experiment is to study the intrinsic strength of PCC aggregates and the second part to study the reversibility of the aggregates.

#### Microscopy and real time fluorescent video imaging (RTFVI)

Fluorescent images were acquired on a Leica DM-IRB inverted microscope equipped with a Hamamatsu intensified charge-coupled device (EB-CCD) camera C7190-21 (Hamamatsu City, Japan), and automated image acquisition software (Metamorph: Universal Imaging Corporation, Downington, PA). Polymer was tagged with an aldehyde reactive fluorescent probe, Alexa Fluor 488, to ensure proper visualization. Alexa Fluor 488 (Invitrogen Inc.) and PVFA/NaAA (0.05% w/w) were stirred together for one hour in deionised water. The solution was then dialyzed for 12 hours using a 3,500 Mw cut-off membrane to remove any free probes. The fluorescent polymer is used to visualize PCC aggregation. Salt (CaCl<sub>2</sub>) was added to the PCC suspension to simulate the papermaking process. Shear is only applied during a few seconds after the addition of salt and polymer to the PCC suspension. Salt (CaCl<sub>2</sub>) and polymer were added simultaneously. Once the aggregation process has been initiated, about 1-1.2 mL of the suspension was poured into a small cuvette, without agitation. The estimated time between the injection of the chemicals (salt (CaCl<sub>2</sub>) and polymer), and the imaging is about 10 seconds; results were corrected accordingly. This real time fluorescent video technique has the advantage of being able to visualize PCC aggregation. Two images were recorded every second, for at least two minutes and more, during an experiment. However, the experimental set up leads to settling of the PCC aggregates, which makes interpretation of the particle size difficult. Many experimental conditions were tried to overcome this, e.g. more aggregation leads to more and faster settling. Numerous PCC concentrations were explored: from 0.1 to 2500 ppm, and the optimum was found to be between 1580 and 1780 ppm. From this method, combined with image analysis, an attempt was made to measure the average number of discrete PCC particles in an aggregate, as a function of time, which is valuable information in the study of the kinetics of PCC aggregation. To get accurate information the video images were treated to improve the contrasts, using the sharpen mode of Image J software.

#### **Image analysis**

For experiments (1 mg and 5 mg PVFA/NaAA/g of PCC), video images were taken from 0 to 45 seconds. These images were analyzed using image analyzer software (Clemex Vision PE version 3.5.). A number of large aggregates were selected using the interactive mode of the image analyzer software. The area of particles was divided by the total area of the image, giving the fractional surface area covered by PCC particles or aggregates. Then, the fractional coverage area was plotted as a function of time.

## RESULTS

## Strength and reversibility of PCC aggregates

## Strength of PCC aggregates (PDA experiments)

PDA experiments were performed to show the relative intrinsic strength of PCC aggregates. Based on previous results [61] the dosages of the chemicals (PVFA/NaAA, C-starch and PEO/Cofactor) were selected to get a similar particle size at the lowest shear rate. Figure 7 shows the normalized apparent PCC aggregate size, expressed as  $\Delta R/\Delta R_0$ , under different shear rates and where  $\Delta R_0$  is the PCC apparent particle size at the lowest shear rate. The shear rates (in reciprocal seconds) were calculated from the volumetric flow rate, Q, using:

$$G = \frac{8Q}{3\pi r^3} \tag{3}$$

1205



Tube flow rate (ml/min.)

**Figure 7.** Normalized changes in apparent particle size  $(\Delta R/\Delta R_0)$  as a function of shear rate (s<sup>-1</sup>) and as flow rate (mL/min) for different polymer treatments: 5 mg PVFA/NaAA/ g of PCC; 2 mg C-starch/ g of PCC and 0.03125 mg PEO/0.143mg cofactor/ g of PCC; cofactor:PEO ratio of 4.5:1. The PCC concentration was 1g/L, temperature was room temperature, no salt was added and the stirring rate was 300 rpm. Black symbols show the apparent particle size after the shear was reversed from high to low level. Top left and bottom right pictures show the PEO/Cofactor/PCC aggregates under the lowest and highest shear rate respectively.

where Q is the flow rate, r the radius of the inner diameter of the flexible tubing (3mm).

Larger aggregates (higher ratio,  $\Delta R$ ) imply stronger aggregates and less break-up under the same shear rate. Figure 7 shows that generally the aggregate strength is similar when they are induced by PVFA/NaAA and starch, while the PEO/cofactor system gives somewhat weaker aggregates at high shear rates. It is worth mentioning that the current cofactor:PEO ratio is 4.5:1, while Goto and Pelton [69], using a different cofactor, reported that the maximum scalenohedral PCC floc strength corresponded to a ratio of 2–3. They found that the flocs broke up when exerting an extensional force of about 100–140 nN. Results from figure 7 show again that a dynamic equilibrium exists between the formation and break-up of aggregates at steady state. The reversibility of the aggregates was verified by measuring the  $\Delta R$  after reversing the high shear rate back to the low shear rate. Figure 7 shows that PVFA/NaAA and starch induced aggregation is partially reversible while PEO/cofactor induced aggregation is not reversible.

# *Reversibility of PCC aggregates (test tubes experiments)*

The reversibility of PCC aggregates was also studied in tests tube experiments. PEI was added to a diluted PCC suspension (1000 ppm), 5 mg PEI/g PCC, followed by manual agitation. PEI alone, which is a low molecular weight cationic polymer, does not aggregate PCC; in fact it acts as a stabiliser [66]. Particle size distributions measured for PCC and PCC+PEI were found to be nearly identical at the beginning and at the end of a 7 months period. When aggregating PCC stabilised by PEI, with PVFA/NaAA, an amphoteric polymer, reversible aggregation was observed (Figure 8). Other experiments showed that PCC aggregates are stable for months in the absence of shear, for PVFA/NaAA and also for C-starch. This implies a dynamic equilibrium between the formation and break-up of PCC aggregates and thus aggregation is reversible for this type of system.



Figure 8. PEI pre-stabilised PCC particles aggregated with PVFA/NaAA: low shear (left), strong manual agitation (middle), and 5 minutes later (right). Room temperature. No added salt.

# Microscopy and video imaging

Numerous real time videos in fluorescent mode were performed to study the kinetics of PCC aggregation. Figure 9 shows typical images from zero up to 45 seconds, for the 1mg PVFA/NaAA / g of PCC, 1mM CaCl<sub>2</sub> system. Because the way the experiments were performed it was not obvious if the



Figure 9. Accumulation of PCC aggregates on bottom of cuvette as a function of time. Experimental conditions: 1940 ppm PCC, 1mg PVFA/NaAA/g PCC, 1 mM CaCl<sub>2</sub>, room temperature. Selected large aggregates are indicated by the circles. These images were enhanced to improve the contrasts.

images in figure 9 result from PCC aggregation and/or sedimentation at the bottom of the cuvette on the glass lamella. Consequently, the fractional surface area covered by the PCC was measured as a function of time (Figure 10). During sedimentation the PCC flux towards the glass lamella surface is j = nv, n is the number of particles per unit volume and v the velocity. Hence, the fractional surface coverage, the surface occupied by the PCC out of the total surface, is  $S = \pi a^2 jt$ , t being the time. Substituting for v the Stokes sedimentation velocity, and expressing n in terms of concentration c, yields:

$$S = \frac{gac\Delta\rho t}{6\eta\rho_{PCC}} \tag{4}$$

where g is the gravitational acceleration, a is the PCC radius, c the PCC concentration,  $\Delta \rho$  the density difference  $(\rho_{PCC} - \rho_{H_2O})$ ,  $\rho_{PCC}$  the density of PCC,  $\eta$  the viscosity of water and t the time. Equation 4 predicts that the fractional surface area should increase linearly with time. Indeed, figure 10



Figure 10. Fractional surface coverage and light intensity as a function of time. PCC was treated with 1 mg PVFA/NaAA/ g of PCC (1940 ppm of PCC), and 5 mg PVFA/NaAA/ g of PCC (1780 ppm of PCC). Both experiments were performed at 1 mM CaCl<sub>2</sub> and room temperature. Dashed line shows the theoretical sedimentation for non-flocculated PCC. The best fit (solid line) corresponds to PCC of 5.0 μm.

shows that S is linearly related to time and supports that sedimentation is the main mechanism for the 1mg PVFA/NaAA/g PCC system ( $r^2 = 0.9999$  for 1 mg PVFA/NaAA/g PCC). Moreover, figure 10 shows that the best fit for the radius of PCC is 5.0 µm, larger than the 4.4 µm of the non-aggregated PCC, implying that a small amount of aggregation has occurred. Because the estimated time between the injection of chemicals (CaCl<sub>2</sub> and PVFA/NaAA) and the imaging is about 10 seconds, this is about the amount of aggregation you can expect in such a short time. Stopping the shear is equivalent to quenching the aggregation.

Furthermore, the light intensity was measured to validate the above trend and to see if polymer adsorption can be measured with this technique. Even though the light intensity follows the same trend as the fractional surface area, very few data points are available and a lot more experiments are needed to draw any conclusion.

This technique, combined with image analysis may be used to estimate the number of discrete PCC particles in an aggregate. For example, the PVFA/ NaAA system at a dosage of 5 mg/g of PCC and 1mM CaCl<sub>2</sub> shows the average number of discrete PCC particles in selected large aggregates to be about 17–18 (Figure 11). Because this technique is exploratory and very time



Figure 11. Experimental average number of discrete PCC particles in selected large aggregates as a function of time. The data to build this graph are not statistical average. Experimental conditions: 1780 ppm PCC, 5mg PVFA/NaAA/g PCC, 1mM CaCl<sub>2</sub> and room temperature.

consuming, large aggregates were selected to demonstrate its usefulness. Consequently, Figure 11 does not intend to give a statistical average. More work is needed to demonstrate the potential of this new method.

# Type of aggregates

Whether open or dense aggregates are suitable for papermaking is not clear yet but we can speculate that the open aggregates would be better, at least for



**Figure 12.** PCC floc sizes for low and high dosages of PVFA/NaAA (0.5 and 5mg/g PCC), C-starch (0.5 and 5mg/g PCC) and PEO/Cofactor (0.05 and 5mg of PEO/g PCC). The cofactor:PEO ratio, 4.5:1, was constant for both PEO dosages. The flocculation efficiency (a, W = 1/a) and the statistical average particle size were taken from Figures 13 and 14 [61]. However, these parameters do not correlate with the above pictures because only one floc or a few flocs are shown.

the optical properties of paper because of the larger surface area to scatter more light.

Figure 12 compares the PCC floc structures and sizes for low and high dosages of PVFA/NaAA (0.5 and 5mg/g PCC), C-starch (0.5 and 5mg/g PCC) and PEO/Cofactor (0.05 and 5mg of PEO/g PCC). The chemical additives were added into a 1L dispersion of 1000 ppm of PCC. The suspension was stirred for 5 minutes at 300 rpm using a 3 cm propeller before an aliquot was taken for image recording. Image recording was performed 1 to 4 hours after flocs reaction. The dispersions were manually gently shaken and 100  $\mu$ l was placed on a microscope glass slide. A cover glass was carefully deposit on the drop and the excess of water was removed with absorbent paper. Photos were taken using dark field illumination.

From Figures 13 and 14 it can be seen that low dosages lead to low floccu-



Figure 13. Particle size as a function of polymer dosage. All experiments were performed using 2000 ppm of PCC suspensions, room temperature and no added salt. The cofactor:PEO ratio, 4.5:1, was constant for all PEO dosages (Adapted from 61) Representative examples of floc sizes induced by C-starch for low and high dosages are shown in Figure 15.



**Figure 14.** Stability ratio (Log *W*) as a function of polymer dosage. All experiments were performed using 2000 ppm of PCC suspensions, room temperature and no added salt. The fastest aggregation rate, obtained from the 5 mg PEO/cofactor/g of PCC system, was used as the reference aggregation rate to compare the performance of the above chemicals on the same basis (Adapted from 61).

lation efficiencies and small flocs and whereas high dosages lead to higher flocculation efficiencies and larger flocs. For low dosages the size of the flocs is due to a dynamic equilibrium between floc formation and break-up, because there is sufficient room for further bridging and flocs should grow without limit if break-up was absent. For higher dosages the floc size may be determined by a competition between polymer adsorption and particle aggregation. Flocs form before the surface is fully saturated by polymer and subsequent polymer adsorption prevents further floc growth because of electrosteric repulsion between the particles [64]. This implies that the floc strength increases with polymer dosage. This explains the difference in floc size for the two dosages in Figure 12. However, from the floc images it is hard to conclude whether flocs get denser or not when they get larger (Figures 12 and 15). Larger flocs contain more particles, many of which overlap in an



**Figure 15.** Optical (left) and SEM (right) images of PCC aggregates induced by C-starch. Top and bottom images show PCC aggregates produced from low and high C-starch dosages respectively. The optical and SEM do not show the same aggregate.

image. Moreover the density of flocs depends on the shear history of the flocculation process and flocs often get denser at high shear [70–74]. This densification could be more pronounced for larger flocs, because the hydro-dynamic forces exerted on them are larger. This might be the reason why there is no obvious correlation between the flocculation efficiencies and floc densities, as it is the case for perikinetic coagulation (Figures 12 to 15).

# CONCLUDING REMARKS

PCC aggregation was studied using static light scattering/diffraction (SLS), real time fluorescent video imaging (RTFVI), photometric dispersion analysis (PDA), image analysis, scanning electron microscopy (SEM) and light microscopy. RTFVI combined with image analysis was used to measure the

number of discrete PCC particles in aggregates. This method has the potential of measuring polymer adsorption on particles. Using RTFVI, it was found that the fractional surface coverage in the area of observation by PCC aggregates increases linearly with time, with the slope determined by the size of the aggregates. PEO/cofactor induced aggregates were weaker at high shear and far more irreversible than those induced by PVFA/NaAA or C-starch. Flocs produced at low polymer dosages were smaller and weaker than those produced at higher dosages.

# ACKNOWLEDGEMENTS

The authors wish to acknowledge the valuable assistance from colleagues at Harvard University: Dr Cliff Brangwynne, Dr. Gijsje Koenderink, Dr. Tomas Angelini, Dr. Carlos Martinez for their assistance on fluorescence video imaging, Dr. Chanjoong Kim and Dr. Daniel Blair for valuable insights. The authors also thank Denis Berthiaume from Cascades Rolland Division and Pascal Allard for the papermaking process, Claude Tremblay for the scanning electron microscopy, Eric St-Pierre for laboratory assistance, and Frédérick Anctil for the image analyses, all from the Research and Development Centre of Cascades Inc. Financial support from NSERC and FPInnovations for an Industrial Research Chair is also acknowledged.

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# **Transcription of Discussion**

# THE STRUCTURE AND STRENGTH OF FLOCS OF PRECIPITATED CALCIUM CARBONATE INDUCED BY VARIOUS POLYMERS USED IN PAPERMAKING

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Bob Pelton McMaster University

Nice work, Roger. 10 or 15 years ago, we published a series of papers where we looked at micro-mechanics of these types of floc. We actually took individual flocs and did a tensile test with small capillary tubes pulling them apart. That is a very tedious thing even for graduates to do, but I have a suggestion. I know a number of groups that are working with highly filled systems where flocs are large and they are easily manipulable under a microscope. What I remember is the amazing range of behaviours of these things which you could assess qualitatively. Some of them you would pull and they would extend to an elongation of 600% or 700% before they broke, and others were like the biscuits that we have at coffee time and they would fail by brittle fracture. I think you can learn a lot about how these polymers behave, qualitatively, just by grabbing onto these flocs and giving them a pull, and seeing whether they are like chewing gum or British cookies.

#### Discussion

# Roger Gaudreault

Thank you very much for this great comment; I reported on your work in the manuscript. By the way, what Bob is talking about is the work that was done with Goto (reference 69 in the paper in the proceedings, ed.) where they used PCC flocculated by PEO and a co-factor. What they reported was the maximum strength of PCC flocs for the PEO / cofactor system, giving values of 100 to 140 nN. They had a ratio of 2 to 3 of cofactor to PEO. I read this paper quite a few times, and if we had more time, I think that it would be a great technique to use, to support the understanding of floc strength. Thank you.

# Jean-Claude Roux University of Grenoble

A very interesting talk, even for a non-chemist like myself. I have one very simple question. You mentioned that you would like to pre-aggregate particles, have you some experimental evidence that pre-aggregation will reduce the limiting effect that you mentioned on the sheet properties?

# Roger Gaudreault

Yes, we have. We did a lot of laboratory work on physical properties, even more than I showed today on the colloidal aspects, and yes it is possible to show that. But I have to admit that the polymer we used for the work on aggregation and physical properties was the one which was developed for GCC (ground calcium carbonate) but for this project we added PCC, as used in our mill. Nevertheless, we decided to go ahead with this polymer. We also tried it with GCC and I can confirm that with GCC it will lower the drop in strength. With PCC the effect was smaller, giving very little improvement in strength properties at constant filler level. I know that the company that we dealt with at that time now has a new polymer which is adapted for PCC. So it is clearly yes – but the polymer we added was not the developed for PCC.

## Jean-Claude Roux

But what about the shear rates, because with the shear rates you may have some decreasing of efficiency as you proved?

## Roger Gaudreault

The work referred to earlier was on handsheets made in our laboratory. But with the shear rate you come to another aspect, which is practical application

to papermaking. We took a lot pulp samples from our paper making process, obtaining a lot of SEM images from: the pulper before screening, the machine chest, the head box, from points before and after the fan pump, the head box and, of course, images from paper samples. What we found is that, as you get closer to the head box and, of course, to the paper, the filler flocs get bigger. Part of the explanation is likely to be the polymers that we normally add at the machine chest and at the fan pump. We did scan our process a few times, and this is written up in the manuscript. Whether these aggregates will persist in papermaking is another question. I do not have the full answer to that but, when we were doing this work, the supplier claimed that there were two mills in the world that were using this chemistry.

## Jean-Claude Roux

Thank you for this complete answer.

# Gil Garnier Australian Pulp and Paper Institute

I am especially interested by the reversibility of your flocculation and I would like you to comment on this in terms of the conformation of the polymers. I will explain: you used three linear polymers of different backbone rigidity, molecular weight, and charge density and one dendrimer. Are you able to correlate the reversibility of the flocculation in terms of the polymer characteristics and the dynamics of adsorption on the surface?

## Roger Gaudreault

We did not concentrate greatly on this issue in the paper. Nevertheless, PEO has a molecular weight of 6 MDa, it is linear and gives weaker PCC flocs at higher shear rates that are irreversible. For a PEO / co-factor induced aggregate formed through polymer bridging, PEO is most likely sitting on two adjacent discrete particles that break apart under high shear. In other words, the PEO will now sit on only one of the particles. Whether the PEO itself is broken or not is another question, although I do not think it is. For the copolymer, it is more interesting because it has a molecular weight of 0.6 MDa and gives PCC flocs that are partially reversible. The copolymer possibly acts through charge neutralization or patch coagulation. Interestingly, we did use OCC (old corrugated containers) pulp fines, we did the same experiment and with a similar polymer we found that the OCC fines flocs were perfectly reversible. So that means that the flocculation using the copolymer, whether it produces a filler aggregate or a fines aggregate, is

reversible. We will have to do more experiments using C-starch, but what we have found so far is that C-starch induced PCC aggregates are partially reversible.

# Juha Salmela VTT

Thank you for a very nice presentation. I have a question which I would like you to answer. You showed a figure (figure 7 in the paper published in the proceedings, ed.) where you have relative floc size as a function of shear rate. So, I have a little problem with the shear rate there, I do not really understand it. In the paper you are using an equation (equation (3) in the paper published in the proceedings, ed.) that is derived for Newtonian fluid, pure fluid but we are dealing with particle suspension, so there is a little problem. What is your comment on this? If you actually measured the shear rate, do you think the figure would be the same?

# Roger Gaudreault

I am 99% sure the answer will be "no". As you know it is quite difficult to calculate the shear rate in such a system and so what we did, and it is written in the manuscript, was to use the equation which was given by the supplier which estimates shear rate from volumetric flow rate. I am sure if we measured it on an absolute basis, or used a more accurate model, we would get a different answer. I am quite confident about the trends but I agree with you that we must have a concern about the absolute values of the shear rate.

# Juha Salmela

But that figure actually might look very different if you have real shear rates because the different suspensions, at the same flow rate, they might have different shear rates.

# Roger Gaudreault

Yes. I'd like to add a comment on that. As you know, there are not too many values in the literature for shear rate. I remember, in a Bob Alince paper, for a beaker, he used 10 reciprocal seconds but we do not have many such data in the literature to tell us where we sit. In the Firth and Hunter paper, they said that from 910 to 2000 reciprocal seconds is a moderate shear.

#### Harshad Pande Domtar

You mentioned a number of ways to increase filler levels and one of them was "on-fibre PCC crystallization". Do you know if someone is doing that commercially?

## Roger Gaudreault

There is a patent on this from Alex Koukoulas but, so far as I have heard, there is nobody using it commercially. You would have to do a better search to be sure.

Harshad Pande

Thank you.