

# ACHIEVING MAXIMUM FILLER RETENTION BY IMPROVING MECHANICAL AND CHEMICAL RETENTION

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## ABSTRACT

Conditions for maximizing chemical and mechanical filler retention were studied through a combination of laboratory, semi-pilot and pilot scale experiments. In the first part of this work, we investigated the impact of particle size on the mechanical retention of particles in a fibre network using a modified laboratory hand sheet former. Quartz particles of well-defined and narrow-size fractions were used to simulate pre-flocculated filler of different sizes. Five different size fractions were studied. The mechanical retention was found to increase linearly with both web fibre grammage for each quartz fraction and with particle size. These results were then validated through pilot-scale production trials where different filler floc sizes were created through pre-flocculation techniques. In the second part of this work, we studied the stability of pre-flocculated filler flocs through a set of semi-pilot scale flow loop trials. Trials were performed by pre-flocculating filler (PCC) with flocculating agents continuously and exposing the filler flocs to controlled levels of hydrodynamic shear created by flow through a partially closed gate valve. Changes in filler floc size were monitored continuously using Focused Beam Reflectance Measurements (FBRM). A clear reduction in the particle size was observed as the pressure drop increased. A major part of the floc

degradation occurred at relatively low shear conditions while under the highest shear conditions, the pre-flocculated PCC floc size was reduced close to the un-flocculated state. In the third part of this work, we investigated the effect of different forms of process related shear on retention polymer stability and its effect on chemical retention. A set of semi-pilot scale flow loop trials were performed to investigate the effect of elongational shear-strain and shear due to velocity differences created inside and outside a dosage nozzle respectively. We show that the effect of elongational strain created inside the dosage nozzle leads to significant retention polymer degradation while shear created outside the dosage nozzle due to velocity gradients has a smaller effect on polymer degradation. We investigate these results with a series of pilot scale production trials and show that high shear conditions created inside the dosage nozzle leads to significant reductions in chemical filler retention. However, pilot trials indicate that shear created outside the dosage nozzle can also have a significant effect on filler retention, although to a lesser extent.

## **INTRODUCTION**

Present day papermaking processes are energy intensive. The majority of this energy is spent on extracting the fibres from the logs, processing and preparing the fibres in suspension, and removing the water that is bound to the fibres in the wet paper web. As a result, the energy consumption during production is approximately proportional to the amount of fibres employed. Conversely, only a small fraction of the total energy is spent on preparing non wood-based components (e.g. mineral filler material) and mechanically removing the water from the space in between the fibres. By consequence, replacing a greater fraction of the fibres in a product with filler material is an effective way of reducing the energy consumption during production. Filler also has a positive impact on paper optical quality and printability.

Filler material, typically on the order of a few microns in size, can be difficult to retain in the paper web. Hence retention aids, defined here as high molecular mass, water soluble polymers are often added to the paper stock in order to improve the efficiency with which the filler materials remain in the paper web. These polymers can work by the process of adsorption [1] and flocculation [2]. Adsorption processes result in the chemical attraction and/or attachment-of filler particles to fibres, e.g. through polyelectrolytic bridges or charge neutralization, which results in what is often referred to as chemical retention. Polymers can also flocculate fillers generating larger filler aggregates which will have a higher mechanical retention.

## **Filler pre-flocculation and mechanical retention**

One strategy to increasing the filler content in paper is to pre-flocculate filler prior to its addition to the furnish. The main reason for developing the concept of pre-flocculating filler has been to be able to maintain strength of the paper at increased filler content. Filler has a well-known negative impact on strength, see e.g. [3–6]. It has been suggested that strength deteriorates for three main reasons – insufficient adhesion between the filler and the cellulose or between filler particles and the introduction of stress concentrations (e.g. cracks) into the sheet by the fillers [6]. Moreover, since filler particles are small they will occupy a large surface and can hinder fibre-fibre contact which is decisive for the strength of the paper.

Pre-flocculation will reduce the effective specific surface area of the filler and could thus limit the negative effect on paper strength. Pre-flocculation has been tested in full scale over the years. Almost 40 years ago clay was pre-flocculated with a high molecular weight synthetic polymer in a full scale trial resulting in increased retention and improved mechanical properties of the paper [7]. Clay has been pre-flocculated with cationic starch to give improved mechanical properties of the paper produced [8]. Also by using starch, but flocculating calcium carbonate, both retention and the mechanical properties of the paper produced have been found to improve [9]. These studies all engage filler-filler flocculation.

Co-flocculation of fines and fillers has also been demonstrated at mill scale [10]. With these studies, strong flocs were achieved which resulted in improved strength properties. Fines and clay were flocculated using a high molecular weight CPAM. It was found that the flocculation was more effective when fines were treated with CPAM prior to adding the clay compared to mixing fines and clay together and there after adding the CPAM.

More recent trials have been performed at pilot scale. Ground calcium carbonate (GCC) was pre-flocculated using starch, producing a 65 g/m<sup>2</sup> paper at a machine speed of 60 m/min [11]. The pre-flocculation resulted in increased retention and improved stiffness and burst strength. GCC has also been pre-flocculated with CPAM and bentonite micro particle, while producing 80 g/m<sup>2</sup> paper (kraft pulp HW/SW 80%/20%) on a pilot Fourdriner machine running at 80 m/min (Stora Enso Imatra) in studies by [12, 13]. The pre-flocculation gave improved retention but the mechanical properties were not investigated. Cooked cationic starch has been added to clay, where-after this material was then spray dried. This resulted in higher tensile strength and bulk of the paper [14].

A full scale pre-flocculation trial, was performed by [15] on a 300 ton-per-day Fourdriner producing coated basestock. The increase in filler retention, due to pre-flocculation, varied between 5 and 26 % depending on the strategy used. Their hypothesis for these differences was that the size of filler flocs affected the filler retention. The pre-flocculation also resulted in increased tensile strength stiffness

and machine performance. Increased retention has also been achieved by [16]. However, no effect on sheet quality was observed when pre-flocculating clay in the production of soft calendared grades from bleached thermo-mechanical pulp (TMP).

The location for pre-flocculated filler addition has also been shown to influence retention, e.g. [12, 13]. Here it was demonstrated through pilot scale trials that it is beneficial to add the pre-flocculated filler (GCC pre-flocculated using CPAM and bentonite micro particle) as late as possible in the process. It was suggested that this is due to the shear-sensitivity of the filler flocs. One key issue to be successful in pre-flocculating filler is to produce filler flocs that are stable enough to survive, or show fast re-flocculation after the high shear forces created within a paper machine.

Many lab-scale studies have been performed investigating the stability and degree of re-flocculation of filler flocs e.g. [17–21]. These studies suggest that the degree of flocculation, floc break-up on the application of shear, and re-flocculation after the application of shear are strongly dependent on the kind of filler and the kind and character, i.e. molecular weight ( $M_w$ ), branching, and charge of the flocculating agent used. This would suggest that it should be possible to produce suitable filler flocs if a suitable filler-flocculant is used. However, all these studies have been performed in beakers with a rotating propeller generating the shear forces. There is no clear correlation between the shear forces of a propeller and the shear forces in the paper machine.

Most of the full and pilot scale studies mentioned above show that pre-flocculation of fillers gives an improved retention. The retention of the pre-flocculated aggregates is likely to be improved since they are larger than individual filler particles and thus will be mechanically retained in the fibre network to a greater extent, i.e., by mechanical filler retention.

As retention of filler particles during papermaking is an immensely important production objective, numerous studies have been performed on this subject. Generally these studies are focused on the effect of chemical additives where the main mechanism is seen to be the ability to attach fillers to the fibre surface, see e.g. [22]. However, the mechanical retention of fillers in paper has received only limited attention in the literature.

The mechanical retention of single filler particles is generally low due to the small size of filler particles compared to the pore size in the fibre network [23]. However, there are agglomerates of filler particles as well as filler particles and fines in the furnish when it leaves the headbox. The size of these aggregates is affected by the chemical and flow environment. These aggregates are much larger than the individual particles and are more likely to be retained mechanically in the fibre network. A model for the mechanical retention of fillers was presented by [24]. The model is based on the probability that a randomly chosen particle meets a pore that is smaller in size than the particle. This model describes entrapment of

particles of a given size in a fibre network of varying grammage. The theory was compared to experimental results using a laboratory sheet former and clay as filler. The theory showed good agreement with the experimental data.

### **Polymer degradation and chemical retention**

Despite the potential for improved mechanical retention through pre-flocculation strategies, chemical retention, i.e. retention through the addition of chemical flocculating agents/polymers, remains the most common approach. Some polymer properties which influence filler retention (for single component retention systems), include polymer molecular weight, degree of branching of macromolecular structure, charge density, and electrolyte concentration [25].

However high molecular mass macro-molecules are shear sensitive and are prone to undergo chain cleavage accompanied by a reduction in molecular mass when exposed to too high levels of shear. When this occurs, the functionality of retention aid polymers are reduced significantly. For example, numerous researchers have observed significant reductions in filler retention when retention aids are subjected to high levels of pre-shear prior to sheet forming using Britt-jar type apparatuses, e.g. [26–28]. The effect of pre-shearing and post-shearing on retention aid performance was studied at lab-scale by [27]. With these studies, a rotary mixer was used to pre-shear a slurry consisting of hardwood kraft pulp, 25% fines, 30% precipitated calcium carbonate (PCC) and a CPAM retention aid. Shear was then applied on-line in the form of pressure pulses during dewatering on a small lab forming unit. They found that retention decreased significantly with increasing levels of pre-shear and decreased slightly with increased levels of on-line shear. Relationships between shear, retention and dewatering were investigated using lab forming unit in conjunction with two different types of PAM by [29]. The effect of increased shear levels was shown to result in decreased filler retention.

It has also been shown that polymer degradation can occur during polymer transfer from fibre to filler during processing, e.g. [26, 30]. With these studies, both Britt-jar and pilot scale flow loop experiments were performed with stocks consisting of softwood fibres (10 g/l) and latex particles (5 g/l); the latex particles which served as a model for either filler or fines. Fluorescent labelled CPAM was added to the fibre stock only and then the latex was added. It was then shown that approximately 80% of the CPAM polymers were transferred from the fibre to the latex particles. The CPAM was then ‘washed off’ the latex particles and gel permeation chromatography (GPC) measurements were performed to measure the molecular weight distribution ( $M_w$ ) of the CPAM solution. Significant polymer degradation was observed during the experiments upon which it was concluded that polymer degradation can occur during the polymer transfer and/or floc rupture processes.

The above studies show that with exposure to conditions of high shear, chemical retention can fail and fillers or their agglomerates are retained mainly by mechanical entrapment (mechanical retention) with other components of the furnish, namely fines or fibres. If both chemical and mechanical retention fail, filler (and fine) material is washed into the short re-circulation loop which can subsequently lead to severe runnability and product quality issues [31].

On a fundamental level, mechanical degradation of polymers refers to the process in which the activation energy required for polymer chain scission is exceeded by the energy imparted on the polymer. During processing and production, this occurs due to exposure to high levels of shear, e.g. during flow through mechanical components such as screens, pumps, valves, and other sudden changes to the flow geometry, and also due to turbulence within the flow. Early research on the subject revealed that the key factors causing polymer degradation included polymer molecular mass, chain extension, shear-strain (in particular elongational shear-strain) and viscosity, e.g. see [32] and the references contained therein. The aforementioned parameters were re-investigated by [32]. Using an experimental dosage rig, they studied the degradation of highly dilute polystyrene polymer solutions ( $M_w \sim 10^6$ ). Ironically, they studied degradation with a lab set-up similar to a retention aids dosage system. With this set-up, the dosage nozzle contraction ratio, angle, and nozzle diameter could be varied thus creating polymer chain extension that could be varied from transient to sudden. Here transient chain extension would result, e.g. during flow through a headbox nozzle, whereas sudden chain extension would occur during flow into the headbox tube package.  $M_w$  distributions of the polymers after flow through the device were measured using GPC. They identified some inconsistencies with the traditionally understood causes for degradation and demonstrated that (1) partially uncoiled chains show much higher than expected degradation (well below the theoretical strain rate values), (2) viscosity plays only a very minor role in degradation, (3) pure elongational strain is not the only key factor causing polymer degradation, and (4) velocity and pressure drop appear to play significant rolls in degradation. An attempt to reconcile some inconsistencies with polymer degradation in transient and stagnation elongational flows – the former similar to flow through a headbox nozzle, the latter similar to dosage into the approach flow was made by [33]. With these studies, 200 ppm polyethylene oxide (PEO) solutions were studied and  $M_w$  distribution measured with GPC. They investigated both sudden and gradual contractions with and without a stagnation point in the flow. They also considered the number of passes through their re-circulatory system, the local strain rate, and Reynolds number,  $Re = \frac{\rho Du}{\mu}$ , where  $\rho$  is the fluid density,  $\mu$  the fluid viscosity,  $u$  the mean fluid velocity, and  $D$  the pipe diameter. They showed that the stagnation point due to cross flow (similar to dosage into the paper-machine approach flow) increases polymer degradation

significantly, however degradation is approximately the same in sudden and gradual contractions. In this same work, they further investigated the relationship between imposed strain rate,  $\epsilon$ , and critical molecular weight for degradation,  $M_{wD}$ , for PEO systems. They showed power law relationships between the two which were dependent on the solvent and flow system.

The polymer degradation phenomenon has also received considerable attention over the last several decades due its implication with a phenomenon known as turbulent drag reduction. More specifically, when added to a turbulent flow, high molecular weight polymers are known to produce massive reductions in turbulent drag even at dilute concentrations, i.e. reductions in pumping costs and energy consumption during transport and processing of industrial flows. Some of the most common drag reducing polymers includes polyacrylamide and polyethylene oxide [34–36]. Drag reduction can be quantified as a decrease in the pressure differential over a fixed length of pipe relative to a non-drag reduced flow, e.g. [34]. The percent drag reduction, DR can therefore be defined as follows

$$\%DR = \frac{\Delta P_0 - \Delta P_p}{\Delta P_0} \times 100 \quad (1)$$

where  $\Delta P_0$  was the pressure drop measured over a fixed pipe segment for flow with pure water and  $\Delta P_p$  was the drag reduced pressure drop measured after polymer dosage. Of particular interest here is the fact that the drag reduction phenomenon vanishes as polymers undergo shear degradation. For example, [37] studied the degradation of high molecular mass polystyrene through recirculation in a flow loop set-up. Drag reduction was monitored continuously during the experiments through differential pressure measurements and samples of the polymer solution were removed at discrete times from which the  $M_w$  was determined using GPC. They showed a continuous reduction in DR over time, i.e. the pressure differential increased towards that obtained for the flow of solvent alone. A clear correlation was made between shifts in the polymer  $M_w$  toward smaller values and losses in DR. More specifically, the degradation of drag reducing polymers can be directly correlated to increases in pressure differential. Since these early experiments, similar experiments yielding comparable results have been performed using, e.g. polyacrylamide [36], and polyethylene oxide [38]. Moreover, [38] studied the degradation of both PEO and PAM polymers in a pipe flow at large Reynolds number with a pipe diameter 27.2 mm. The fluid was not recirculated in these experiments, but samples were extracted at multiple points along the pipe length for measurement of the  $M_w$  using GPC. The pressure drop, i.e. DR, was also measured between each sample extraction point in the flow. They showed that polymer degradation occurs within the pump, at a contraction within the flow, and along pipe length due to turbulence. By fitting data to theory

for the maximum drag force exerted on a polymer chain, they showed that degradation is proportional to  $Re^{3/2}$ .

The above mentioned studies clearly identify several key sources for polymer degradation, many of which mimic those found in most modern paper machines. Moreover, implications for the destruction of pre-flocculated filler are also associated with these same high shear environments. With the objective of achieving high filler retention in paper products, it is therefore critical to gain a deeper understanding of the relationships between process conditions, the shear associated with these processes, and the effect on filler retention. It is therefore the purpose of this work is to investigate the filler retention phenomenon from a process oriented approach. Implementation of optimal conditions for mechanical retention are investigated and related to the process fluid mechanics of the paper machine. The underlying causes for loss of chemical retention are investigated and related to fluid mechanics of the paper machine. It is the main goal of this work to gain a deeper understanding of filler retention through bridging chemical, mechanical and process phenomena typically implemented in the modern production process.

## **EXPERIMENTAL DETAILS**

The experiments performed in this work spanned the range of lab, semi-pilot, and pilot scale. The effect of particle size on mechanical retention was investigated using a modified laboratory hand sheet former, referred to as the Rapid Drainage Device (RDD). The effect of shear on pre-flocculated filler (micro-) floc size distributions and on retention polymer degradation was studied on the Innventia semi-pilot scale flow loop facility. Laboratory and semi-pilot experiments were then validated through pilot scale paper production trials using the Innventia FEX paper machine.

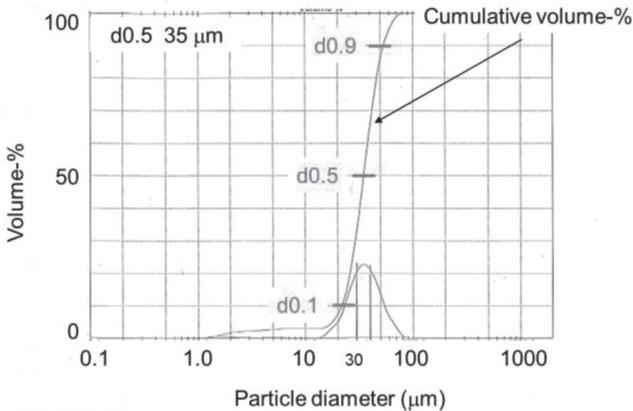
### **Filler pre-flocculation**

Filler flocs formed from filler and chemicals will change in size and shape with time. They will also often have wide size distributions making them hard to study. Quartz particles of well-defined and narrow-size fractions were therefore used to simulate filler flocs of different sizes. These quartz particles were supplied by Particle Technology, UK. Particle fractions were characterized using a light scattering technology, Master Sizer (Malvern Instruments, UK), see Table 1.

In order to achieve similar sheet grammages of quartz particles for the different experimental conditions, the amount of particles added to the RDD was higher at lower fibre grammages as well as when using small quartz particles. Additionally,

**Table 1.** Compilation of particle sizes of the quartz particle fractions measured with Master Sizer. d0.1, d0.5 and d0.9 refer to the particle sizes with which 10, 50 respective 90% of the volume of particles are smaller than, see Figure 1

Median size d0.5 ( $\mu\text{m}$ )	d0.1–d0.9 ( $\mu\text{m}$ )
2.7	0.9–8
10.2	5–17
35.0	22–54
48.9	31–72
103	74–140



**Figure 1.** Particle size distribution (plain and cumulative respectively), measured with Master sizer, of the quartz particle fraction with median size (i.e. d0.5) of 35  $\mu\text{m}$ .

in order to investigate if the amount of particles had an impact on mechanical retention, different amounts were added in separate experiments. The added amount was from 0.1–1.6 g which corresponded to theoretical filler grammages of 10–160  $\text{g}/\text{m}^2$  under the assumption of 100% retention.

A commercial TCF-bleached not refined birch kraft pulp (Trade name: Golden Birch) from Södra Mörrum, Södra Cell, Sweden was used in the experiments. The pulp had a fines content of 4.6% measured with BDDJ, a Schoppler-Riegler (SR) value of 15.8 and a Water Retention Value (WRV) of 1.11  $\text{g H}_2\text{O}/\text{g pulp}$ . Fibre grammages from 2–80  $\text{g}/\text{m}^2$  were prepared in order to study the impact of fibre layer thickness on retention.

## **Rapid Drainage Device**

The Rapid Drainage Device (RDD) is an experimental apparatus originally designed to measure the dewatering of a fibre suspension [39]. The RDD, see Figure 2, is based on the same principle as a conventional laboratory hand sheet former. The major modification is the introduction of a long pipe acting as a suction leg, which creates an elevated dewatering vacuum. This suction leg is divided into sections, which makes it possible to change the length and thereby adjust the dewatering vacuum. A wire is mounted at the bottom of the tank, which has a cross section of about 1 dm<sup>2</sup>.

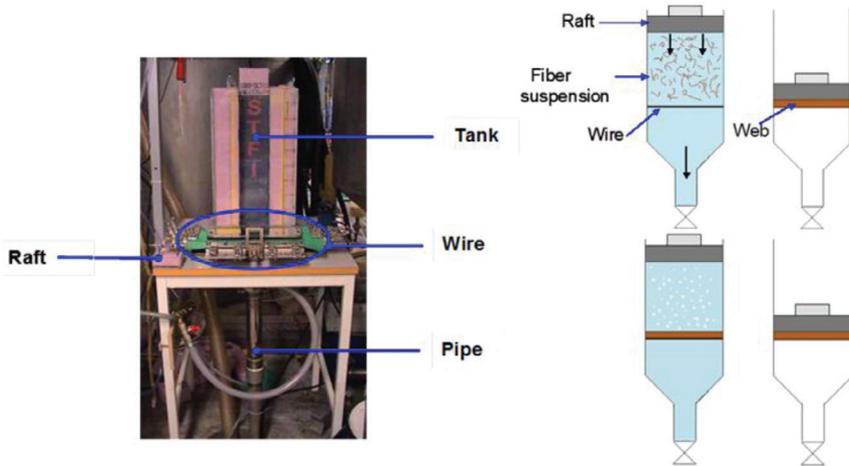
During the main part of the experiments the height of the suction leg was 275 cm corresponding to a dewatering pressure of 27.5 kPa. To study the impact of elevated dewatering speeds, some experiments were performed using a suction leg of 415 cm, which corresponds to a dewatering pressure of 41.5 kPa. The wire used was an Albany Ultra 5000 – PK332, SSB (Albany International), which has an air permeance of 1.8 m/s and a hole size of 450 µm.

## **Experimental procedures**

The experiments were performed by first forming a fibre mat on the wire and there after adding the filler particles. The reason for this approach was two-fold; first it decouples the impact of filtration (which may be regarded as mechanical retention) from other phenomena such as hetero-flocculation between fibre fines and filler, and second it eliminates the uncertainty that the size of the filler particles may influence the formation of the fibre mat. An additional reason is the fact that stratified forming is very likely to find a strong market in the near future. The technique of stratification makes it possible to add different components in different layers in the headbox. For example, if filler were added in the middle layer, it would be retained by a surface fibre mat in the same way as with our experimental set up.

The procedure of the mechanical retention experiments in the RDD is schematically illustrated in Figure 2. The experiments were done by:

- 1) Producing a sheet of pure fibre in the RDD by filling the tank with water (3.2 L) and adding a known amount of fibre. This was followed by dewatering, causing a sheet to be formed on the wire.
- 2) The tank was refilled with water (3.2 L), by adding water just above the fibre sheet while keeping the dewatering pressure on. This caused the fibre sheet to remain intact on the wire. Quartz particles, in a known amount, were then added to the tank, after which gentle stirring was performed. The water containing quartz particles was then drained through the fibre mat. Finally the formed fibre mat containing retained quartz particles was removed and dried at 105°C.



**Figure 2.** Left: The Rapid Drainage Device (RDD). Right: Schematic illustration of the procedure of the mechanical retention experiments in the RDD. At the top, production of a fibre layer by adding fibres to the RDD tank and dewatering. At the bottom, retention experiment by adding quartz particles to the RDD tank and dewatering.

The dry weight ( $m_{tot.}$ ) and ash content of the sheet were determined. The ash content was recalculated to quartz particle content ( $m_{q.p.}$ ). The quartz particle retention ( $R_{q.p.}$ ) was then calculated as:

$$R_{q.p.} = \frac{m_{q.p.}}{m_{q.p.added}}, \quad (2)$$

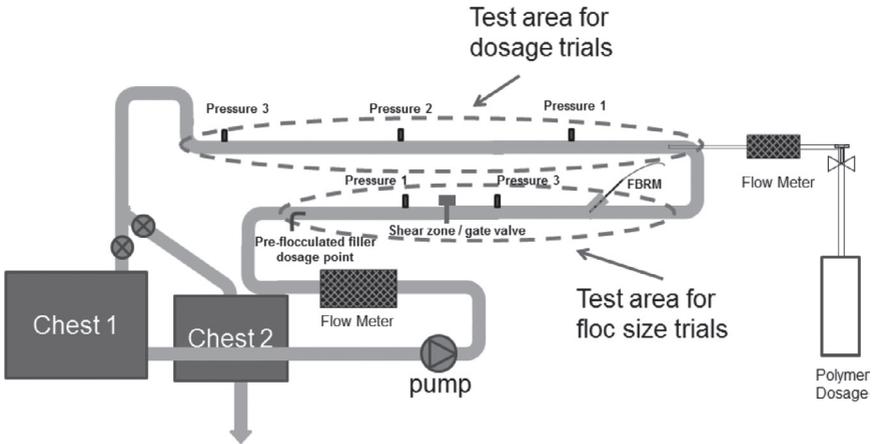
where  $m_{q.p.added}$  was the amount of quartz particle added to the RDD. The fibre grammage  $w_f$  was calculated as:

$$w_f = \frac{m_{tot.} - m_{q.p.}}{A_{RDD}} \quad (3)$$

where  $A_{RDD}$  was the area of the wire in the RDD.

### The Flow-Loop Facility – Effect of shear on pre-flocculated filler and polymer stability

The semi-pilot scale experiments were performed in the re-circulatory pipe flow facility of Innventia AB. A schematic diagram of this facility is shown in Figure 3. The main part of this facility consisted of two long sections of cylindrical Perspex pipe, with length 3.0 m and inner diameter 57mm. The stock flow was fed from an



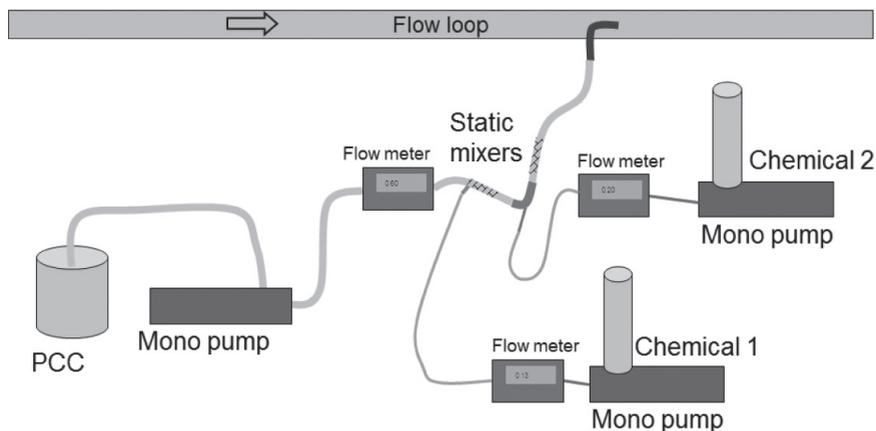
**Figure 3.** Schematic diagram of the flow loop facility.

open reservoir, approximately  $1 \text{ m}^3$  in volume, and pumped by an ITT 4.2 kW variable frequency drive centrifugal pump (Flygt pump 3102– 152 mm impeller). Flow was measured through the device with an ABB magnetic flow meter (Fisher & Porter, model no. 10DS3111). The trials with pre-flocculated filler were performed with the lower horizontal part of the flow loop while the trials with retention polymer stability were performed with the upper horizontal part of the flow loop. All data was logged continuously while the facility was in operation using LABVIEW.

### Dosage system for pre-flocculated filler

To ensure that the contact time between filler and flocculating agent as well as the mixing in the pre-flocculation system was constant during the trials, a dosage system with continuous addition of filler and flocculating agent was developed. The dosage system is shown in Figure 4. Filler was pumped from a barrel and the flocculation agent was added just before a static mixer. One or two flocculation agents could be added separately. The filler flow and the chemical flows could be individually controlled. To avoid excessive flocculation and thereby uneven filler dosage in the flow loop, the hose was filled with static mixers from the dosage point of chemical to the inflow to the flow loop.

To expose the filler flocs to controlled shear forces in the flow loop a gate valve was used. To achieve different levels of shear the opening was adjusted. Shear levels up to 170 kPa were achieved. The pressure drop over the gate valve was measured continuously with a differential pressure transducer (Fuji FKX22,  $6 \pm 1/6 \text{ kPa}$  and



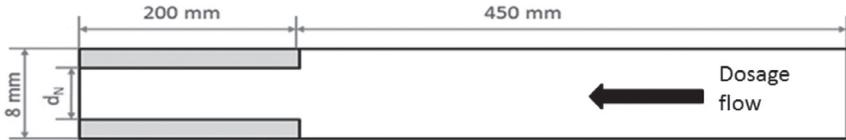
**Figure 4.** Schematic of the pre-flocculated filler dosage system.

FKCX35,  $130 \pm 3/130$  kPa). Since the pressure drop is proportional to energy this value can be used to estimate the shear energy loss.

Filler floc size distribution was measured in the flow loop using the Focused Beam Reflectance Measurement (FBRM) technique (Mettler Toledo). FBRM operates by scanning a highly focused laser beam at fixed speed across particles in a suspension and it gives particle size (chord length) and number of particles (counts per second) in the suspension. A detailed description of FBRM can be found in, e.g. [43].

### Dosage system for retention aids

Retention aids dosage was made concentrically with the main flow by inserting a long brass pipe, 8 mm inner diameter, 10 mm outer diameter, through the centre of the upper 90 degree elbow. The polymer suspension was injected into the main flow with a progressive cavity pump (Rolikon SCF10211R8) which was controlled manually and monitored with an ABB magnetic flow meter, (Fisher & Porter, model no. 10DS2112A). After dosage was made, the mixed suspension of stock and polymer was not allowed to recirculate so that the concentration of polymer in the test section remained constant. Pressure sensors were mounted at three points along the test section (Fuji FKX22,  $6 \pm 1/6$  kPa and FKX35,  $130 \pm 3/130$  kPa), specifically positioned at 0.4 m, 1.1 m and 2.5 m downstream the addition point. Thus the length of pipe corresponding to the measurement section was 2.1 m. Polymer dosage was made through one of three different pipes with inlet nozzle diameter 8 mm and outlet nozzle diameters,  $d_N$ , of either 3 mm,



**Figure 5.** Schematic of the retention aids dosage nozzle.

1.5 mm and 1 mm, each representing increasing levels of elongational strain respectively, see Figure 5.

The maximum flow rate of the polymer dosage pump was approximately 4 l/min. Depending on the bulk flow and nozzle diameter, the velocity ratios, defined as the ratio of velocity in the nozzle to bulk velocity in the main pipe, were different for each pipe diameter as shown in Table 2. The trials were performed with water as the bulk flow.

Polymer degradation was estimated as changes in drag reduction measured downstream the dosage point according to Equation 1. Specifically, a relative decrease in drag reduction was assumed to imply an increased level of polymer degradation. Pressure drop measurements were made to monitor the drag reduction while varying the dosage speed ratio and nozzle diameter. Approximately 10–12 measurements were gathered at each trial point and subsequently averaged. The Reynolds numbers considered in these trials were approximately 37500 to 112500, based on the bulk flow pipe diameter, bulk flow velocity and the density and viscosity of water. In reality, the viscosity corresponding to the flow of water and retention aid can differ considerably from that of pure water alone, therefore these values of Reynolds number indicate only an order of magnitude and not an exact value. However, at these velocities the flow is turbulent, therefore the water based Reynolds number should still give reasonable characterization of the flow conditions in the pipe.

**Table 2.** Available dosage speed ratio range for each of the three dosage nozzle diameters

<i>Nozzle diameter</i>	<i>Bulk Velocity</i>	<i>Dosage Speed Ratio</i>
3.0 mm	1 m/s	1 to 9
	2 m/s	1 to 4
	3 m/s	1 to 3
1.5 mm	1 m/s, 2 m/s, 3 m/s	4 to 12
1.0 mm	1 m/s, 2 m/s, 3 m/s	4 to 12

Polymer degradation was also shown through measurement of the molecular weight distributions using the size exclusion chromatography (SEC) method with a Column TSK-GEL (Tosoh Corporation) and a differential refractometric detector RID-10A (Shimadzu Corporation). The eluent used was 0.3 M NaOAc (sodium acetate) and 0.3 M HAc (acetic acid). The calibration polymer used was polyethylene glycol of a known molecular weight. Samples were collected after dosage through each of the different dosage nozzles at a dosage speed ratio of 4. One additional test was made for the highest strain nozzle at a dosage speed ratio 10.

### **Pilot Production FEX Trials**

Pilot scale paper production trials were performed on the FEX pilot paper machine at Innventia AB, at a machine speed of 600 m/min.

### **Paper machine set-up**

#### **Headbox**

The 330 mm wide STFI-Valmet headbox was used. From the CD-distribution channel, a 7-row pipe package, with 11 pipes in each row, feeds the headbox nozzle. Pipe inlet diameters are 13 mm after 60 mm extending with a step to 24 mm diameter and finally contracting to a 12 mm high and 27 mm wide rectangular outlet area. The headbox nozzle entrance height is 130 mm with a plain nozzle outlet, without a parrot's beak.

#### **Dewatering**

Twin-wire roll dewatering was employed with a roll diameter 1635 mm.

#### **Pressing**

Wet pressing was made in three nips:

1. Roll nip, double felted, press load 60 kN/m
2. Shoe nip, press load 400 kN/m. Single felted with felt on bottom side.
3. Shoe nip, press load 700 kN/m. Single felted with felt on top side.

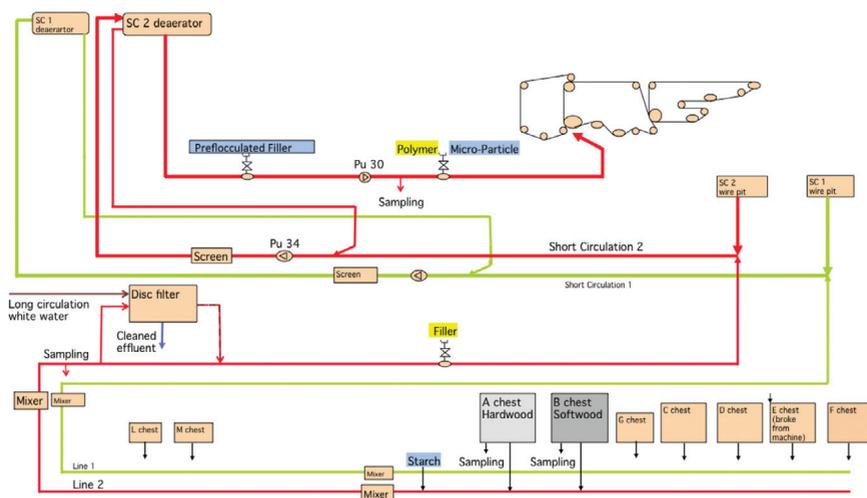
#### **Drying**

Off-line drying was performed in two versions:

- 1-Cylinder FEX Dryer for fully restricted web shrinking in MD and CD.
- 10-Cylinder FEX Dryer for sample roll drying.

## White water system

The principle of the system is shown in Figure 6, with addition positions marked.



**Figure 6.** Schematic of the FEX-System (press section not shown). Blue markings (darker tint) at additions for Filler Flocculation Trial and yellow (lighter tint) markings at additions for Polymer Degradation Trial.

## Trial parameters

**Table 3.** Materials and process data for the pilot-scale FEX trials

<i>Parameter</i>	<i>Filler-Preflocculation/ Mechanical Retention Trial</i>	<i>Polymer degradation/ Chemical retention Trial</i>
Basis Weight, g/m <sup>2</sup>	80	60
Fibre raw material	50/50 Hardwood/Softwood Dried Sulphite	80/20 Hardwood/Softwood Dried Sulphate
Refining levels, deg SR	19/23	26/29
Filler, %	PCC, 26 – 33	GCC, 20
Retention System	Starch + Micro-Particle (EKA)	Polymer, Nalco 74508
Addition levels	Starch: 8 kg/ton	Polymer: 900 g/ton

Jet thickness, mm	11	12.5
Jet Speed, m/min	622	635
Wire Tension + Nominal Dewatering Pressure	5 kN/m; 6.25 kPa	8 kN/m; 10 kPa
Nominal Mix – Wire Speed Difference, m/min	– 15	– 25

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### **Retention evaluation**

Filler retention (total) was evaluated as the ratio between the amount of filler in the product and the amount of filler delivered from the headbox, i.e.

$$\text{Filler retention [\%]} = \frac{\text{Web speed [m / min]} \times \text{Web width [m]} \times \text{Basis weight [g / m}^2\text{]} \times \text{Filler content [\%]}}{\text{Headbox flowrate [l / min]} \times \text{Filler concentration [g / l]}} \quad (4)$$

This method ensures a more precise evaluation of filler retention, compared with the conventional method of evaluating “first pass retention”, which is based on sampling in the short circulation. The problem with this is that due to local filler sedimentation effects, it is not always possible to collect a relevant white water filler content sample. Instead, sampling after the head-box pump will give reliable filler content values. Further, “total retention” also includes the retention in the last part of the wire section as well as in the press section, which is not the case for “first pass retention”.

### **Filler-Preflocculation/Mechanical Retention**

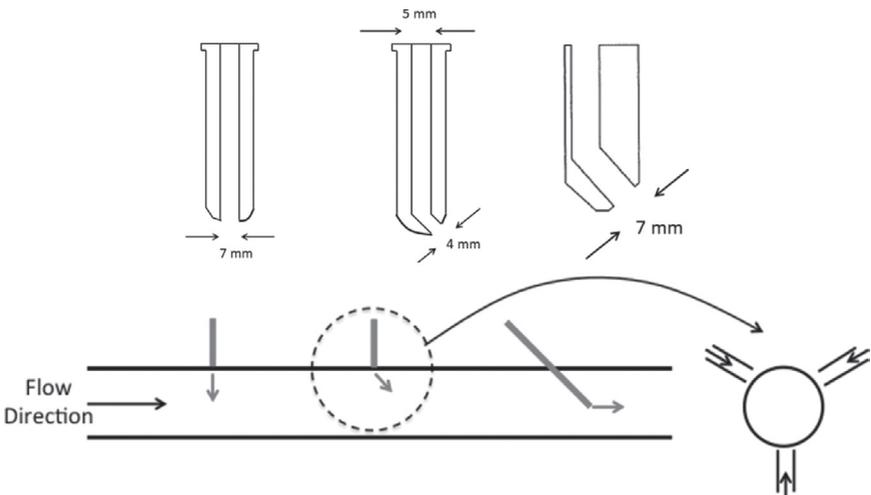
The first set of trials was performed to investigate the effect of precipitated calcium carbonate (PCC) filler floc size on retention level, see Figure 6 and Table 3. The retention system included initial addition of starch, and final micro-particle addition after the headbox pump. Three different concepts for filler pre-flocculation, giving different sizes of filler flocs, were tested. The flocculated filler was added after the deaerator in the short circulation. Mean particle size was measured in the flow downstream the headbox pump using FBRM.

### **Polymer degradation/Chemical retention**

A second set of trials was performed to investigate the effect of different types of shear imposed on retention aid polymers during dosage, see Figure 6 and Table 3. Ground calcium carbonate (GCC) was used as filler. The filler was in this case added after the introduction of recovered fine material from the disc filter.

Cationic-polyacrylamide (CPAM, NALCO 74508) was used as retention aid polymer. The dosage speed ratio  $v_r$ , i.e. the ratio of retention aids velocity to the mean stock velocity in the approach flow pipe, was used as an operational variable in all trial cases. Retention aids dosage was made after the headbox pump, to avoid any possible effects of this equipment on retention polymer degradation. The approach flow pipe diameter was 150 mm at this location and the mean stock velocity was approximately 2.5 m/s (2600 l/min). The estimated retention aid dwell time was 5.5 sec prior to wire dewatering.

Three different dosage nozzle designs were investigated, each of which created different forms of shear on the polymers during dosage, see Figure 7. The three dosage strategies considered are named and described as follows, (a) single side-wall dosage, i.e. a single dosage nozzle mounted into the approach flow pipe with dosage made perpendicular to the stock flow. This nozzle created a quasi-stagnation point with the approach flow at the point of dosage. (b) triple side-wall dosage (FEX standard), i.e. three dosage nozzles mounted symmetrically around the approach flow pipe with dosage made at a 45° angle into the stock flow. These nozzles created the lowest degree of shear on the polymer system. (c) centreline dosage, i.e. a single dosage pipe installed inside the approach flow pipe such that dosage was made concentrically with the stock flow. A sudden contraction was built into the inside of this nozzle thereby creating large elongational shear-strain



**Figure 7.** Schematic diagrams of the three dosage nozzle set-ups mounted into the approach flow pipe during the FEX trials. Shown here are Left: Single side-wall dosage nozzle, Centre: Triple side-wall dosage nozzle and Right: Centerline dosage nozzle.

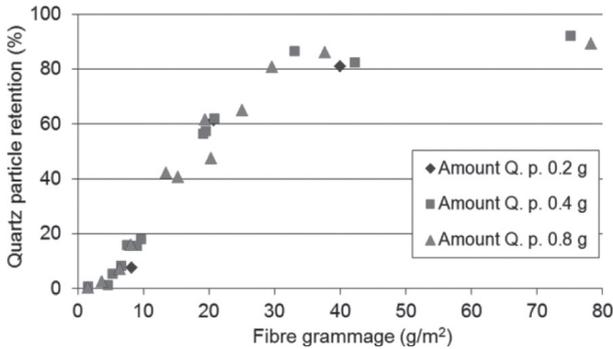
levels during dosage. The nozzle outflow diameters were 4 mm for the triple side-wall dosage nozzles and 7 mm for the single side-wall and centreline dosage nozzles. These diameters resulted in approximately equal total dosage area, i.e. equal retention aids mass flux for a given dosage velocity. During the trials, only one of the three dosage systems was mounted at any one time. The other two were completely removed from the approach flow pipe. Five different relative dosage speed ratios,  $v_r$ , were considered for each dosage configuration. To re-iterate, the dosage speed ratio is defined as the ratio of the absolute, mean speed in the dosage nozzle divided by the mean speed in the approach flow pipe, where mean speed refers to the volume flow rate divided by the pipe area. However, it should be pointed out that the actual local ratio of dosage speed to approach flow speed will vary for the different dosage strategies due to differences in impingement angle, e.g. 90° in the single side-wall, 45° in the triple side-wall, and concentric in the centreline dosage. The dosage speed ratio was varied by increasing the dilution flow so that equal retention aids levels were maintained throughout the trials. With the single side-wall and triple side wall dosage, the dosage velocity ratios considered were  $v_r = 0.6, 1.1, 2.7, 6.2$  and 8.9. With the centreline dosage, dosage speed ratios included  $v_r = 0.6, 1.1, 2.7,$  and 6.2. The reasons for the difference were due to the fact that the time to reach machine equilibrium became increasingly too large with the centreline dosage strategy as  $v_r$  was increased. Similarly, filler retention was becoming too low, as indicated by a very high headbox concentration measured during these trials. Thus the largest setting of for  $v_r$ , i.e. 8.9, was not completed.

## **RESULTS**

### **Mechanical retention in the Rapid Drainage Device**

The results presented in all the figures are from experiments using a dewatering pressure of 27.5 kPa. An increase in dewatering pressure to 41.5 kPa did not produce any obvious effect on retention. Five fractions of quartz particles were evaluated. Each fraction had a fairly steep particle size distribution, the median sizes are given in Table 1. The size of the filler used in production of fine paper and publication paper is generally around 2  $\mu\text{m}$ , for example specified as 40 or 60 volume-% of the particles are smaller than 2  $\mu\text{m}$ . However, the fillers are, as discussed above, normally flocculated by the retention aids.

Typical retention results for the particles with median size of 35.0  $\mu\text{m}$  at a dewatering pressure of 27.5 kPa are shown Figure 8. The retention is plotted as a function of the grammage of the fibre mat for three different amounts of quartz particles added to the RDD. Each point in the graph represents a single experiment in the RDD. The results suggest that retention is independent of the amount (i.e.

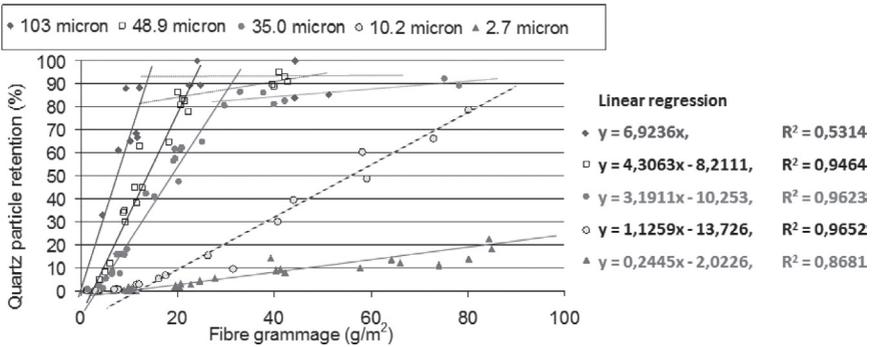


**Figure 8.** Quartz particle retention as a function of grammage of the fibre mat for the quartz particle fraction with a median size of 35.0  $\mu\text{m}$ . Amount Q. p. refers to the added amount of quartz particles in the RDD.

concentration) of particles but linearly dependent on the fibre mat thickness up to a retention of roughly 90%, which is denoted the “limit retention”. Moreover, the results show that a certain fibre mat grammage is required in order to retain particles in the mat. An increase in fibre grammage can lead to fewer and smaller pores in the fibre network and thus an increase in the mechanical retention of the particles.

The quartz particle fractions did contain particles considerably smaller than the median particle size, see Table 1 and Figure 1. For example in the quartz particle fraction with median size 35  $\mu\text{m}$  (d0.5), 10 volume-% of the particles were smaller than 22  $\mu\text{m}$  (d0.1). These identified amounts of quartz particles considerably smaller than median particle size, are suggested as the major reason for the “limit retention”. Additionally, the fibre network probably contains pores that are considerably larger than the average pore size of the sheet. These larger pores would result in a decrease in mechanical retention and would also contribute to the difficulty of reaching 100% retention.

The mechanical retention for all tested quartz particle fractions as a function of the grammage of fibre mat is plotted in Figure 9. It can be seen that the mechanical retention increased linearly with fibre grammage for each quartz fraction and that the mechanical retention increased with particle size. For the quartz fractions with specified median sizes of 35  $\mu\text{m}$  and larger, the limit retention can be clearly identified and ranges from 80% to 90%. As previously discussed, this limit retention is most probably due to the fact that a significant fraction of particles were smaller than median particle size. For all quartz particle fractions, except for the fraction of largest particles, a certain fibre mat grammage was required in order to retain particles, and this is referred to as the “critical fibre grammage”. The critical fibre grammage can be estimated from each curve’s interception with the x-axis and



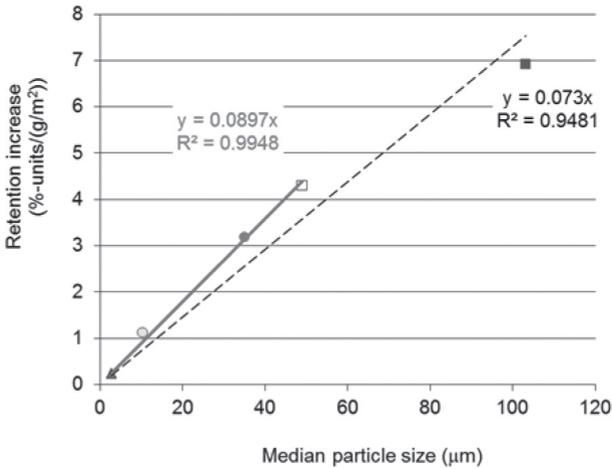
**Figure 9.** Retention for quartz particle fractions with different median sizes as a function of grammage of the fibre mat. Linear regressions are given for each quartz particle fraction, using the linear part between “critical fibre grammage” and “limit retention” of each set of measurements.

tends to be highest for the smallest particles. It was around 10 g/m<sup>2</sup> for the two particle fractions smallest size, around 2 g/m<sup>2</sup> for the mid-sized fractions (median size 35.0 and 48.9 μm) and tended to have reached zero for the fraction of largest particle size. The pore size of the wire in the RDD was 450 μm, and the particles should not have been captured directly of the wire, not even for the fraction of largest particle size.

The slopes of the linear part of the retention curves, i.e. between critical fibre grammage and limit retention, were determined by linear regressions. The regression coefficients (R<sup>2</sup>) were between 0.86 and 0.97 for all fractions except the fraction with the largest particles, which had R<sup>2</sup>=0.53. The increase in retention related to fibre grammage, i.e. the slopes of the retention curves for each quartz particle fraction, was found to be linearly dependent on the median particle size, see Figure 10 with a slight deviation for the fraction with the largest particles. The Mechanical Filler Retention (MFR) seems to be linearly dependent on grammage of the fibre layer ( $w_f$ ) above the critical fibre grammage ( $w_{f,c}$ ) and the slopes of these lines (i.e. retention increase) are linearly dependent on the size of the quartz particle (D) (Figure 10). This implies that MFR will be linearly dependent on the product of ( $w_f - w_{f,c}$ ) and D, and can be described by the following expression:

$$MFR = Const \cdot (w_f - w_{f,c})D \quad (5)$$

The constant (Const.) will most probably be affected by the fibre properties, fines content and machine technical parameters such as type of wire but also the dewatering and the formation. Equation 5 is an empiric relation based on a large number



**Figure 10.** The increase in retention related to fibre grammage (i.e. the slopes of the curves in Figure 9) as a function of median particle size. The linear regression (solid line) is valid for all particle fractions. The linear regression (dashed line) is obtained by omitting the largest particle size (103 µm). For an explanation of the symbols, see Figure 9.

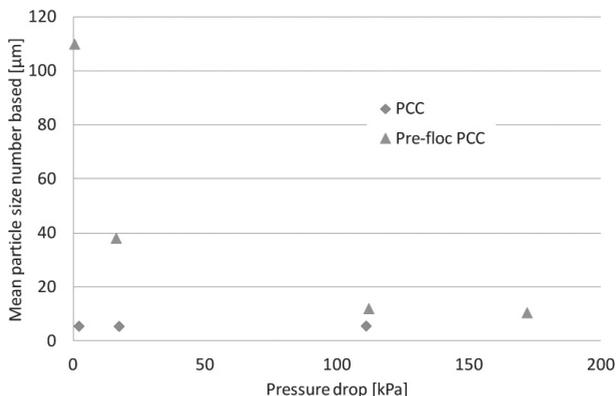
of experimental data. It is interesting to conclude that this expression is consistent with the theory suggested by [24] despite the fact that that theory was developed for a system where fibre and filler coexisted in the suspension before the sheet was formed and the filler particles were entrapped in the sheet. In the present study, the fibre sheet was formed before filler was added, and the formation of the fibre sheet was thus independent on the size and content of the filler particles.

### Semi-pilot scale flow loop trials

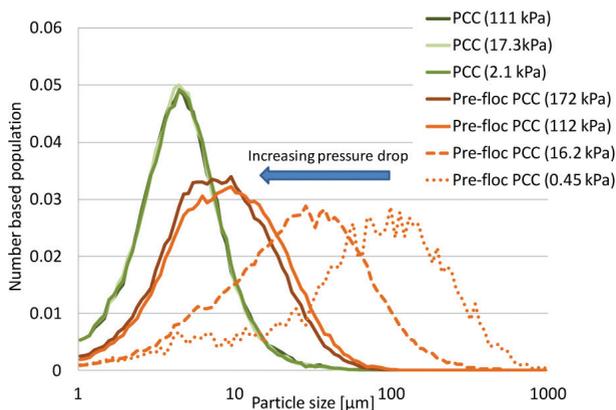
#### *Effect of high shear on pre-flocculated filler stability*

Results from trials where a gate valve was used to generate and apply different shear levels to pre-flocculated filler are shown in Figures 11 and 12. The filler was pre-flocculated with flocculating agents in a continuous dosage system. Trial points without adding chemicals to the PCC, i.e. no pre-flocculation were also run, denoted “PCC”. The floc size was measured with FBRM.

As expected, the mean particle size of the un-flocculated PCC was not affected by the pressure drop over the gate valve. The pre-flocculated filler had a large mean particle size when the gate valve was open (generating low pressure drop) and increases in the pressure drop led to a decrease in the mean particle size. At pressure



**Figure 11.** Particle size at different pressure drops measured in the flow loop. The main stream consisted of water. Un-flocculated and pre-flocculated PCC, respectively, were fed into the main stream. Particle size was measured with FBRM.



**Figure 12.** Particle size distributions of un-flocculated and pre-flocculated PCC at different pressure drops measured in flow loop, i.e. the same trial points as in Figure 11.

drops higher than 100 kPa the mean particle size for pre-flocculated filler was nearly the same as for un-flocculated filler. The FBRM measurements have a great advantage, giving not only the mean values but also particle size distributions. The particle size distributions for the trial points in Figure 11 are shown in Figure 12.

In the trial with un-flocculated PCC, the particle size distributions remained constant as the pressure drop was increased. For the pre-flocculated PCC there was a clear change in the particle size distribution when the pressure drop increased,

showing that the largest particles were ruptured. A major part of the floc degradation occurred at relatively low pressure drops, seen as the large difference in particle size distribution when pressure drop increased from 0.45 to 16.2 kPa and then further to 112 kPa. Increasing the pressure drop from 112 to 172 kPa only gave a minor change in particle size distribution and even at the highest pressure drop a considerable part of the filler was still flocculated. These effects are more apparent in the particle size distribution curves than from the mean values. The fact that the flocs were relatively large at the lowest pressure drop and decreased with increasing pressure drop down to a certain size, where further increased pressure drop gave very small decrease in particle size, suggests that the main mechanism for floc stability is floc strength and that the flocs that exist after the highest pressure drop may be considered as primary flocs.

### *Effect of high shear on retention polymer degradation*

In this section we identify conditions for polymer degradation experimentally using a pilot scale flow loop. We investigate two primary sources of shear-strain during dosage, namely the effect of elongational strain created inside the dosage nozzle and the effect of shear-strain created by velocity differences between flows inside and outside the dosage nozzle. In these experiments, elongational strain was created inside the dosage nozzle by a sudden contraction from an initial nozzle diameter of 8 mm to smaller nozzle outlet diameters of 3 mm, 1.5 mm or 1 mm, or equivalent sudden contraction ratios, i.e. the ratio of initial to exit nozzle diameter,  $R = 2.7, 5.3, \text{ and } 8$  respectively. With the sudden contraction, a smaller nozzle outlet diameter corresponds to a larger level of elongational strain. Shear-strain outside the dosage nozzle was created by increasing the dosage speed ratio.

In order to show rigorously that polymers are degrading under the high shear conditions imposed by the dosage nozzle, samples of the injected polymer were collected after dosage through each of the nozzles and the molecular weight distribution was measured using size exclusion chromatography (SEC) and differential refractometric detector. Shown in Table 4 are the mean values for molecular weights collected from each of the dosage nozzle contraction ratios at a dosage velocity ratio of 4. The number average molecular weight,  $M_n$ , shows a clear decrease as the contraction ratio, i.e. acceleration in each nozzle, increases. Moreover, the polydispersity, i.e. the heterogeneity in molecular sizes is shown to increase. These results re-iterate those already shown in the literature, namely that high molar mass retention polymers undergo chain cleavage after exposure to high shear, e.g. [37].

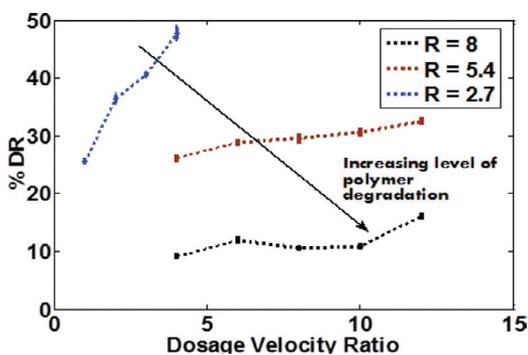
Polymer degradation was then correlated to measurements of drag reduction, where a relative decrease in drag reduction corresponds to an increased degree of polymer degradation. The effect of nozzle diameter on DR as a function of dosage

**Table 4.** Average molecular weight measurements for CPAM polymers measured with SEC after dosage through the different nozzles with different contraction ratios. The corresponding dosage speed ratio is 4 except for the final row where the dosage speed ratio is 10.

Nozzle Contraction Ratio	Weight average molecular weight, $M_w$	Number average molecular weight, $M_n$	Polydispersity ( $M_w/M_n$ )
2.7	$1,495 \times 10^7$	$1,494 \times 10^6$	10,01
5.4	$1,338 \times 10^7$	$1,097 \times 10^6$	12,2
8	$1,209 \times 10^7$	$0,806 \times 10^6$	15
8 (speed ratio 10)	$1,200 \times 10^7$	$0,570 \times 10^6$	21,2

speed ratio for dosage into pure water is shown below, see Figure 13. The error bars in this figure indicate the 95% confidence interval.

Figure 13 shows several interesting trends. The first observation is that DR increased in all dosage nozzles with increase in the dosage speed ratio. However, this effect is far less significant in the smallest dosage nozzle. This would suggest that the increase in shear-strain created at the interface between the inner and outer flows due to increase in the dosage speed ratio is relatively small and has only a minor effect on polymer degradation. In the largest nozzle, a maximum DR of 47.76 % was reached. The cause for the increase in DR with increase in dosage speed ratio is most likely due to the higher turbulence generated by the large velocity difference which subsequently creates better mixing conditions, e.g. [42]. It should be mentioned that the increase in polymer concentration is expected to play only a minor role in increasing the DR, given that in all cases we are



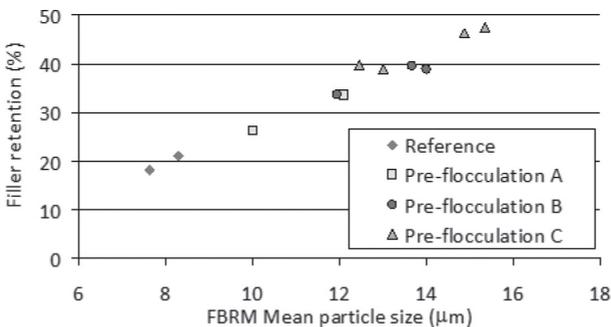
**Figure 13.** Comparison of drag reduction as a function of dosage speed ratio for the three different dosage nozzle contraction ratios, R. Dosage is made into pure water with a bulk flow speed of 2 m/s.

already at or above the concentration corresponding to maximum drag reduction [34]. The second key observation in Figure 13 is the severe reduction in DR as the dosage nozzle outlet diameter decreases. To reiterate, by decreasing the dosage nozzle outlet diameter we are effectively increasing the elongation strain inside the nozzle. These results indicate the significant impact of elongation strain inside the nozzle on retention polymer degradation.

## Pilot scale production trials

### Mechanical Retention

Pilot-scale production trials on the FEX paper machine confirmed the results observed with the RDD. Specifically, a linear relation between filler retention and median particle size during the production of fine paper using pre-flocculated filler, see Figure 14. Three different concepts for pre-flocculation were used. Mean particle size were measured in the flow to the headbox using FBRM. This was a homogeneous headbox, i.e. no stratification was used in this FEX trial, and hence the size measurements were made on a suspension containing fibre and filler. The relationship defined by Equation (5) could be simplified to  $MFR = Const^b \cdot D$ . The filler content of the sheets produced varied between different trial points from 26 to 33%. These differences did not affect the retention which is in agreement with the results from the RDD-experiments where different amounts of particles gave the same level of retention. The linear relation between filler retention and mean particle size suggests the importance of mechanical retention on the paper machine. Moreover, if filler pre-flocculation strategies are employed, this result further



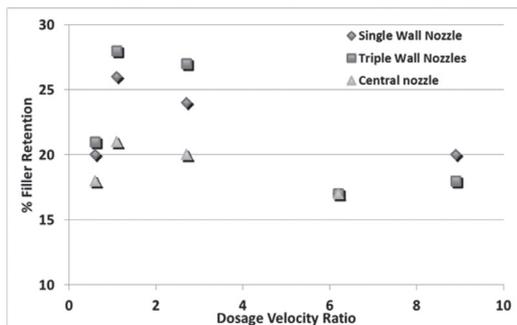
**Figure 14.** Filler retention versus mean particle size measured with FBRM (number weighted value) in the flow to the headbox during a FEX-trial producing fine paper using pre-flocculation of filler. Three different concepts for pre-flocculation were tested and are denoted A, B and C.

stresses the importance of preserving filler-floc size, in particular by minimizing exposure to points of large hydrodynamic shear in the paper machine.

### Chemical Retention

The effect of shear created within the retention aids dosage nozzles on chemical filler retention is investigated with pilot scale production trials. Figure 15 shows plots of the percent filler retention as a function of dosage speed ratio for each dosage strategy. A clear maximum in filler retention was observed at a dosage speed ratio of 1.1 for all three dosage strategies. This result is due to a minimum in shear-strain created by differences between the inner and outer flows outside the dosage nozzles at this dosage speed ratio. More specifically, when the dosage speed ratio deviates from unity, the shear layers between the inner and outer flows become increasingly larger and the highly shear sensitive retention aid polymers are more likely to degrade and perform poorly. However, when the dosage velocity ratio is near unity, i.e. when the inner and outer flows are of equal velocity, the local shear is reduced and the retention aid polymers are less likely to undergo shear degradation. In this situation filler retention is clearly improved.

The different types of shear created within each nozzle were also shown to influence retention significantly. In particular, the triple side-wall dosage gave the highest filler retention level while the centreline dosage nozzle gave the lowest. The improved performance of the triple side-wall dosage configuration is due to two factors, namely better mixing of the retention aids due to the fact that there are three times as many addition points, but also largely due to the low shear levels created within this nozzle. In particular, the nozzle is free from internal sudden contractions and therefore creates minimal elongational strain within the



**Figure 15.** Percent filler retention vs. dosage velocity ratio for the single side-wall, triple side-wall and centreline dosage strategies.

nozzle, but also the 45° impingement angle eliminates stagnation point type strain, as discussed in the earlier sections. On the other hand, the centreline dosage gave the poorest filler retention over all speed ratios. This is believed to be largely a consequence of the sudden contraction within this nozzle. In this region, high levels of elongational strain are generated which increase the probability for polymer degradation. Thus, retention polymers are most likely degrading prior to exposure to the stock and retention is therefore low. The single side wall nozzle gave intermediate retention. With this nozzle, large shear-strain is introduced at the point of impingement with the flow which creates a quasi-stagnation point. This has also been shown at lab scale to result in polymer degradation [32].

It is interesting to compare results from the experiments performed on the pilot scale flow loop, where the dosage speed ratio did not have a significant effect on polymer degradation, with the production trials, where dosage speed ratio did have a significant impact on filler retention. The differences here are believed to originate from two different sources. One difference might be explained by noting the large effect of dosage speed ratio on filler retention with the non-concentric nozzles, i.e. the side and triple nozzles, compared to the relatively smaller dependence observed with the centreline dosage. With the side-wall dosage nozzles non-linear shear is created at the point of impingement with the main flow and this could create large, speed ratio dependent shear levels. A second effect may be understood by considering the chemical interaction between the cationic retention aid and the anionic substances within the stock, e.g. the fibre. As discussed in the literature, cationic polymers can attach to fibres and degrade during transfer to other fibres and/or filler. The increase in speed ratio may enhance this effect thus increasing the chance for polymer degradation and therefore reducing the total filler retention levels. Nonetheless, these trials show the strong adverse effect of applying excessive shear on the retention system at particular points in the process on chemical retention of filler during production.

## **DISCUSSION**

The retention of filler in products is an essential need for efficient and low cost production of paper products. The production process is however complex, difficult to control, and can vary significantly from one mill to the next – even for identical paper grades. We have attempted here to demonstrate the adverse impact of high shear conditions located in the ‘wrong places’ in relation to filler retention in products. High shear, which can come in the form of process equipment, e.g. valves, pumps, screens, or by poor design of process equipment, e.g. dosage nozzles, has been shown to inhibit chemical retention through mechanical degradation of the retention polymers, as well as mechanical retention, through

destruction of optimal filler floc size. In particular, the findings presented here demonstrate the importance of maintaining pre-flocculated filler size during processing. Mechanical filler retention is shown to be effective, particularly given the ease for which chemical filler retention can fail due to polymer degradation. However, filler floc size must be preserved, which is possible through control of shear conditions in process flows. Similarly, chemical retention is shown to be effective only when retention polymer integrity is maintained. This too is possible through better control of strain induced shear. In particular, it was shown that retention aid polymers can be destroyed as early as the within the dosage nozzle, thus resulting in degradation of the additive before it even has the chance to make contact with the stock. Together, these three studies demonstrate the importance of controlling process flow conditions, namely minimizing sources for shear and when handling flocculants and pre-flocculated filler. Moreover, failure to do so is shown to have adverse effects on retention, and therefore overall process efficiency. Thus a process oriented approach is always essential for high quality production.

## **CONCLUSION**

This work has investigated factors affecting filler retention in paper products using a process oriented approach. Conditions for optimal mechanical retention have been identified using a laboratory device, the rapid drainage device (RDD). Using a semi-pilot scale flow loop, process conditions have been identified which impair chemical and mechanical retention, namely high shear sources located at particular points in the process flow. Pilot-scale production trials were then used to support the laboratory and semi-pilot scale findings.

In the first part of this work, the effect of mean particle size on mechanical retention within a fibre network was investigated using the RDD. The experimental results showed that mechanical filler retention (MFR) increases linearly with particle size and grammage of the fibre layer above the critical grammage for particles of sizes up to at least 50  $\mu\text{m}$  in this experiment. The relation was also found to be valid in a pilot scale (FEX) trial, where fine paper was produced using a technique for pre-flocculation of filler.

In the second part of this work, filler pre-flocculation stability was studied through flow loop trials. The filler was pre-flocculated in a continuous dosage system and exposed to different controlled levels of shear created by a partially closed gate valve and the size distribution of the filler flocs monitored continuously using FBRM. The filler floc size was observed to decrease significantly with increased shear forces. The flocs remained relatively large at the lowest pressure drop and decreased with increasing pressure drop down to a certain size, where further increased pressure drop gave very small decreases in particle size.

This suggests that the main mechanism for floc stability is floc strength and that the flocs exist after the highest pressure drop may be considered as primary flocs.

In the third part of this work, we investigate the effect of shear-strain during retention aids dosage on chemical retention. The effect was studied first through a set of dosage trials on a flow loop where the effect of shear created by differences in the relative dosage velocity as well as elongational strain created inside the dosage nozzle on polymer degradation was studied. It was shown that the shear-strain created by relative dosage velocity had a small effect on polymer degradation. However, large levels of polymer degradation were observed when the elongational strain in the dosage nozzle was increased. A set of pilot scale production trials were performed where different (single component) retention aids dosage nozzles were implemented and filler retention was measured in the final product. Three different retention aids dosage strategies were studied, each imposing a different type of shear-strain on the polymers and the relative dosage velocity was varied. Maximum filler retention was observed when the dosage velocity was approximately equal the stock velocity, i.e. when the shear outside the nozzle was minimized. It was also shown that the nozzle creating the lowest level of shear strain internally resulted in the highest filler retention, while the nozzle creating large internal shear-strain resulted in the lowest filler retention.

These findings demonstrate the importance of maintaining pre-flocculated filler size during processing. MFR is shown to be effective, particularly given the ease for which chemical filler retention can fail due to polymer degradation. However, filler floc size must be preserved, which is possible through control of shear conditions in process flows. Moreover, chemical retention is shown to be effective only when retention polymer integrity is maintained. This too is possible through better control of strain induced shear. Together, these three studies demonstrate the importance of controlling process flow conditions, namely by reducing shear and elongational strain when handling flocculants. Moreover, failure to do so is shown to have adverse effects on retention, and therefore overall process efficiency. Thus a process oriented approach is a must for high quality production.

## **ACKNOWLEDGEMENTS**

This work was performed within the Future Papyrus and the Web Structure & Runnability Innventia research clusters. EKA Chemicals, Stora Enso and the Swedish Energy Agency are sincerely thanked for financing the Future Papyrus cluster. Andritz, Holmen, Klabin, Stora Enso and the Swedish Energy Agency are sincerely thanked for financing the Web Structure and Runnability research cluster.

## REFERENCES

1. Wåberg 2000 Polyelectrolyte adsorption onto cellulose fibres – a review, *NPPRJ* 15(5) 586–597.
2. Dickenson and Eriksson 1991 Particle flocculation by adsorbing polymers, *Adv. Colloid interface sc.*, 34, 1–29.
3. Bown, R. (1997). A review of the influence of pigments in papermaking and coating. *Trans. of the 11th Fundamental Research Symposium “The Fundamentals of Paper-making”*, Cambridge, Sept 1997, 83–137.
4. Beazley, K. M. (1985). Fillers-a brief technological review. *Paper Technology and Industry* (October): 267–268.
5. Beazley, K., (Ed.) (1993). *Papermaking Fillers: An update*. Pira Reviews of Pulp and Paper Technology, Pira International, Leatherhead, UK.
6. Eklund, D. and Lindström, T. (1991). *Paper Chemistry-An introduction*, Chapter IX. DT Paper Science Publications, Grankulla, Finland.
7. Riddell, M.C., Jenkins, B., Rivers, A., Waring, I. (1976). Three developments at Wolvercote paper mill. *Paper Technology and Industry*, April 1976.
8. Mather, R.D. and Jones, J.P.E. (1982). Production of paper at high filler levels. 1982 Tappi Papermakers conference, 5–8 April, 1982, Atlanta, USA, Tappi Press, USA..
9. Brooks, K. and Meagher, J. (1982). The increasing role of calcium carbonate in the paper industry. *Paper* 4, October, 1982.
10. Gavelin, G. (1985). Coflocculation of fines and filler particles. *Paperi ja Puu* 67(11), 649–653.
11. Mabee, S. and Harvey, R. (2000). Filler flocculation technology – Increasing sheet filler content without loss in strength or runnability parameters. 2000 Tappi Papermakers Conference and Trade Fair, Vancouver, Canada, Vol. 2, 797–809, Tappi Press, USA.
12. Holm, M. and Manner, H. (2001). Increasing filler content of fine paper by using preflocculation. *Mednarodni Letni Simpozij International Symposium*, Bled, Slovenia, 14–16 November 2001, 167–170.
13. Holm, M. and Manner, H. (2003). Stability of preflocculated calcium carbonate filler flocs. 57th Appita Annual Conference, Melbourne, Australia, 5–7 May 2003, 337–342, Appita, Australia.
14. Zhao, Y., Kim, D., White, D., Deng, Y., Patterson, T., Jones, P., Turner, E., Ragauskas, A.J. (2008). Developing a new paradigm for linerboard fillers. *Tappi Journal* 7(3), 3–7.
15. Mabee, S. (2001). Controlled filler preflocculation – Improved formation, strength and machine performance. 2001 Papermakers conference, Cincinnati, USA, 11–14 March 2001, Tappi Press, USA.
16. Tomney, T, Pruszynski, P.E., Armstong, J.R., Hurley, R. (1997). Controlling filler retention in mechanical grades. 83rd Annual Meeting Technical Section – Paper, People, Progress, Montreal, Canada, 28–31 January 1997, Preprints B, B367–B372, Canadian Pulp and Paper Association, Canada.

17. Blanco, M.A., Tijero, J., Hooimeijer, A. (1995). Study of flocculation process in papermaking. 1995 Papermakers Conference, Chicago, USA, 23–26 April 1995, 455–463, Tappi Press, USA.
18. Fuente, E., Blanco, A., Negro, C., San Pio, I., Tijero, J. (2003). Monitoring flocculation of fillers in papermaking. *Paper Technology* 44(8), 41–46, 48–50.
19. Goto, S and Pelton, R. (2000a). The link between strength and shear sensitivity for filler flocs formed with retention aid. *Tappi Journal* 83(4), 82.
20. Goto, S and Pelton, R. (2000b). The link between strength and shear sensitivity for filler flocs formed with retention aid. 2000 TAPPI Papermakers Conference and Trade Fair, Vancouver, Canada, 16–19 April 2000, Book 2, 523–538, Tappi Press, USA
21. Krogerus, B. (1993). Dynamic flocculation studies on fibre fines and filler clay. *Nordic Pulp and Paper Research Journal*, 8(1), 135–140.
22. Lindström, T. (1989): Some fundamental chemical aspects on paper forming. In: *Fundamentals of Papermaking*. John Wiley & Sons, London, UK, 311.
23. Helle, T. (1982): On the evaluation of the forming characteristics of papermaking wires. *International Water Removal Symposium*, 67, 93–97.
24. Dodson, C.T.J., Sampson, W.W. (1997): A model for the retention of particles in evolving fibre networks. In: *Fundamentals of papermaking materials – Proc. 11th Fundamental Research Symposium*, Cambridge, UK, Sept. 1997, vol. 2, 1161–1174.
25. Hubbe, M., Nanko, H., McNeal, M., (2009): Retention aid polymeric interactions with cellulosic surfaces and suspensions: A review, *BioResources*, 4, p. 850–906.
26. Tanaka, H., Swerin, A., Ödberg, L. (1993) Transfer of cationic retention aid from fibers to fine particles and cleavage of polymer chains under wet-end papermaking conditions, *Tappi Journal*, 76(5), 157–163.
27. Tripaththaranan, T. Hubbe, M, Heitmann, J., & Venditti, R. (2004): Effect of idealized flow conditions on retention aid performance: Parts 1 and 2. *Appita Journal*, 57(5,6), pp. 404–410, 448–454.
28. Hubbe, M., Wang, F., 2002, Where to add retention aids: Issues of time and shear, *TAPPI Journal*, 1, 29–33.
29. Wedding, M., Helmer, R., Raverty, W., Irvine, G., 2008, Laboratory simulation of chemical addition, mixing shear, and paper properties of unbleached kraft pine needles, *Appita*, 61, 133–140.
30. Ödberg, L., Tanaka, H., Swerin (1993) Kinetic aspects of the adsorption of polymers on cellulosic fibres, *NPPRJ*, Issue 1, 1993, 6–9, 47–50.
31. Dunham, Tubergen, Govoni, Alfano 2000 The effect of dissolved and colloidal substances on flocculation of mechanical pulps, *JPPS*, 26(3), 95–101.
32. Nguyen, T. & Kausch, H. (1992) Chain extension and degradation in convergent flow, *Polymer*, 33(12), 2611–2621.
33. Islam et al (2003) *Inertial effects of polymer chain scission in planar elongational cross-slot flow*, *Macromolecules*, 37, 1023–1030.
34. Ptasiński PK, Nieuwstadt FTM, van den Brule BHAA, Hulsen MA. (2001): “Experiments in turbulent pipe flow with polymer additives at maximum drag reduction”, *Flow Turbulence and Combustion*, 66, 2, 159–182.

35. Deslouis, C., Tribollet, B., Tihon, J., Near-wall turbulence in drag reducing flows investigated by the photolithography-electrochemical probes, *J. Non-Newtonian Fluid Mech.* 123 (2004) 141–150
36. Liberatore, M.W., Baik, S., McHugh, A.J., Hanratty, T.J., Turbulent drag reduction of polyacrylamide solutions: effect of degradation on molecular weight distribution, *J. Non-Newtonian Fluid Mech.* 123 (2004) 175–183.
37. Hudson, D. & Zakin, J. (1980) *Flow assisted degradation in dilute polystyrene solutions*, *Poly. Sc. & Eng.* 20(7), 517–523.
38. Elbing, B., Winkel, E., Solomon, M., & Ceccio, S. (2009) Degradation of homogeneous polymer solutions in high shear turbulent pipe flow, *Exp. Fluids*, 47, 1033–1044.
39. Granlöf, L., Holmqvist, C. (2009): Filtration experiments using the Rapid Drainage Device. STFI-Packforsk Report No.19, Improved Formation II, Internal report.
40. Kerekes, R. J. and Schell, C. J. (1992). Characterization of fibre flocculation regimes by a crowding factor, *Journal of Pulp and Paper Science*, 18, 32–38.
41. Lucisano, M., Krochak, P., Hansson, Å., Lofthus, J., Norman, B. (2011) 2D Total grammage and filler content maps using moveable radiation emitters and detectors, *Progress in Paper Physics Conference*, Graz, Austria.
42. Norman, B., Tegengren, Å. Mixing of thick stock and white water. EUCEPA, 1988 Harrogate conference centre, Harrogate UK, Vol 1, 52–56, (1988).
43. Blanco, A., Fuente, E., Negro, C., Tijero, J., 2002, Flocculation monitoring: Focused Beam Reflectance Measurement as a measurement tool, *Canadian Journal of Chemical Engineering*, 80, 1–7.

## Transcription of Discussion

# ACHIEVING MAXIMUM FILLER RETENTION BY IMPROVING MECHANICAL AND CHEMICAL RETENTION

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I would like to know what is the effect of the average pulp suspension velocity, since it can modify things to a certain extent and we understand the rheology of the pulp suspension. Have you tried to modify this engineering parameter? And what can you recommend as the best range of velocities in the approach-flow system of the paper machine?

*Paul Krochak*

Yes, we looked at this; it's a good question and there is some effect, although it is not large. There seems to be a little bit of a middle ground where it is optimal, and so I only showed results for  $1 \text{ m s}^{-1}$ , or a water based Reynolds number of approximately  $12 \times 10^3$ , which is quite low if compared to a real approach-flow which could have a Reynolds number up to around  $5 \times 10^5$ . We do see a little bit of an effect and it is probably positive. We definitely know that the critical parameter when we talk about speeds is the speed ratio, and actually I can go one step further and say that it's actually momentum ratio. But we have done tests where we have increased the speed, increased both speeds of dosage and main flow, and we have not seen a huge difference.

*Discussion*

*Jean-Claude Roux*

So you believe that these effects can also be obtained at a higher velocity?

*Paul Krochak*

Yes.

*Gil Garnier*      Monash University

Paul, if I wanted to get a very high retention, I would take a chunk of calcium carbonate and wrap the paper around it, but I am not sure that will produce a good product! An alternative is to go back to the GCC and get big chunk of filler, but again, I am not sure I will produce good paper.

My question is: what is the ideal filler size and filler distribution in paper to, first, maximise the retention, second, to maximize the properties of paper? Just to guide you, are we looking at individual filler particles on fibres or big chunks of filler in pores?

*Paul Krochak*

Yes, that is a really good question but all we've looked at here was total filler retention. We did not go into formation, we did not go into paper properties, although, for example, strength – basic tensile properties – do improve. Of course, if we start talking about paper properties, then usually we come down to things like formation and we get into the question of mixing and I think this is another very deep conversation. What I was hinting at with the retention aids is that you cannot forget mixing and you cannot forget formation and you cannot forget uniformity. You are right, we have to consider the mixing, we have to consider the integrity of what we are adding to get out the nice formation and the nice paper properties.

*Roger Gaudreault*      Cascades

Can you comment on the surface coverage of polymer on filler, polymer on fibre?

*Paul Krochak*

No, because we have not done that. I did cite some literature when I discussed this in the main article.

*Roger Gaudreault*

A last quick question: can you translate the pressure drop into shear rate because we usually use reciprocal seconds in paper making?

*Paul Krochak*

It is proportional, I believe, to the mean velocity.

*Juha Salmela*      VTT

I have a question about the graph where you showed the speed ratio and filler retention (figure 15 in the paper). You have three different dosing systems, one in the centre of the pipe and two at the sides, so local shear is probably, as you said, very important. In the central dosing, you are actually putting the polymers into zero average shear rate, a plug-flow region, so there is no local high shear field around the dosage nozzle. So it is plug flow and this means zero velocity gradient – is this correct?

*Paul Krochak*

We did not go down to zero

*Juha Salmela*

But anyway, there is a low shear rate: local average shear rate at the centre of the pipe is low and close to the wall, it is very high. So the average shear field is very different in these three different dosing systems. So my question is, have you looked at changing the x-axis from absolute velocity ratio, which is a kind of average value to something like local shear rate? Isn't there a better way to characterise the local shear field and the size of the effect of polymer degradation?

*Paul Krochak*

If I understand your question, you are asking whether we could use a different parameter, for example, the maximum shear?

*Juha Salmela*

Yes, I think that this data could collapse more nicely if you, instead of using just velocity ratio, used local shear rate or something similar.

## *Discussion*

*Paul Krochak*

It is something worth considering. We actually published something on this last year<sup>1</sup>. We did some CFD simulations and we showed that the maximum point of shear is not in the centre of the channel, it happens at different points based on the dosage strategy.

*Bob Pelton*      McMaster University

10 or 15 years ago, we did a lot of work on polymer flocculation of PCC. We performed direct measurements of floc strength – single floc pulling experiments – and the main conclusion from that work is that you can get an enormous range of floc properties depending on the chemistries you use in the polymers. So you can make flocs that are very brittle and are like cookies that just fall apart when you pull on them. You can also make flocs that act like a piece of chewing gum that are enormously resistant to shear forces. So I think if I was trying to move this field ahead, a good area might be to try preforming flocs and putting a lot more effort into the various polymer chemistries. I think the result that you are showing us here looks like a fairly traditional polymer, which is very, very shear-sensitive. So if I was moving forward, I would change the polymer chemistry.

My question is: there are a lot of theories on mechanical filtration, including nice work done at FPIInnovations, and also, I think, at Innventia, on modelling the bed characteristics of fibre mat formation. Have you compared any of your results to the theories of mechanical filtration?

*Paul Krochak*

Firstly a comment on your first comment. I agree that this is very basic, and it is very interesting to look at different chemical systems because there seems to be very little known about a lot of them.

In reply to your question, yes we have, and I think we included a short section in the manuscript on how this compares to similar models that are out there.

<sup>1</sup>P. Krochak, S. Schack, and G. Fasci, “New insights into retention aids dosage and mixing”, *Nordic Pulp and Paper Research Journal* 27 no 2 pp. 192–201 (2012).