# In Situ Precipitated Calcium Carbonate in the Presence of Pulp Fibers – A Beating Study

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*Authors' contributions*

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*Original Research Article*

## ABSTRACT

The paper industry around the world is in search for new ways to decrease production costs. New approached with additives such as new developed *In Situ* precipitated paper fillers materials have the potential to reduce production cost and increase profit margins.

*In Situ* precipitated calcium carbonate filler with 20.9% and 41.7% filler material was produced in a large-scale laboratory unit using a eucalyptus pulp fiber suspension with a 1.7% fiber solids content.

Laboratory beating tests were performed with a Valley Beater and APFI Mill using pure eucalyptus pulp with no filler content as the based trial and the two-laboratory manufactured *In Situ* precipitated filler pulps.

Valley Beater and PFI Mill laboratory beating machines show similar differences/trends for the breaking length, tear and burst index.

EC-pulp with no filler has the highest strength for breaking length, tear and burst index. With increasing filler level breaking length, tear and burst index decrease. Filler containing pulp shows a decrease in beating time for the same beating level. 20 minutes for the Valley Beater and 15000 revolutions for the PFI mill show highest change in pulp fiber beating level sufficient for paper making operation.

Valley Beater and PFI Mill laboratory equipment operate different and an exact comparison of the beating curves is not possible. Based on the amount of pulp fiber needed for experiments the

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Valley Beater for large amounts and the PFI mill for smaller amounts should be selected.
The SEM pictographs of the Valley Beater and PFI Mill beating trials from 0 stage to the high beating stage at 80 minutes for the Valley beater and 60000 revolutions for the PFI Mill show similar results. No damage to the fibers is noticeable at the unbeaten level. With increasing beating level. At a magnification of 430 times the fiber structure shows an increasing dense fiber structure with less visible pores. Magnification of 2500 times reveals increasing damage to the fiber wall and fiber surface.

## 1. INTRODUCTION

Increasing production costs caused by raising energy costs, stringent environmental laws, globalization and high competitiveness and pressure on profit margins among commodity grades require the paper industry around the world to search for new ways to decrease production costs [1,2]. Roughly 420 million metric tons of paper products were produced in 2018 [3]. To save production cost paper companies target less expensive raw material and additives to replace more expensive fiber materials. As paper manufacturer shifted from acid to alkaline papermaking processes in the 1970's in Europe and in the 1980's in North America, Precipitated Calcium Carbonate (PCC) has become the preferred filler material for the printing and writing grade paper industry sector [4]. At present time paper products require worldwide over 8 million tons of filler material [5].

The major paper fillers used in papermaking are Ground Calcium Carbonate (GCC) and PCC. PCC is the largest category of filler in North America, with nearly 70% of the market share. The second most common filler type, with a market share of 15%, is Kaolin, followed by GCC with 13%. Titan dioxide's estimated market share is about 2%. The use of Silica / Silicates accounts for 0.3% and Talc and Aluminum Trihydrate together account for approximately 0.1% [7].

The use of fillers, especially PCC, is mainly driven by production cost issues, because paper fillers materials are less expensive than fiber, allowing reduced production costs, improved optical paper properties, dimensional stability, and better sheet formation and printability as well as increased machine speed on the paper machine and coating application side [7]. However, applying filler material causes a decrease of the paper's strength and lowers the product quality. [4,5,7]. Over the last decades and today the paper manufacturers attempted to

increase the calcium carbonate based ($CaCO_3$) filler in a sheet of paper due to its savings potential of up to $ 4.0 per ton of paper produced for each 1% increase in filler content [7].

PCC at present time commercially applied in slurry or powdered form to the papermaking suspension in the blend chest in wet-end section of the paper mill and at the fan pump shortly before the fiber suspension is entering the paper machine head box after which the sheet forming process occurs [8].

Before the fiber suspension enters the wet-end the mechanical preparation of the fibers by beating has been completed. Interaction of fillers and beating has been of interest by various researchers since the 1970's mainly on $TiO_2$. *In Situ* manufactured mineral fillers in the presence of pulp fibers prior to beating had been not the focus of past research [5].

Beating or refining, of pulp fiber is the mechanical treatment and modification of fibers so that they can be formed into paper or board of desired properties. The main target of refining is to improve the bonding ability of fibers so that they form strong and smooth paper sheets with ideal properties for converting and printing.

The most commonly used refining or beating method is to treat pulp fibers in the presence of water with metallic plates of fillings in disc (disc refiner), cylindrical (cylinder refiner) or conical (conical refiner) form. The plates or fillings are grooved so that the bars that treat fibers and the grooves between bars allow fiber transportation through the refining machine [9].

Fig. 1. Shows simplified the rotor and stator pulp fiber interaction during the beating process. First, pulp fibers are collected on the leading edges of the rotor and stator bars as shown in the fiber pick-up stage in Fig. 1. a). During the pulp fiber pick-up stage, the consistency is typically 3%−5%. When the leading edge of the rotor bar

approaches the leading edge of the stator and moves over the stator bar an edge to surface treatment shown in Fig. 1.b) is initiated. During the edge to surface treatment, the pulp fibers are compressed and receives a forceful strike. As a result, most of the water is compressed out of the pulp fibers. Simultaneously, short fibers with low flocculation ability are likely to be separated and flow into the grooves between the bars. Only those fibers remaining between rotor and stator surface are compressed between the two metallic bar surfaces and receive refining. After this, both leading edges slide along the pulp fibers and press them against the flat bar surface of the rotor and stator. Most refining is performed during this surface-to-surface stage, shown in Fig. 1.c), when the bar edges give mechanical treatment and friction between fibers. This stage continues until the leading edges reach the tailing edges of the opposite bars. During the edge-to-surface stage, the pulp fibers are still pressed between the flat bar surfaces until the tailing edge of the rotor bar has passed the tailing edge of the stator bar, releasing the fibers into the grove of the filling during the release stage shown in Fig. 1.c).

Refining affects fibers in many ways, with the most important effects being a) cutting and shortening of fibers, b) external fibrillation, the partial removal of the fiber wall, while still leaving the fiber wall attached to the fiber, c) internal changes in the wall structure, variously described as internal fibrillation, delamination or swelling, d) production of fines by complete removal of parts from fiber walls, creating small debris in the pulp fiber suspension. Other effects include curling or straightening the fiber, creation of nodes, kinks, slip planes, and micro compressions in the cell wall, or separating cell wall layers from each other, and redistribution of hemicelluloses from the interior of the fiber to the exterior, and abrasion of the fiber surface at the molecular level to produce a more gelatinous surface.

As a result of the above effects, fibers are collapsed after refining (flattened) and made more flexible, and their bonding surface area is increased allowing more hydrogen bonds between the individual fibers.

The results of beating can be measured in a change of dewatering or resistance to drainage of a given pulp fiber suspension, called Canadian Standard Freeness (CSF) as well as a change in measurable mechanical fiber and sheet properties [9].

The following research project has the objective to investigate the effect of *In Situ* Precipitated Calcium Carbonate (ISPCC) filler material on pulp fiber dewatering and mechanical fiber properties by beating. Tests were performed using two different laboratory beating devices (Valley Beater and PFI Mill) for the evaluation of dewatering and mechanical paper properties (breaking length, burst and tear).

## 2. MATERIALS

For this research project producing ISPCC hardwood pulp in the form of Bleached Eucalyptus Kraft Pulp (BEKP) from CMPC Celulosa was used. Calcium hydroxide $(Ca(OH)_2)$ powder was obtain from Lhoist North America. Industrial grade carbon dioxide $(CO_2)$ gas was used with a 99% purity, supplied in a pressurized container containing 50 lbs. (22.68 kg) of gas.

### 2.1 Precipitation System

For the production of the *In Situ* precipitated calcium carbonate (ISPCC) in the presence of pulp fibers, a Large-Scale Laboratory Precipitation (LSLP) shown in Fig 2. Was used [2].
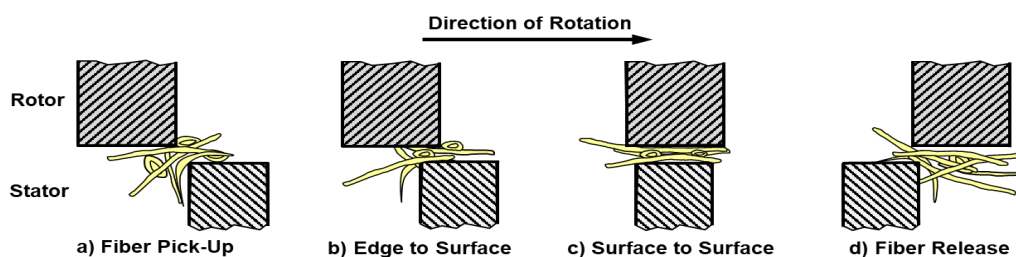


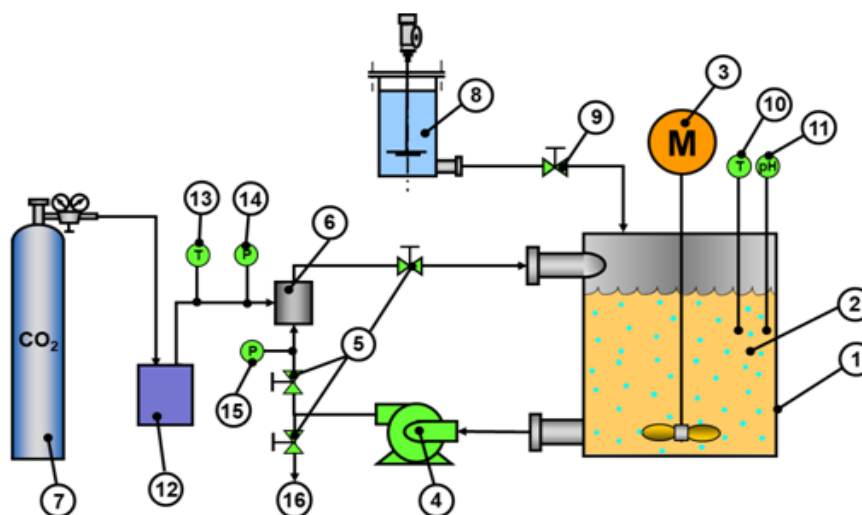**Fig. 1. Rotor stator beating interaction [10]**

**Fig. 2. Large Scale Laboratory Precipitation (LSLP) system: 1) 1000 l tank, 2) Pulp fiber suspension, 3) 0.375 kW propeller mixer 4) 0.75 kW impeller pump, 5) Ball valve, 6) Static mixer, 7) $CO_2$ Tank with pressure transducer and flow adjustment, 8) lime tank, 9) Dosing valve, 10) Temperature Probe, 11) pH Probe, 12) Gas heater, 13) Gas temperature probe, 14) $CO_2$ pressure Gauge, 15) Pressure gauge, 16) Transfer pipe [2]**

## 2.2 Operation of Large-Scale Precipitation System

For this research project a ISPCC filler content of 20% and 40% was targeted. First 8 kg of EC pulp fibers are pulped in 4 batches with 40 l each, at a consistency of 5% using a laboratory pulper. The resulting 160 l EC pulp fiber suspension is then transferred into the LSLP system tank (1) and diluted to a consistency of 1.70% (470.5 liter) by adding 310.5 l $H_2O$ to into the tank (1). Second, a $Ca(OH)_2$ suspension with 20% dry solids content containing 2 kg (20 l) is being prepared and added from the lime tank (8) into tank (1). The variable speed propeller mixer (3) is used to mix the resulting suspension of EC pulp fibers and Ca $(OH)_2$. Pulp suspension flow in tank (1) is adjusted in that way that good recirculation of the pulp suspension is ensured by an mixing vortex indentation in the center of 100 mm (4 in) on the tank surface. The mixing propeller (3) is kept in operation for the whole precipitation process to ensure good mixing of the pulp suspension and the precipitated ISPCC pulp. After approximately 5 minutes of mixing recirculation pump (4) is started and the pulp suspension is recirculated with about 70 l/min (18.5 gal/min). Fourth, the pressure regulator of the Carbon dioxide ($CO_2$) storage tank (7) is opened and the $CO_2$ gas flow adjusted to 60.0 cfm (1.7 l/min) and a pressure of 68948.0 Pa (10.0 psi) above the pressure reading on pressure gauge (15) using pressure gauge (14). The $CO_2$ gas exiting the $CO_2$ storage tank (7) transfers into a $CO_2$-heater (12) to maintain a $CO_2$ temperature between 20°C and 30°C. The temperature of the $CO_2$ is measured with temperature probe (13). $CO_2$ gas exiting the $CO_2$-heater is then transferred into the static mixer assembly (6) using a 0.5" (12.7 mm) inside diameter clear PVC hose. Six Sulzer-SMF mixing elements with 25 mm in diameter are used in the static mixer assembly (6) to mix the pulp suspension and $CO_2$ without causing plugging. The LSLP system is operated this way and temperature and pH values are monitored with probes (10) and (11) respectively. The LSLP system operation in stopped when pH of the recirculated pulp fiber suspension reaches a value of 7.5. A 45 l suspension sample is taken from the precipitated HP suspension for further testing of beating and testing of mechanical paper properties. To reach the second ISPCC target another $Ca(OH)_2$ suspension with 20% dry solids content containing 2 kg (20 l) is being prepared and added from the lime tank (8) into tank (1), and the precipitation process is initiated for a second time as described above. After the pH reached 7.5 another 45l sample is taken for beating and testing mechanical properties.

## 2.3 Testing Methods

Beating of pulp (Valley beater method) in accordance to T200 sp-06 "Laboratory beating of pulp (Valley beater method)" [10]. Handsheets preparation was done according to T205 sp-06

"Forming handsheets for physical tests of pulp" [11]. The ash was measured after T211 om-02, "Ash in wood, pulp, paper and paperboard: combustion at 525°C [12]. Physical testing of handsheets was performed in accordance to T220 sp-06, "Physical testing of pulp handsheets" [13]. Freeness of pulp was measured as Canadian Standard Freeness (CSF) according to T227 om-09 "Freeness of pulp (Canadian standard method)" [14]. Consistency of a pulp suspension was measured with TAPPI T240 om-07 "Consistency (concentration) of pulp suspensions" [15]. Beating of pulp (PFI mill method) was performed in accordance to T248 sp-08 "Laboratory beating of pulp (PFI mill method)" [16].

Conditioning of the paper samples was done according to T402 sp-08, "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products" [17]. Burst Index was measured in accordance with T403 om-02 :Bursting strength of paper" [18]. Basis weight was measured with T410 om-08. "Grammage of Paper and Paperboard (weight per unit area)" [19]. Moisture content of pulp was determined by T412 om-06 "Moisture in pulp, paper and paperboard" [20]. Tear resistance was measured according to T414 om-04 "Internal tearing resistance of paper (Elmendorf-type method)" [21]. Tensile strength was performed following T494 om-06, "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" [22].

For measuring temperature and pH of the pulp suspension an Accumet AP85 instrument was used.

## 2.4 Pulp Beating Methods

For this research project a laboratory Valley Beater T200 sp-06 and a PFI Mill T248 sp-08 were used. Both laboratory machines are used in established laboratory methods of Technical Association of the Pulp and Paper Industry (TAPPI).

### 2.4.1 Valley beater method

T200 sp-06 requires a sample weighing 362 ± 3.0g oven dry (OD) fiber material for a beater run. The sample is diluted to 23 l which corresponds to a fiber consistency of 1.57 ± 0.04%.

After the 23 l sample is filled in the Valley Beater (Fig. 3.), the beater is run for three minutes with no load. When the pulp is properly disintegrated, the clamp from the lever arm is removed, and the standard 5500-g weight is added to the lever arm and the beating process is started. After successive time intervals (20 minutes for this research project), a 1200-mL sample is withdrawn from the beater to yield a total of five samples at approximately equal freeness intervals. Each withdrawal provided a sample of 18.8 g OD to yield sufficient pulp for TAPPI freeness determination in accordance with T227 om-09 "Freeness of Pulp," and for making 12 standard 1.2 g handsheets in accordance with T205 sp-06 "Forming handsheets for physical tests of pulp".

### 2.4.2 PFI mill method

T248 sp-08 requires a specimen weighing 24.0 ± 0.25 g oven dry (OD) for each beating run.

For the EC pulp tests without ISPCC, EC pulp fibers were soaked in 500 mL of distilled water at room temperature for a minimum of four hours. The soaked pulp was torn into pieces sized approximately 25 × 25 mm. It is essential that the pulp was thoroughly softened by soaking to ensure that disintegration has no negative effect on beating. After soaking the EC pulp samples were transferred to the disintegrator and distilled water at 20 ± 5°C was added to give a total volume of 2000 ± 25 mL; the consistency of the EC pulp was then 1.2%. After a disintegration time of 10 min, the pulp was checked and found to be completely disintegrated.

After disintegration, the pulp suspension was dewatered using a Büchner funnel using a coarse filter paper to achieve approximately 20% consistency. To avoid loss of fines, the filtrate was again filtered through the fiber mat until clear. The thickened pad was weighed and diluted with water to a total mass of 240 ± 0.5 g, corresponding to a 10% stock consistency. Following this, the pulp was peeled from the filter and placed in a 400-mL beaker.

From the ISPCC pulp containing 20.9% and 41.7% ISPCC filler pulp a 10% OD EC fiber pulp suspension with a total mass of 240 ± 0.5 g was prepared taking in account the ISPCC filler level.

After the pulp suspension is prepared for beating, the PFI mill (Fig. 4 a & b) was adjusted to a temperature of 23 ± 2°C using hot water and the gap between the rotor an housing was checked to be 0.2 mm before the pulp was added. Next,

the 10% pulp suspension was transferred to the beater housing and distributed as evenly as possible over the wall of the housing (Fig. 4b). The PFI mill is closed, started, the weight applied for beating, and the revolution counter was simultaneously started. After the required number of revolutions for the roll, the beating was discontinued by removing pressure from the roll. The motors were shut off and the roll was centered. Both the roll and housing cover were lifted.

Next, all pulp is transferred into a 2000-mL beaker and diluted with distilled water to 2000 ml, followed by disintegrating in a disintegrator at 10,000 revolutions. The consistency of the pulp suspension is now 1.2% based on OD fiber content. The pulp was now ready for TAPPI freeness determination in accordance with T227 om-09 "Freeness of Pulp," and for the making handsheets in accordance with T205 sp-06 "Forming handsheets for physical tests of pulp".

## 2.5. Scanning Electron Microscopy

JEOL JSM-5800 LV low vacuum scanning electron microscope was used for surface evaluation of a paper handsheet containing ISPCC prepared according to TAPPI testing standard T205 sp-06 [13].

## 3. RESULTS AND DISCUSSION

All tests for this research were performed in according to the in Section 2.3. referenced TAPPI methods. All results stayed in the precision statements for the referenced TAPPI methods.

### 3.1 Manufacture of Hybrid Pulp

Fig. 5. shows the development of ph and temperature during the ISPCC manufacturing process. As it can be seen in Fig. 2. the EC pulp fiber suspension and 2 kg $Ca(OH)_2$ suspension was precipitated for 25 minutes until the pH value dropped below 7.5. At the beginning of the process, the suspension has an initial pH value of 12.2 caused by the $Ca(OH)_2$. In the first 15 Minutes the pH value drops just slightly. Between 15 and 20 minutes, a significant drop in pH is noticeable with a pH below 7.5 after 23 minutes. The temperature is just slightly increased during the precipitation process from 15.8°C to 17.1°C. The ISPCC pulp now has a filer content of 20.9%.
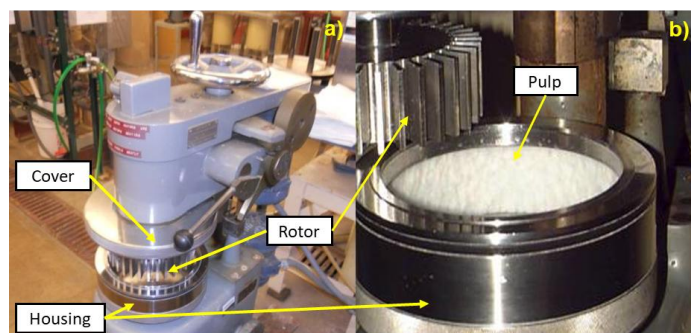


**Fig. 3. Valley beater [23]**

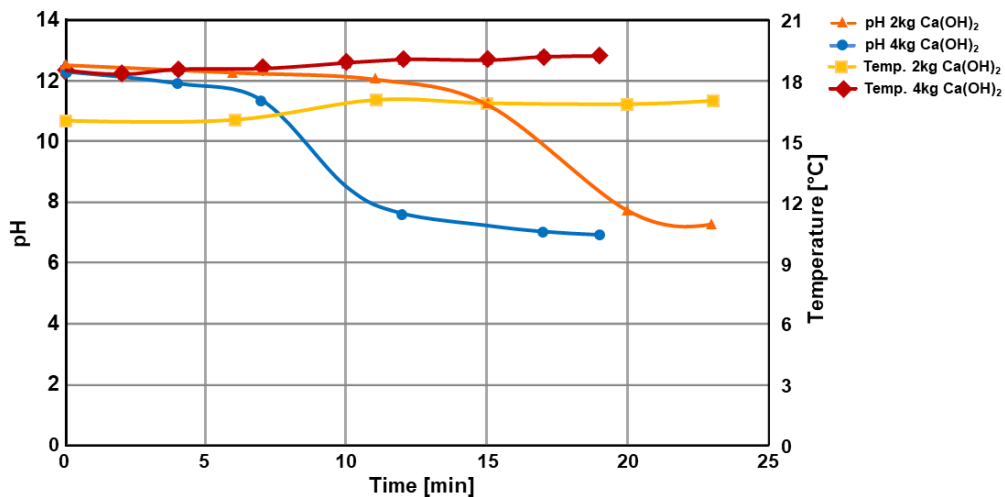

**Fig. 4. PFI Mill [24]**

**Fig. 5. Development of pH and temperature for manufacturing ISPCC**

In the second step, an additional 2 kg of $Ca(OH)_2$ suspension was added to the ISPCC pulp fiber suspension and ISPCC precipitated for a second time. This time the precipitated process was faster (Fig. 2.), which could be linked to dissolved $CO_2$ that remained in the pulp suspension after $Ca(OH)_2$ conversion into $CaCO_3$ reached a neutral pH during the first trial. However, more in detail investigations on this finding needs to be done in the future. After 7 minutes a significant drop in pH value could be noticed with a final pH below 7.5 after 18 minutes. The temperature increased during the precipitation process to 19.7°C. The ISPCC pulp now has a filer content of 41.7%. Both ISPCC pulp suspension are used for the beating and following mechanical paper properties study.

## 3.2 Beating Study

In this chapter the behavior of the ISPCC pulp, in the following called Hybrid Pulp (HP) with 20.9% and 41.7% filler was analyzed during beating and compared to EC pulp without filler content. For the analysis, beating curves were generated with two different beaters (Valley beater and PFI mill).

### 3.2.1 Valley beater study

The Valley Beater beating curve is shown in Fig. 6. For the EC pulp with no filler content and HP pulp with 20.9% and 41.7% filler content. Each Valley Beater run provided enough pulp samples for the Because of the subsequent analyses.

The beating curve starts at 0 minutes for the no filler containing EC pulp and the 20.9% and 41.7% filler containing HP pulp (unrefined pulp sample). The beating level goes up to 80 minutes (highly refined sample) in intervals of 20 minutes for all three pulp samples.

The HP pulps have a higher initial dewatering ability (CEF-value) with increasing filler content as the EC pulp with no filler.

The dewatering ability of all pulps decreases with beating time and increases after 40 minutes for the HP pulp with 41.7% filler content and about 55 minutes for the HP pulp with 20.9% filler content. The EC pulp with no filler content did not reach the reverse point after 80 minutes of beating. The HP pulp reaches a lower CSF value earlier than the EC pulp with less beating time or higher CSF value after the reverse point. This indicated that for HP pulp less beating is needed and therefore less energy is consumed to reach a certain CSF value after the initial CSF value of the EC pulp with no beaten is reached.

In Fig. 7, 8, and 9 show the beating curves development in 20 minutes increments for the breaking length index, the tear Index and burst index respectively over a beating time of 80 minutes.

It can be seen in Fig. 7. that the breaking length index increases with increasing beating for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content, with the EC pulp having the highest breaking length index gain over the 80 minutes beating time, followed by the HP pulp with 20.9% and 41.7% which are very similar. After 40 minutes of beating both HP pulps show a lover gain of breaking length, whereas the HP pulp with 41.7% did not show an increase after 60 minutes of beating.
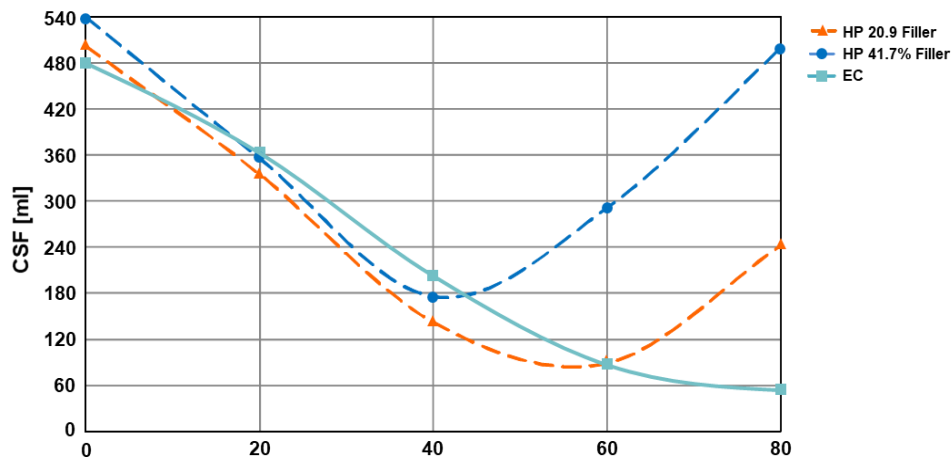
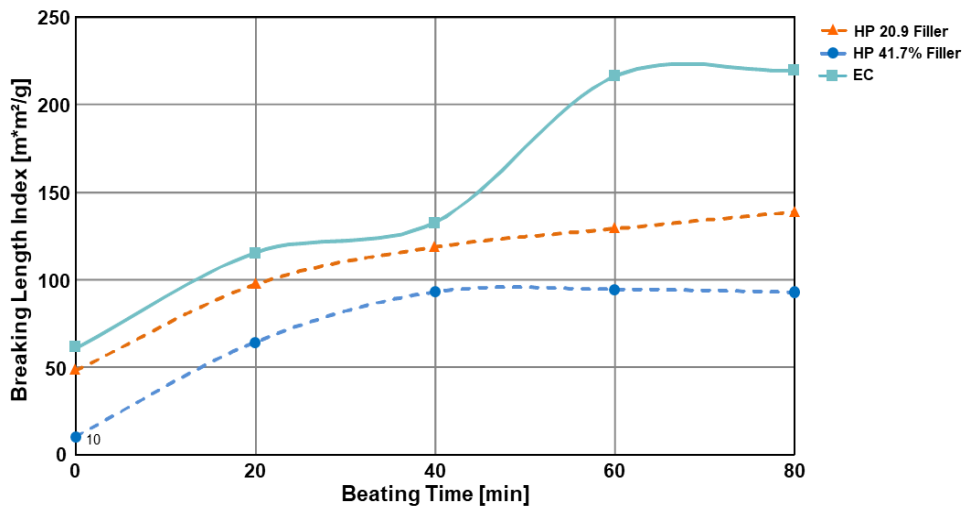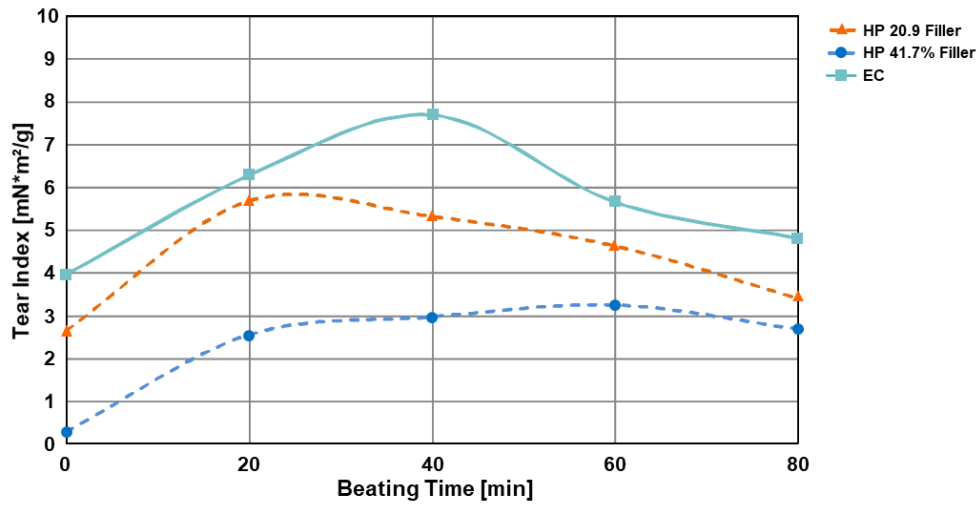**Fig. 6. Valley beater beating curve**



**Fig. 7. Valley beater breaking length index**

Fig. 8. shows that the tear index curves based on beating time are similar for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content. The maximum for the EC pulp, HP pulp with 20.9% and 41.7% filler content is at a beating time of 40 minutes, 20 minutes and 60 minutes respectively. All three pulps show a decrease in burst index after a beating time of 40 minutes for the EC pulp, 60 minutes for the HP pulp with 41.7% filler content and 20 minutes for the HP pulp with 20.9% filler content Fig. 9. shows that the burst index increases with beating time for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content with the maximum at 60 minutes of beating. All three pulps show a decrease in burst index after a beating time of 60 minutes. The EC pulp has the highest burst index gain over the 60 minutes beating time, followed by the HP pulp with 20.9% and 41.7%. After 60 minutes of beating all three pulps show a decrease in burst index.

**3.2.2 PFI mill beating study**

The PFI Mill beating curve is shown in Fig. 10. For the EC pulp with no filler content and HP pulp with 20.9% and 41.7% filler content. Because of the small capacity of the PFI mill each run provided just enough pulp for the subsequent analyses. Therefore, for each test point of the curve in Fig. 10. A new sample set is needed to be prepared and tested.

The refining curve starts at 0 revolutions for the no filler containing EC pulp and the 20.9% and 41.7% filler containing HP pulp (unrefined pulp sample). The beating level goes up to 60,000 revolutions (highly refined sample) in intervals of 15000 revolutions for all three pulp samples.

**Fig. 8. Valley beater tear index**
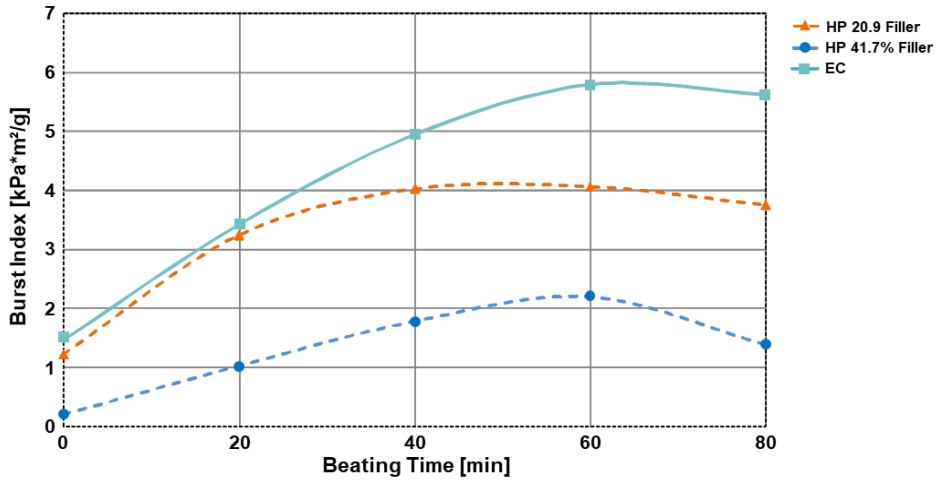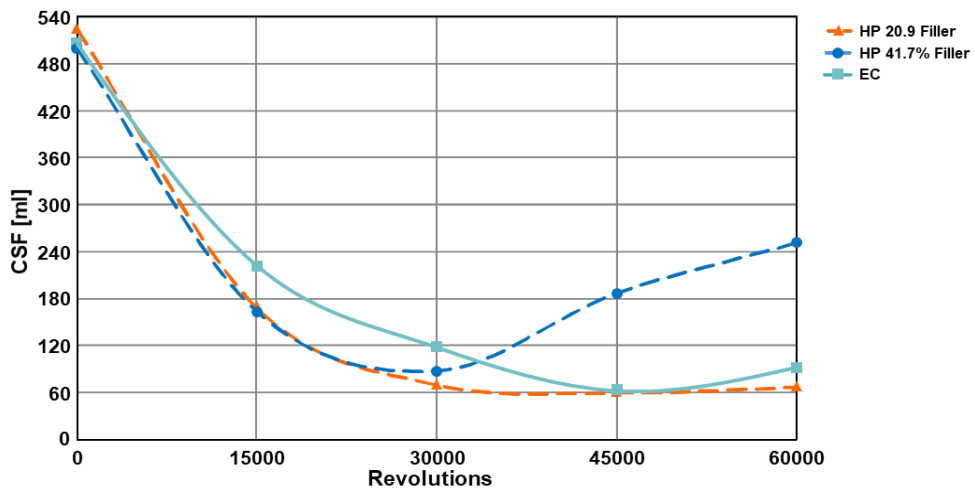


**Fig. 9. Valley beater burst index**



**Fig. 10. PFI mill beating curve**

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The HP containing pulps have a higher initial dewatering ability (CEF-value) with increasing filler content as the EC pulp with no filler.

The dewatering ability of all pulps decreases with beating time and increases after 30000 revolutions for the HP pulp with 41.7% filler content and at 45000 revolutions for the EC pulp with no filler content. The HP pulp with 20.9% filler content increases its CSF value slightly after 45000 revolutions. The HP with 20.9% and 41.7% filler content reaches a lower CSF value earlier than the EC pulp with less beating time or higher CSF value after the reverse point. This indicated that for HP pulp less beating is needed and therefore less energy is consumed to reach a certain CSF value after the initial CSF value of the EC pulp with no beaten is reached.

In Fig. 11, 12, and 13 the beating curves development in 15000 revolution increments for the breaking length index, the tear Index and burst index can be seen over 60000 revolutions.

It can be seen in Fig. 11. that the breaking length index increases with increasing beating for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content, with the EC pulp having the highest breaking length index gain over a 45000 revolution of beating. Followed by the HP pulp with 20.9% and 41.7% at beating revolutions of 45000 and 30000 respectively. After 45000 revolutions of beating for the EC pulp with no filler and HP with 20.9% and 30000 revolutions of beating forth HP pulp with 41.7% filler content the breaking length index decreases. All three pulps show the highest breaking length index gain at 15000 revolution of beating.

Fig. 12. shows that the tear index increase based on beating time is similar to the breaking length index increase for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content. The maximum tear index for the EC pulp and the HP pulp with 20.9% filler content is at a revolution of 45000. The HP pulp with 41.7% has his maximum at a beating revolution of 30,000. All three pulps show a decrease in tear index after a beating time of 15000 revolutions for the HP pulp with 20.9% filler content and 30000 revolutions of beating for the EC and HP pulp with 41.7% filler content. All three pulps shoe the highest tear index increase for a beating time of 15000, a minimum at 45000 and an increase of tear index at 60000 revolutions of beating.

Fig. 13. shows that the burst index increase with beating time is similar to the breaking length index increase for the EC pulp and the HP pulp with 20.9% and 41.7 % filler content. The maximum for the EC pulp and the HP pulp with 20.9% filler content is at a revolution of 45000. The HP pulp with 41.7% has his maximum at a beating revolution of 30,000. All three pulps show a decrease in burst index after a beating time of 45000 revolutions for the EC and HP pulp with 20.9% filler content and after 30000 revolutions for the HP pulp with 41.7% filler content. All three pulps shoe the highest burst index increase for a beating time of 15000 revolutions.

### 3.2.3 Beating study summary

When comparing the beating curves of the Valley Beater and the PFI Mill all two laboratory machines show similar differences/trends for the breaking length, tear and burst index.
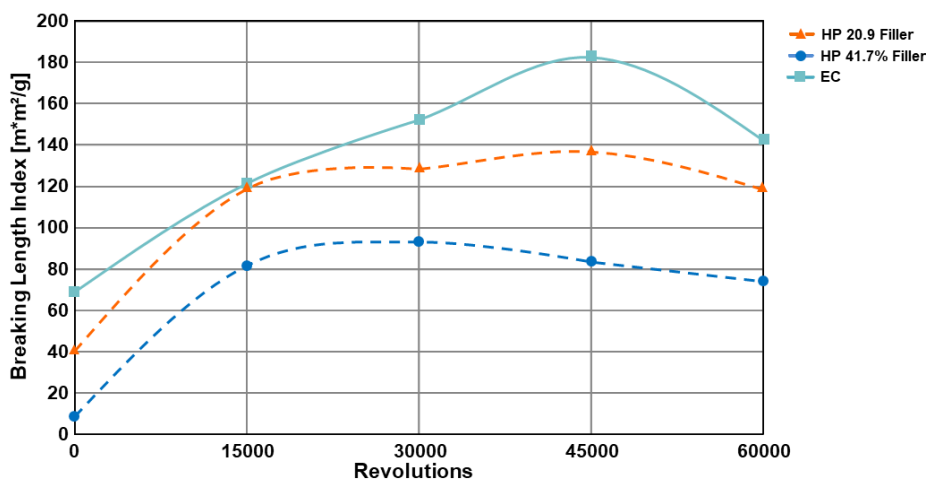


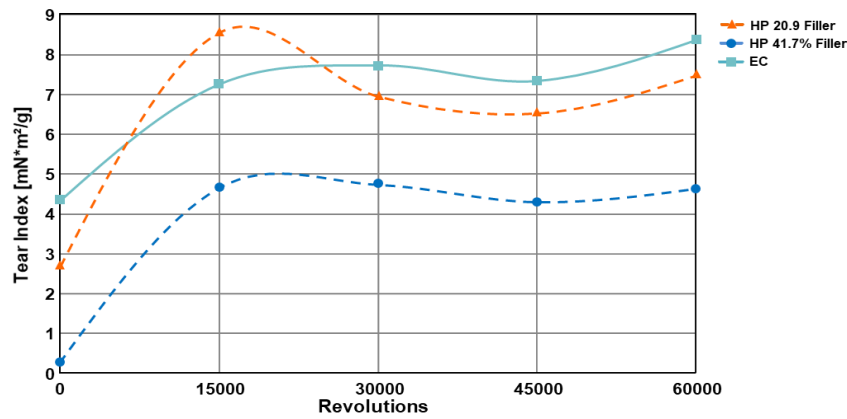**Fig. 11. PFI mill breaking length index**
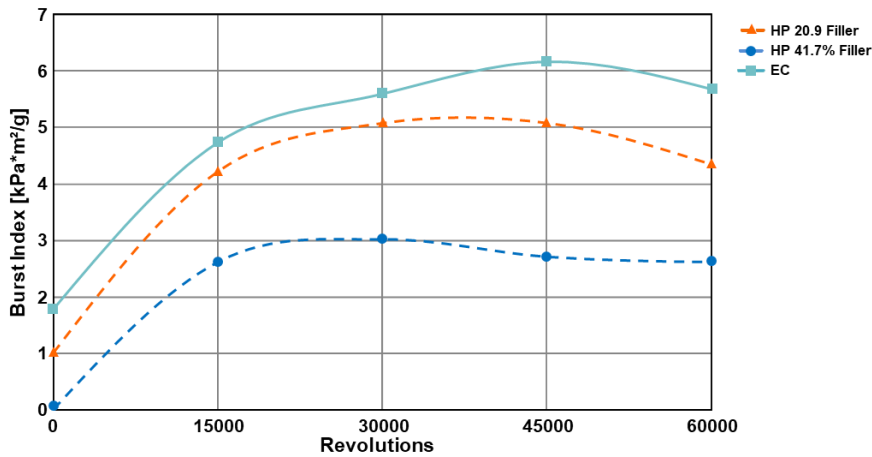
**Fig. 12. PFI mill tear index**



**Fig. 13. PFI mill burst index**

All curves show that the pure EC-pulp has the highest strength for breaking length, tear and burst index, because EC-pulp doesn't have any added fillers. The HP with a filler content of 41.7% shows the lowest breaking length, tear and burst index. Because the Valley Beater and the PFI Mill operate different an exact comparison of the beating curves is not possible. For beating larger amounts of pulp and a more in-depth investigation the Valley Beater is the better laboratory solution due to the large amount of beaten pulp produced at a given time. The PFI mill is the better machine if only smaller amount of pulp is needed for the investigation, however multiple beating trials need to be performed which can be very time intensive.

## 3.3 Effect of Beating on Fiber Structure with Scanning Electron Microscopy

In the following section Scanning Electron Microscope (SEM) pictures were taken from the handsheets made from the Valley Beater and PFI Mill beating tests using the 20.9% ISPCC filler pulp fibers. For better analysis, all sample pictures were taken at a magnification of 430 and 2500 times.

The 430x magnification illustrates the surface structure of the handsheet and allows to see the fiber web bonding structure with the ISPCC.

The 2500x magnification offers a detailed view of the individual fibers. At this magnification the surface of the fiber wall can be better analyzed.

### 3.3.1 Valley beater scanning electron microscopy

SEM pictures were prepared for the unrefined state at 0-minutes beating time and for 20 minutes, 40 minutes, 60 minutes and 80 minutes beating time. The pictures show an increasing fiber damage at the fiber surface from the

unrefined state (0 minutes), up to an extremely refined state (80 minutes) at the 2500 magnification level. Furthermore, it can be observed that the fiber tissue is increasingly cross linked and the free space in the fiber tissue is decreasing. Fig. 14. and Fig. 15. shows the untreated fibers of the refining curve, when the fibers are still in the unrefined state. Therefore, it can be said that no refining energy was transferred to the fibers, and n no damaged fiber walls is visible. This picture with the unrefined fibers correlates well with the weak paper strengths of the sample handsheet. Fig. 16. and Fig. 17. shows the pulp after a refining time of 20 minutes. Here, the fiber has experienced a significant amount of refining energy. Furthermore, the pulp in this picture is characterized by an extreme increase in external fibrils which ensure that the fiber structure can be better linked together. A bonding of the fibers occurs between the cross point of two fibers. In this case, the external fibrils bond with each other as well. The whole structure is now more compact, and it indicates an increased amount of

bonding in the fiber network. This is also evident by the paper's strength at this refining level. **Error! Reference source not found.**shows the refining curve after 40 minutes.  At the top left side of the image, external fibrils are very visible. At a magnification of 2500x, a stronger cross-linked structure than in the previous refining stage is observable.

In the 60-minute refining stage shown in Fig. 20 and Fig. 21. the larger surface area of the fiber wall is evident.  The structure of the network of fibers is more uniform and the pores are smaller. The fibers are also more damaged. After a refining time of 80 minutes, shown in Fig. 2.2 and Fig. 23., no pores are barely visible in the tissue structure at a magnification of 430x,  of the handsheet. Furthermore, in Fig. 23., bigger external fibrils can be seen. In conclusion, the SEM images allow a visual examination of the refining curve. Increasing refining causes an increasing of the surface of the fibers, and as a result the whole fiber structure is progressively better cross-linked.
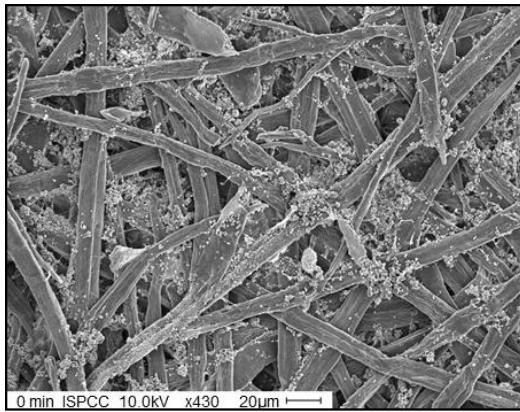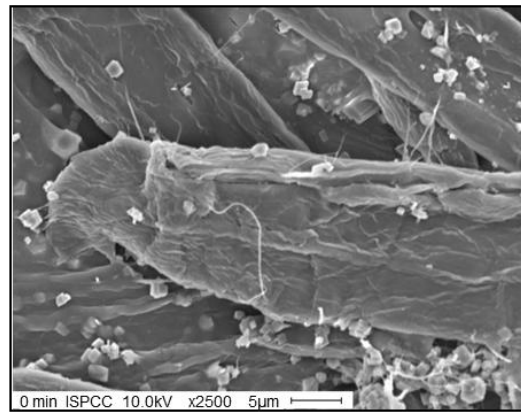


**Fig. 14. Valley Beater, 0 min., x430 [25]**

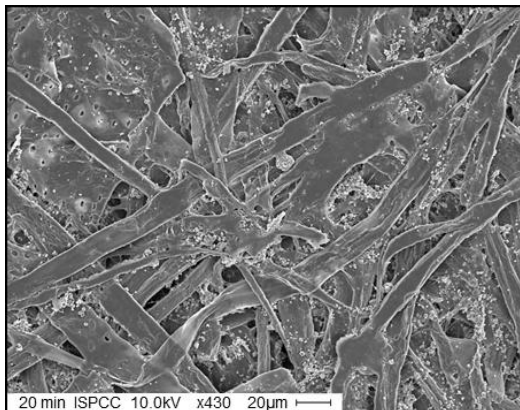

**Fig. 15. Valley Beater, 0 min., x2500 [26]**



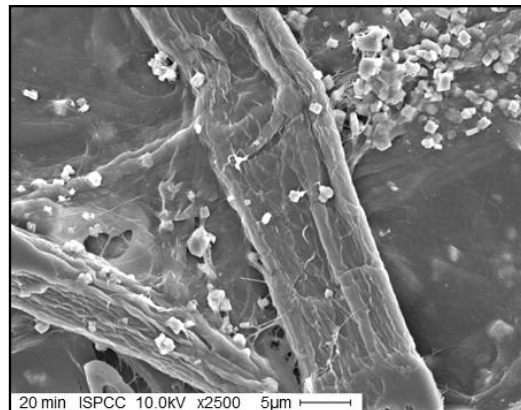**Fig. 16. Valley Beater, 20 min., x430 [27]**



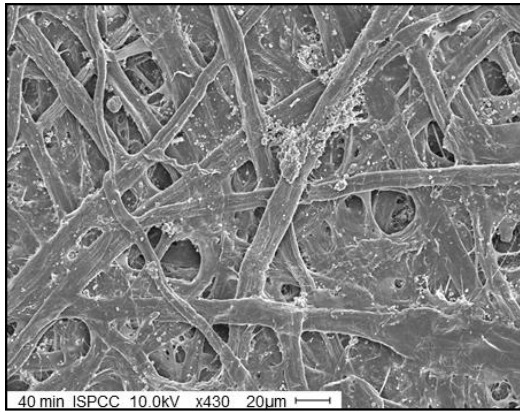**Fig. 17. Valley Beater, 20 min., x2500 [28]**
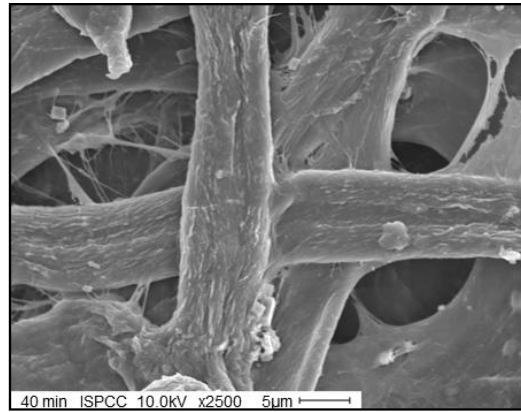
**Fig. 18. Valley Beater, 40 min., x430 [29]**



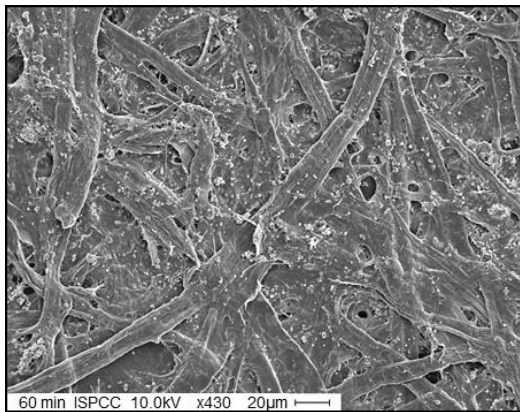**Fig. 19. Valley Beater, 40 min., x2500 [30]**



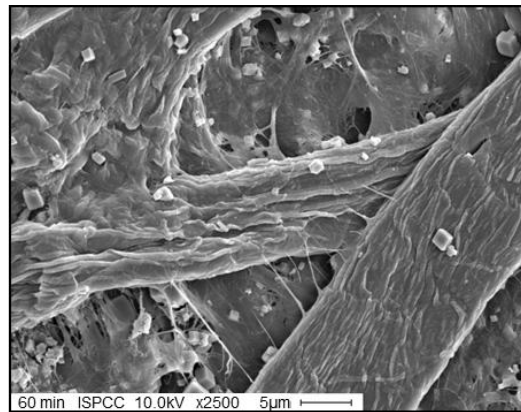**Fig. 20. Valley Beater, 60 min., x430 [31]**



**Fig. 21. Valley Beater, 60 min., x2500 [32]**
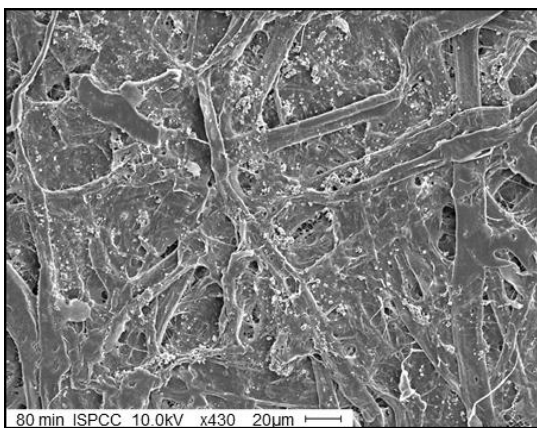


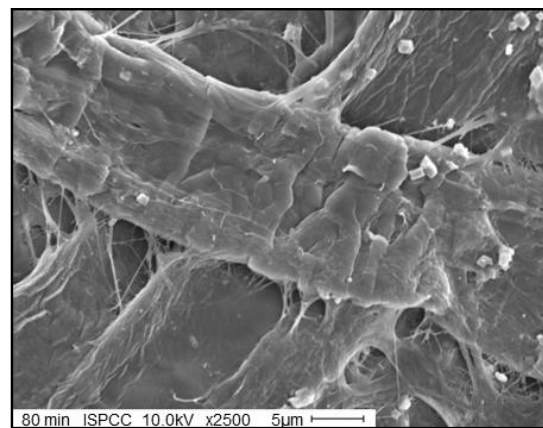**Fig. 22. Valley Beater, 80 min., x430 [33]**



**Fig. 23. Valley Beater, 80 min., x2500 [34]**

### 3.3.2 PFI mill scanning electron microscopy

SEM pictures were prepared for the unrefined state at a beating with 0, 15000, 30000, 45000, and 60000 revolutions. The pictures show an increasing fiber damage at the fiber surface from the unrefined state (0 revolutions), up to an extremely refined state (60000 revolutions) at the

2500 magnification level. Furthermore, it can be observed that the fiber tissue is increasingly cross linked and the free space in the fiber tissue is decreasing. **Error! Reference source not found.** depicts the untreated fibers of the beating curve, when the fibers are still in the unbeaten state with no energy transferred to the fibers.

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At the beginning of the beating curve, shown in Fig. 24. and Fig. 25., an unrefined sample is shown. In this view one can observe the untreated fibers in the sheet structure. Furthermore, in this figure, agglomerations of ISWPCC can be recognized. Even at a magnification of 2500x, no damage to the surface of the cell wall is visible. At the 15000-revolution beating level, shown in Fig. 26. And Fig. 27. an extreme difference can be recognized. The mechanical damage caused by beating can be seen on the fiber wall. Furthermore, an increase in external fibrils in the central area of the picture is quite visible. At the beating level of 30,000 revolutions, represented in Fig. 28. And Fig. 29., only a few fibers remain unrefined. In Fig. 30. and Fig. 31., a larger external fibrillation can be seen, and extreme damage to the fiber wall is clearly visible. The last stage of the beating at 60000 revolutions represented by Fig. 32. And Fig. 33., it is evident clearly how drastically the fiber wall is damaged during refining. The fiber structure is much more cross-linked. In addition, the surface is beaten to such a high degree that no pores are visible.
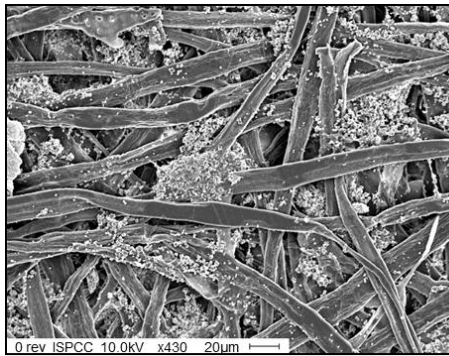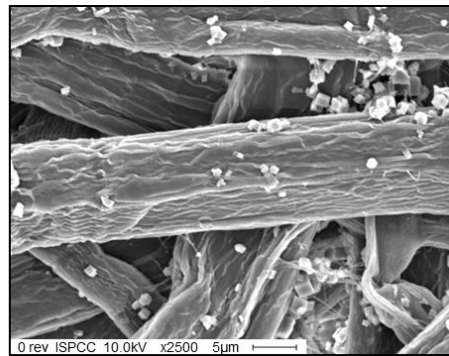


**Fig. 24. PFI MILL, 0 REV., X430 [35]**
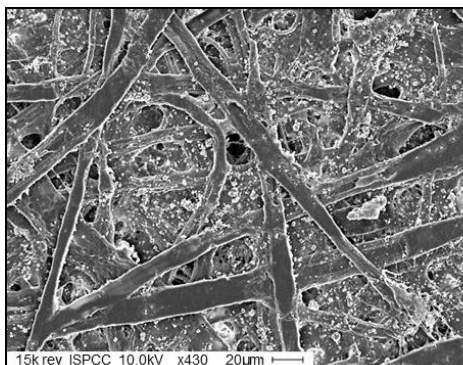


**Fig. 25. PFI MILL, 0 REV., X2500 [36]**
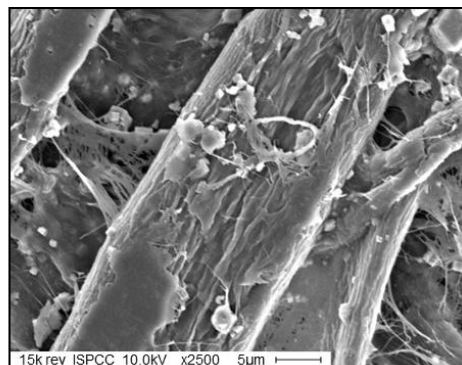


**Fig. 26. PFI MILL, 15000 REV., X430 [37]**



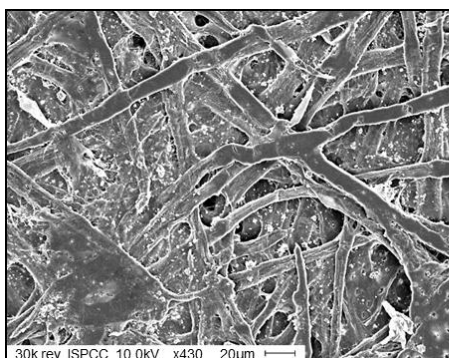**Fig. 27. PFI MILL, 15000 REV., X2500 [38]**



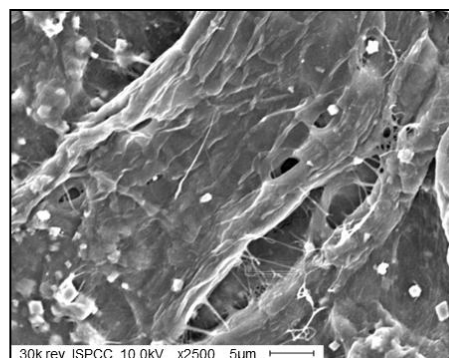**Fig. 28. PFI MILL, 30000 REV., X430 [39]**



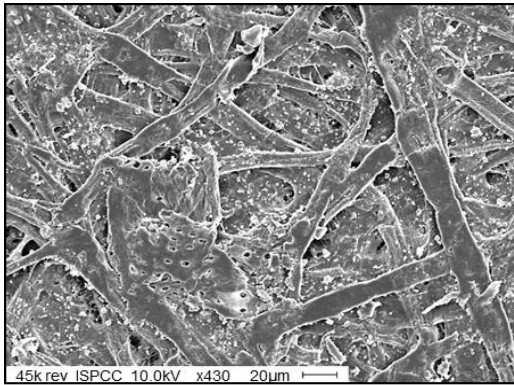**Fig. 29. PFI MILL, 30000 REV., X2500 [40]**

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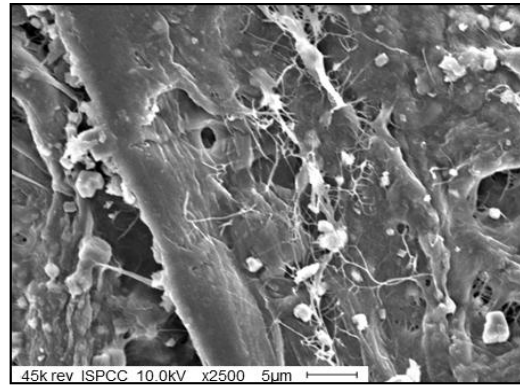**Fig. 30. PFI MILL, 45000 REV., X430 [41]**



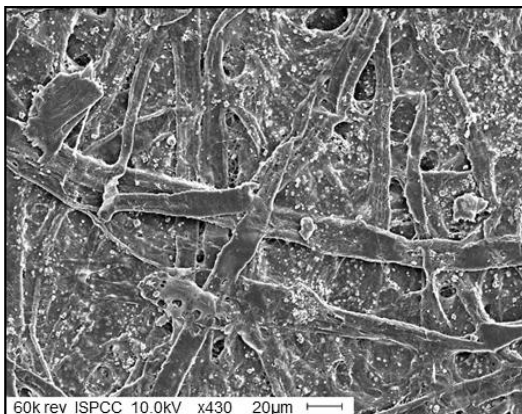**Fig. 31. PFI MILL, 45000 REV., X2500 [42]**



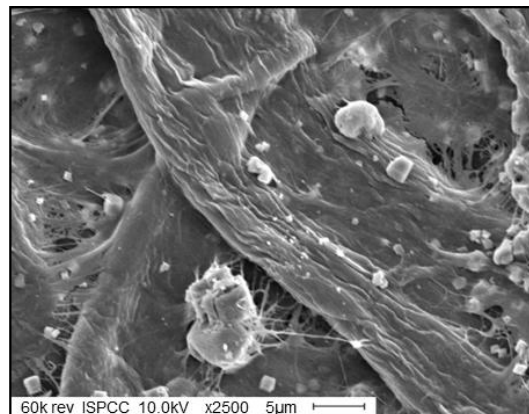**Fig. 32. PFI Mill, 60000 rev., x430 [43]**



**Fig. 33. PFI Mill, 60000 rev., x2500 [44]**

### 3.3.3. Summary valley beater and PFI mill scanning electron microscopy study

The SEM pictographs of the Valley Beater and PFI Mill beating trials from 0 stage to the high beating stage at 80 minutes for the Valley beater and 60000 revolutions for the PFI show similar results. No damage to the fibers is viable at a magnification of 2500 and agglomerations of ISPCC can be found. With increase of beating an increasing damage to the fiber wall can be recognized at the 2500 magnification level. In addition, an increase in external fibrils is visible with increased beating. Furthermore, with increasing in beating the fiber structure at a magnification of 430 shows an increasing dense fiber structure with decreasing pores and no pores visible at the highest beating level of 80 minutes and 60000 revolutions for the Valley Beater and PFI Mill respectively.

## 4. CONCLUSION

In a stirred pulp fiber suspension with 1.7% solids content a 20% $Ca(OH)_2$ suspension was added and calcium carbonate filler with the addition of $CO_2$ was precipitated *In Situ* with the fibers present. The starting pH was 12.2 and the final pH was below 7.5 after precipitation. The final filler content produced during the two production runs was 20.9% and 41.7%.

Laboratory beating tests were performed with a Valley Beater and APFI Mill using pure eucalyptus pulp with no filler content as the based trial and the two laboratory manufactured *In Situ* precipitated filler pulps.

When comparing the beating curves of the Valley Beater and the PFI Mill all two laboratory machines show similar differences/trends for the breaking length, tear and burst index.

All curves show that the pure EC-pulp has the highest strength for breaking length, tear and burst index, because EC-pulp doesn't have any added fillers. The pulp with a filler content of 41.7% shows the lowest breaking length, tear and burst index.

Valley Beater and the PFI Mill laboratory equipment operate different an exact comparison of the beating curves is not possible. For beating larger amounts of pulp and a more in-depth investigation the Valley Beater is the better laboratory solution due to the large amount of beaten pulp produced at a given time. The PFI mill is the better machine if only smaller amount of pulp are needed for the investigation, however multiple beating trials need to be performed which can be very time intensive.

The SEM pictographs of the Valley Beater and PFI Mill beating trials from 0 stage to the high beating stage at 80 minutes for the Valley beater and 60000 revolutions for the PFI show similar results. No damage to the fibers is visible at a magnification of 2500, and agglomerations of ISPCC can be found. With increase of beating an increasing damage to the fiber wall can be recognized at the 2500 magnification level. In addition, an increase in external fibrils is visible with increased beating. Furthermore, with increasing in beating the fiber structure at a magnification of 430 shows an increasing dense fiber structure with decreasing pores and no pores visible at the highest beating level of 80 minutes and 60000 revolutions for the Valley Beater and PFI Mill respectively.

## ACKNOWLEDGEMENTS

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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20. TAPPI T412 om-06 Moisture in pulp, paper and paperboard.
21. TAPPI T414 om-12. Internal tearing resistance of paper (Elmendorf-type method).
22. TAPPI T494 om-06. Tensile properties of paper and paperboard (using constant rate of elongation apparatus).
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24. Doelle K. PFI Mill. pdf-file.
25. Valley Beater SEM Micrograph, 0 min., x430. pdf-file.
26. Valley Beater SEM Micrograph, 0 min., x2500. pdf-file.
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