

OPTIMIZATION OF CHEMICAL USE FOR HIGHLY FILLED MECHANICAL GRADE PAPERS WITH PRECIPITATED CALCIUM CARBONATE

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Response surface methodology was used with four factors to screen for the best starch and optimize the use of chemicals in order to maximize precipitated calcium carbonate (PCC) filler retention in a peroxide-bleached TMP suspension. Three commercial starches were used in conjunction with colloidal silica and flocculant. The PCC loading level and the interactions between PCC level, starch, flocculant, and silica were investigated, and empirical models were constructed. The empirical process models were then employed to predict the retention and drainage. It was found that medium-charged cationic starch (S858) gave the highest total and filler retention, whereas high-charged cationic starch (S880) resulted in the best drainage. The ash content of the handsheet can be pushed up to 40% using the retention system with medium (S858) and high (S880) charged cationic starch. The high-charged cationic starch (S880) gave stronger paper, probably because of its higher affinity with the fiber and fines.

Keywords: Highly PCC filled paper; PCC retention; Response surface methodology; Paper properties; Starch partition

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INTRODUCTION

Mechanical grade papers benefit from the use of calcium carbonate filler because of gains in brightness, a key quality determinant of the performance-to-cost ratio (Ionides 2004). In general, paper produced with higher filler content has improved brightness and opacity. The replacement of wood fibres with less expensive mineral filler such as precipitated calcium carbonate (PCC) has an economic benefit, and it also mitigates to a certain extent the shortage of wood fibres. The paper industry has been able to manufacture paper with significant levels of filler loading with the use of existing machinery and relying on advances in wet end chemistry technology. However, the addition of increased amounts of filler reduces the strength and requires an effective retention system (Li et al. 2002). Starch is usually added to compensate for the strength loss (Baker 2005). The effective retention of starch in the paper sheet is a significant step to determine its performance. Cationic and amphoteric starches were found to be retained in the sheet primary through forming ionic bonds between cationic groups in the starch derivatives and carboxyl groups in pulp fibres or fines (Yoshizawa et al. 1998; Malton et al. 1998). In addition, a number of parameters also affect the starch performance in a

papermaking system (Blennow et al. 2003; Shirazi et al. 2003; Wågberg and Kolar 1996). Consequently, the papermaker needs to evaluate the performance of a starch product in order to make a judicious choice of the type of starch, starch dosage, and addition point. It should be noted that fiber fines are also effective as strengthening agents (Xu and Pelton 2005). Fines have the ability to bridge the filler-induced voids present in the fiber/fiber binding domain. Subramanian et al. (2008) explored the benefits from fiber fines and discussed a composite paper concept that contains up to 50-60 % PCC.

While starch is added primarily for the purpose of strength enhancement, it is also known that a properly selected starch can provide the additional benefit of performing as a retention aid and in some cases does not necessitate the need for a fixation agent (Modgi et al. 2007, 2008). Microparticle or nanoparticle retention aid systems have also been developed to help deal with retention/drainage and formation challenges related to increased amount of filler. There is extensive information on these retention systems in the literature (Alince et al. 2001; Hubbe 2005; Ovenden and Xiao 2002; Rojas and Hubbe 2004; Wiputri and Englezos 2007). In the past decades, many variations of the microparticle systems have been developed to further improve their performance. These include modifications of the physical and chemical structure of silica nano-particles.

It is of interest to explore whether it is possible to increase the level of loading beyond the current typical limit of about 25% by taking advantage of recent developments in starch and nanoparticle technologies. The objective of the present study was to evaluate the ability of three new starches to be used in conjunction with a new nanoparticle retention system to retain increased amounts of PCC. In order to optimize the chemical dosages, “laboratory trials” were carried out in which mill wood fiber suspensions were utilized. Laboratory retention and drainage tests have been traditionally carried out on a trial and error basis using a conventional “change one factor at a time” approach. This experimentation method is time consuming and not capable of reaching the true optimum because interaction among variables is neglected (Singh et al. 2009). To resolve this problem, response surface methodology (RSM) with a central composite design was employed to optimize the addition strategy of chemicals and evaluate their effects. An empirical process model was then constructed to predict the retention and drainage results. In addition, handsheets were prepared and their ash content, breaking length, and burst index were determined. In addition, the partition behavior of starch between fiber and fines was also studied.

MATERIALS AND METHODS

Pulp Furnish

The pulp used in the experiments was peroxide-bleached TMP that had a pH of 6.9 ± 0.2 and was supplied by a leading pulp and paper mill in British Columbia. It was a mixture of spruce, pine, and fir. PCC used in this work was an acid-tolerant PCC obtained from Specialty Minerals Inc (Bethlehem, Pennsylvania, USA). It had an average particle size of $2.71 \pm 0.15 \mu\text{m}$, brightness of 98% ISO, and a zeta potential of $-15 \pm 5 \text{ mV}$ at a concentration of 0.002 wt % in DDW, and the pH was 8.7 ± 0.1 .

Chemicals

Cationic tapioca starches with different nitrogen contents (CATO 304, Alias S304, 0.22-0.26 %N; S858, Alias S858, 0.55-0.60 %N; S880, Alias S880, 0.90-1.10 %N) were used in the experiments. These starches were supplied by National Starch ULC and had an average molecular weight of 3 million (Surrey, BC, Canada). Prior to use, the starches were cooked following the procedure provided by National Starch ULC. Cationic flocculant (acrylamide copolymer, average molecular weight is 10 million) supplied by Eka Chemicals (Magog, QC, Canada) was used. It had a branched structure and a charge density of 2.1 meq/g as determined by polyelectrolyte titration using 0.001N anionic PVSK. Silica with a mean size of 5 nm was supplied by Eka Chemicals (Magog, QC, Canada) as a 8.1 wt % suspension. Distilled and deionized water was used for the preparation of the polymer solutions. Potassium polyvinyl sulphate (PVSK) was used to determine the starch partition behavior between fiber and fines. It was received as a 0.001 N solution from BTG Americas (Pointe-Claire, QC, Canada).

Starch Cooking Procedure

Starch suspension (1.67 wt %) in a jar was placed in a boiling water bath, ensuring that the level of the bath water exceeded the level of the slurry in the jar. For the first few minutes, the starch slurry was continuously stirred until reaching the gel point. Once the gel point was reached, a rolling boil was sustained in the bath for a total of 30 minutes. Care was taken to top up the jar to avoid the net evaporation of water during the cook cycle. The suspension was stirred approximately every 10 minutes to help break down any un-burst grains until the 30 minutes cook cycle was reached. After the starch was cooked, it was cooled down to room temperature. Cooked starch prepared according to this procedure was used within 24 hours.

Process Water

Process water was the water obtained by centrifuging the pulp collected from the storage chest following the bleach tower. The pulp was placed in a screen bag and uniformly loaded into the centrifuge (Bock, Toledo, USA). During the centrifugation process, the water from the outlet was collected, while the pulp left in the screen bag was discarded. It was expected that the process water contained dissolved and colloidal substances. The average particle size of materials suspended in process water was found to be 388 μm as determined by the Malvern Mastersizer 2000. In addition, the zeta potential and the cationic demand were found to be equal to -16.5 mV and 2.2 $\mu\text{eq/g}$, respectively. This process water was used for the dilution of the pulp to simulate the papermaking process as much as possible (Wiputri 2008).

Retention and Drainage Experimental Procedure

Retention and drainage experiments were performed using the DFR-04 device from BTG Americas Inc. (Pointe-Claire, QC, Canada). The main components of the DFR-04 device are the dosing unit, stirring chamber, wire screen, and the balance. In addition, for retention measurements there is a two-way outlet valve with the RET 20 Lab sensor. For drainage measurements, there is a filtrate outlet. The dosing unit allows for the automatic addition of various chemicals to the pulp suspension. The sequence of

addition, the timing of such additions, and data collection were programmed in advance using the accompanying software.

A 50 mesh (200 μm hole) screen was used for the retention and drainage measurements, which were carried out following the procedure shown in Fig. 1. Y is the ratio between the weight of PCC and the weight of fibres. For retention measurements, the DFR-04 was first calibrated using a 1% TMP suspension loaded with PCC. The water in the filtrate was first removed through the vacuum filtration, and the fiber/fines left on the filter paper were collected. Then the fiber/fines were placed in a 100 °C oven for two hours to determine their dry weight. Then the solids were ashed using a 575 °C furnace for 12 hours. Details on the use of DFR-04 can be found in Modgi's Ph.D. thesis (2007).

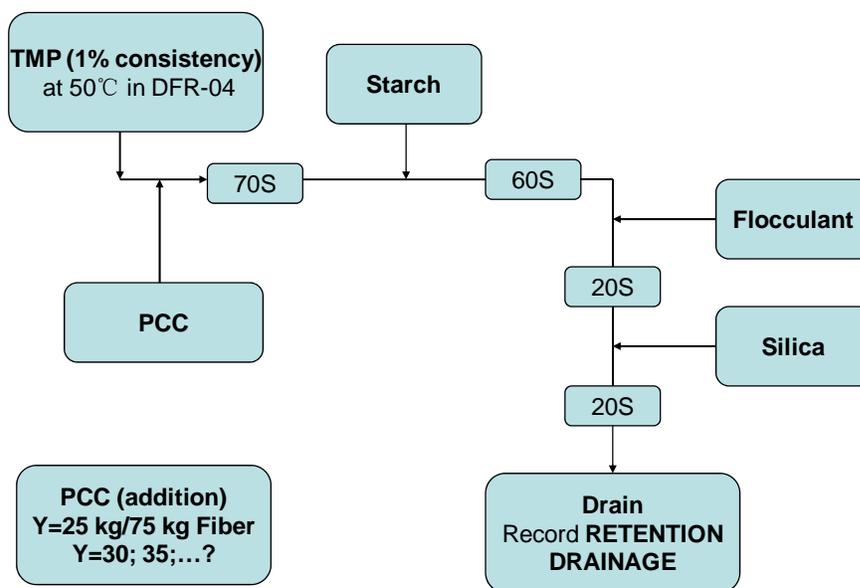


Fig. 1. Block flow diagram for the retention and drainage experiments

During retention experiments, 1 kg of TMP pulp at 1% consistency and at 50 °C was first placed inside the stirring chamber. The additives were then added to the pulp suspension and allowed to mix (see Fig. 1). Retention was measured according to the TAPPI Standard Method T261 cm-94. Each run was repeated three times, and the average total retention and filler retention are reported. For the drainage measurements, a sample of 1 kg of TMP pulp at 1% consistency and at 50 °C was filtered through a screen, and the filtrate weight was determined gravimetrically. The drainage weights reported were the weight of filtrate collected over 60 seconds.

Retention and Drainage Experimental Design

Response surface methodology using the central composite design (CCD) was used to study the effects of the PCC loading levels, dosages of starch, flocculant, and silica for higher PCC content in the final paper product. The experimental design and the

analysis of the results were performed by using JMP IN 4.0 (SAS Institute Inc., Cary, North Carolina). Analysis of variance (ANOVA) was carried out to study the effect of each factor and construct the prediction model. The simplified prediction model was obtained based on the P value (probability) with 95% confidence level.

According to the design, the total number of experiments is $2^n + 2n + n_0$, where n is the number of independent variables ($n=4$) and n_0 is the number of experiments at the central point ($n_0=6$). A 24 full factorial central composite design with five coded levels was used (Singh et al. 2009). The levels of the factors studied are shown in Table 1. The minimum and maximum ranges of chemicals were chosen on the basis of papermaking practice.

Table 1. Levels of the Factors Studied

Factor	Components	Levels of Factor Studied				
		a (-2)	-1	0	+1	A (2)
X_1	PCC (%)	25	30	35	40	45
X_2	Starch (kg/t)	8	9	10	11	12
X_3	Flocculant (kg/t)	0.1	0.2	0.3	0.4	0.5
X_4	Silica (kg/t)	0.2	0.3	0.4	0.5	0.6

The quadratic model for the prediction of the total retention, filler retention and drainage was expressed as follows (Singh et al. 2009),

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i \leq j}^n \sum_j \beta_{ij} X_i X_j + \sum_{i=1}^n \beta_{ii} X_i^2 \quad (1)$$

where β_0 is the intercept. The coefficients β_i , β_{ij} , and β_{ii} represent the linear, interaction, and quadratic effects, respectively.

Pulp Separation for Starch Adsorption Experiment

The Bauer-McNett classifier was used to separate the fiber and fiber fines, following TAPPI Standard T 233 cm-95, 1995. The pulp component that passed through the 200 mesh was taken as the fiber fines. The other component was identified as fibers.

DTPA Chelation Stage

Wood fibres have very strong ion exchange properties with metal ions, which mostly are bonded tightly with the pulp fibers. The metal ions have negative effects during chemical adsorption process on the fibers. Chelation was achieved with diethylene triamine pentaacetic acid (DTPA) at an addition level of 0.5% DTPA on oven dry pulp at a pulp consistency of 10%, and a temperature of 50 °C for 30 minutes before the adsorption experiments in an effort to remove most of the bonded metal ions from the fiber surface (Ni 2005). The pulps were then washed with deionized distilled water to remove the metal ions and unreacted DTPA.

Starch Partition Behavior between Fiber and Fines

Adsorption experiments of cationic starches on cellulose fibers/fines were carried out at 50 °C without further adjustment of the pH value of the pulp during the experiment. The consistency of the pulp suspension used was 0.1%. The fibers were left in contact with the starch solutions for five minutes under constant stirring at 200 rpm. This time was found in our laborator (Preissinger 2009) to be adequate for starch to reach the steady state adsorption on fibers and agrees with literature (Shirazi et al. 2003a). After filtration through a filter paper, the equilibrium concentration of cationic starch was determined by colloidal back titration with potassium polyvinyl sulphate (PVSU) solution, using the Particle Charge Detector (PCD, Müttek, Herrsching, Germany) (Sang and Xiao 2008). The blank experiment (no fiber) was also carried out following the above procedure. The amount (A) of adsorbed starch in mg/g was calculated with equation 2,

$$A = \frac{(V_B - V_S)}{V_B} \times \frac{M_P}{M_F} \quad (2)$$

where V_B is the PVSU volume consumed for the blank sample, V_S is the PVSU volume consumed for the adsorption sample, M_F is fiber mass, and M_P is the mass of added starch.

Handsheet Making Apparatus

A modified former was used to prepare handsheets (Montgomery 2010). Vacuum was used to simulate the actual papermaking process. This was done to study how the pulp suspension and filler distribution were affected when the forming fabric passes over a suction box. Briefly, the apparatus is constructed of a 3" diameter clear acrylic circular cylinder below a forming fabric. Another circular cylinder is attached above the forming fabric, and a gasket is placed around the outside to provide an airtight seal. A vacuum chamber is connected to the bottom of the test chamber by a 3/4" PVC pipe and electrically actuated solenoid valve. The vacuum chamber pressure can be adjusted to the desired pressure by an attached vacuum pump (Montgomery 2010).

Handsheet Properties Measurement

Typically in the pulp and paper industry the TAPPI T 494 om-96 method is employed to determine the tensile properties of paper. The standard sample length for the TAPPI method is 100 mm. The handsheet made from the apparatus in the present study had a diameter of around 3" (76 mm). Therefore, it was impossible to follow the TAPPI method. The COM-TEN Universal tester is another laboratory-scale apparatus used for performing tensile strength. The advantage is that it can be used for smaller length samples. Tensile tests of two office printing paper samples were carried out on both the L&W tensile tester and the COM-TEN Universal tester to check the reliability of the COM-TEN Universal tester. The tensile strength for paper sample 1 was 23.02 ± 0.43 MPa, as measured by L&W tensile tester. The corresponding tensile strength was 25.35 ± 0.79 MPa, as measured by the COM-TEN Universal tester. The tensile strength for paper sample 2 was 41.21 ± 0.63 MPa, as measured by L&W tensile tester. The corresponding tensile strength was 39.58 ± 0.89 MPa, as measured by COM-TEN Universal tester. It was concluded that the Com-Ten instrument was adequate to perform the tensile testing.

In this paper, breaking length, burst index, and ash content of the handsheet are reported. Breaking length, a measurement of tensile strength of paper, is the length beyond which a strip of paper of uniform width would break under its own weight if suspended from one end. Burst index is the quotient of the bursting strength of a paper and its grammage in the conditioned state as defined in the standard method of test. The burst index of the handsheets was determined according to TAPPI T 403 om-02. Ash is the residue left after complete combustion of paper at 575 °C. It is generally expressed as percent of original test sample and represents filler content in the paper. The ash content of the handsheets was determined according to TAPPI T211 om-93.

RESULTS AND DISCUSSION

A total of 30 experiments for each one of the three starches (S304, S858, S880) were conducted. In addition, another 30 experiments were also carried out to determine the corresponding drainage values for each starch. Table 2 shows the retention and drainage results for all three starches. As seen from the measurements, the retention aid program using medium charge density starch (S858) gave the highest retention, whereas the starch S880 gave best drainage performance. The S304, which has the lowest nitrogen content, gave the poorest retention and drainage. Not surprisingly, the maximum retention and drainage values were obtained at the highest dosages of starch, flocculant, and silica for all these three starches. In the following part, the significant factors based on the analysis of variance (ANOVA) are presented for starch S858 and S880 separately in order to distinguish the effect of each factor and their interactions. Based on the ANOVA results, the regression models were also constructed.

ANOVA for the Retention System Using S858

Table 3 shows the significant factors based on the analysis of variance results for the retention system using S858. All the main effect terms were found to be extremely significant for all these three responses. The three interaction effects involving starch S858 were found to be statistically significant in filler retention. A very significant synergism between starch S858 and silica was responsible for the total and filler retention improvement. The interactions between PCC and silica, as well as flocculant and silica were found to play a significant role in improving the drainage performance. Khosrevani et al. (2010) studied the effect of the cationic starch-anionic nanosilica system on the retention and drainage using a 85% bleached chemical eucalyptus/15% bleached chemical softwood pulp system. Their observations indicated that the nanosilica performance relied on the introduction of nanoparticles into the cationic starch-fines-fibers network, converting the fiber mat on the forming wire into a porous structure that is responsive to retention and drainage. In the present study, when the silica was added in the TMP suspension with starch and flocculant, the interaction mechanism became more complicated. This happens probably because the microfloculation of fines and fillers, which converts the fiber network to an open structure similar to the fines-free ones, took place with the help of the cationic polyelectrolyte and nano-particles.

Table 2. Full Experimental Design and the Responses

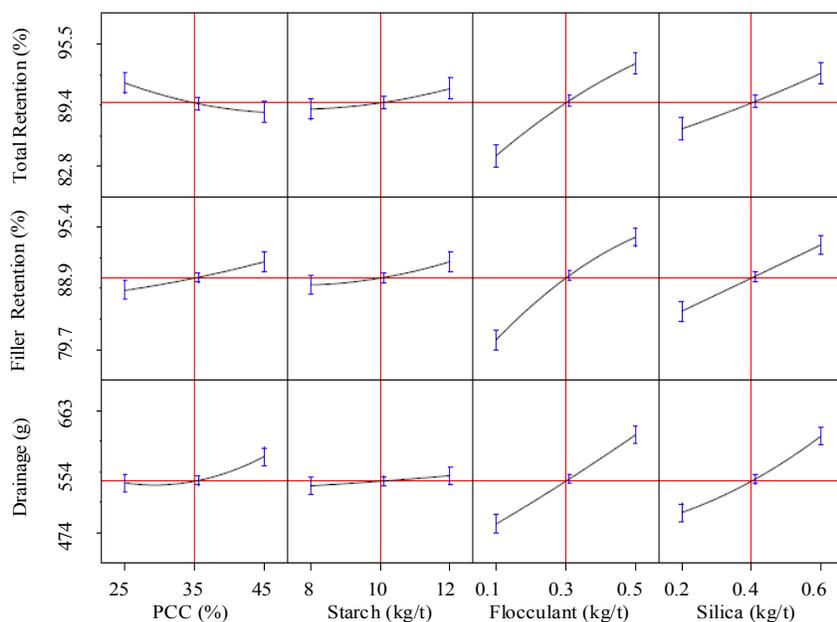
Sample ID	Pattern	PCC (%)	Starch (kg/t)	CPAM (kg/t)	Silica (kg/t)	Total Retention (%)			Filler Retention (%)			Drainage (g)		
						S304	S858	S880	S304	S858	S880	S304	S858	S880
1	a000	25	10	0.3	0.4	86.1	91.2	89	83.9	86.8	82.3	386	555	591
2	----	30	9	0.2	0.3	82	86.1	83.4	73.2	80.9	75	325	492	534
3	---+	30	9	0.2	0.5	82.9	88.4	84.7	74.8	84.9	77.6	365	528	628
4	--+-	30	9	0.4	0.3	88.6	91.3	84.4	85.3	89.1	77	352	554	628
5	-++	30	9	0.4	0.5	90.2	93.1	84.6	87.8	92.7	77.5	380	632	721
6	+-+	30	11	0.2	0.3	84.5	88.3	87	77.5	84	81.4	371	505	615
7	+++	30	11	0.2	0.5	85.2	89.9	87.5	79.6	88.9	83	367	547	651
8	++-	30	11	0.4	0.3	89.3	90.6	85.7	86.1	88.6	79.6	377	552	654
9	+++	30	11	0.4	0.5	91.6	95.5	88.2	89.9	95.4	83.8	390	602	780
10	0a00	35	8	0.3	0.4	86.4	88.6	83.8	84	87.8	80.6	368	540	590
11	00a0	35	10	0.1	0.4	77.6	83	85.5	70	79.7	83.1	344	492	529
12	000a	35	10	0.3	0.2	83	86.4	83.4	79.6	84.2	79.9	323	507	559
13-1	0000	35	10	0.3	0.4	86.5	89.6	84.8	84.6	89	81.3	386	554	656
13-2	0000	35	10	0.3	0.4	87.2	89.6	84.8	85.2	88.9	81.3	386	554	656
13-3	0000	35	10	0.3	0.4	86.5	89.6	84.8	84.6	88.9	81.3	386	554	656
13-4	0000	35	10	0.3	0.4	86.4	88.8	84.8	84.7	88.1	81.3	387	554	656
13-5	0000	35	10	0.3	0.4	86	89.4	84.8	84	89.2	81.3	378	554	656
13-6	0000	35	10	0.3	0.4	86	89.4	84.8	84	89.2	81.3	381	554	656
14	000A	35	10	0.3	0.6	85.1	92.3	89.4	83.4	92.9	88.6	396	619	707
15	00A0	35	10	0.5	0.4	91.4	93.9	88	92	94.7	86.9	396	618	708
16	0A00	35	12	0.3	0.4	88.4	90.6	88.6	87.5	90.5	88.4	391	566	689
17	+---	40	9	0.2	0.3	79.4	85.1	81.1	77.6	85.1	78.9	334	501	573
18	+++	40	9	0.2	0.5	81.5	86.9	82.9	80.1	87.8	81.5	359	565	637
19	++-	40	9	0.4	0.3	87.2	90	84.1	88.7	91.3	83.7	387	573	673
20	+-+	40	9	0.4	0.5	89.7	92	82.7	91.1	93.5	81.3	405	638	730
21	+++	40	11	0.2	0.3	81.1	84.6	83.3	79.6	84.6	81.9	358	509	595
22	++++	40	11	0.2	0.5	83.9	90	88.5	83.4	90.8	89.3	385	571	710
23	+++	40	11	0.4	0.3	89	89.7	84.1	89.9	91.1	83.3	397	576	668
24	++++	40	11	0.4	0.5	91.9	92.7	88.7	93.4	94.4	88.9	419	663	763
25	A000	45	10	0.3	0.4	83.3	88.2	85.3	86	90.8	87.7	407	585	624

The prediction profiles are shown in Fig. 2. The 95% confidence intervals for the predicted values are also shown by error bars above and below each marker. As seen, the PCC had a negative effect on the total retention, while for the filler retention and drainage, the effect was positive. The positive effect of increased PCC amount on the drainage is because PCC is easier to dehydrate than the fiber. Flocculant and silica played more significant roles than starch, based on the steepness of the three prediction curves for the chemicals. It is also noted that flocculant and silica improved the responses throughout the entire experimental dosage range.

Table 3. Significant Factors for the S858 Retention System

Factor	Total Retention	Filler Retention	Drainage
PCC	Extremely Significant	Extremely Significant	Extremely Significant
Starch	Extremely Significant	Extremely Significant	Significant
Flocculant	Extremely Significant	Extremely Significant	Extremely Significant
Silica	Extremely Significant	Extremely Significant	Extremely Significant
PCC*Starch	---	Significant	---
PCC*Silica	---	---	Significant
Starch*Flocculant	---	Significant	---
Starch*Silica	Very Significant	Very Significant	---
Flocculant*Silica	---	---	Significant
PCC*PCC	---	---	Significant
Flocculant*Flocculant	---	Significant	---

---: Not Significant

**Fig. 2.** Prediction profiles for the retention system using S858

ANOVA for the Retention System Using S880

The significant factors based on the analysis of variance for the retention system using S880 appear in Table 4.

Table 4. Significant Factors for the S880 Retention System

Factor	Total Retention	Filler Retention	Drainage
PCC	Very Significant	Extremely Significant	Significant
Starch	Extremely Significant	Extremely Significant	Extremely Significant
Flocculant	---	---	Extremely Significant
Silica	Extremely Significant	Extremely Significant	Extremely Significant
Starch*Silica	Significant	Significant	---

---: Not Significant

For the total retention and filler retention responses, the change of flocculant dosages did not have any statistically significant effect, which is different from its behavior in the retention system with starch S858. This is probably because starch S880 has a much higher charge density than S858. In addition to functioning as strength agent for final paper and fixing agent for dissolved and colloidal substances, starch S880 also partly replaces the function played by the flocculant in retention. A significant interaction effect between starch S880 and silica was found, which may contribute to improve the total and filler retention. This interaction effect was also found for S858 and silica. All main effect terms were extremely significant for the drainage. The prediction profiles as shown in Fig. 3 clearly show the effect of each factor. The slope of S880 is much greater than that of S858. This is probably because of the higher charge density of S880 than S858; more cationic charge was introduced to the flocculation system for the same starch dosage increment. More significant flocculation would occur, resulting in improved retention under the same starch dosage increment. The slope of flocculant was much smaller than those in the retention system using starch S858 for the total retention and filler retention response.

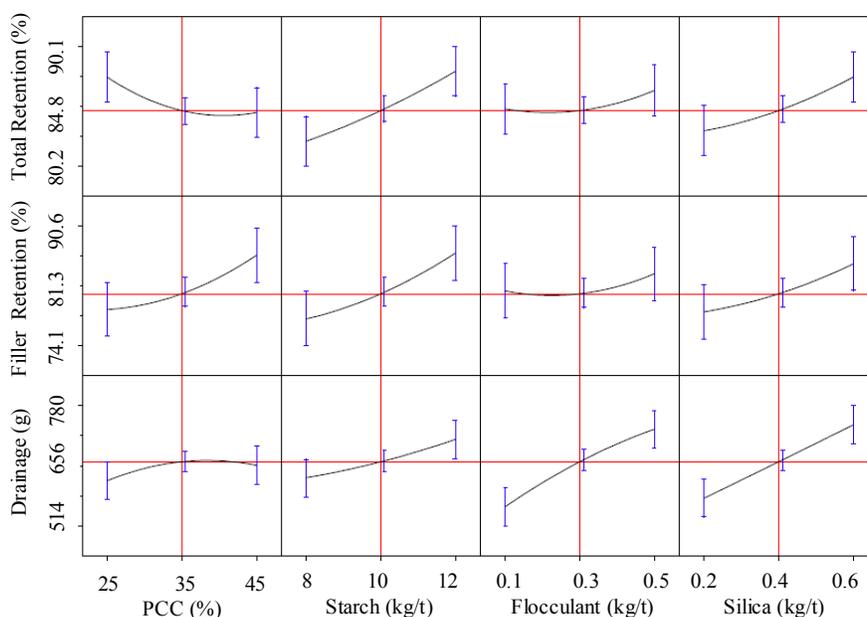


Fig. 3. Prediction profiles for the retention system using S880

Model Construction and Validation

The regression model was constructed to predict the actual operating system. The estimated parameters for all main and crossed effects are reflected in equations shown in Table 5 for the retention system using S858 and S880. X_1 , X_2 , X_3 and X_4 are defined in Table 1.

To validate the accuracy of regression model, six additional experiments at the patterns (Table 6) other than those shown in Table 2 were performed, and the results were compared with the model predicted value. The experiment IDs in Fig. 4 correspond to those in Table 6. As seen from Fig. 4, the agreement was very good.

Table 5. Regression Model for the Retention System Using S858 and S880

	S858 Prediction Equation	S880 Prediction Equation
Total Retention	$Y=89.4-0.763X_1+0.529X_2+2.39X_3+1.44X_4+0.438X_2X_4$	$Y=84.8-0.729X_1+1.45X_2+1.11X_4+0.681X_2X_4$
Filler Retention	$Y=88.9+0.919X_1+0.748X_2+3.29X_4+2.13X_4-0.378X_1X_2-0.416X_2X_3+0.553X_2X_4-0.335X_3^2$	$Y=81.3+1.86X_1+2.26X_2+1.65X_4+0.969X_2X_4$
Drainage	$Y=554+10.2X_1+3.92X_2+34.3X_3+29.5X_4+4.50X_1X_4+4.75X_3X_4+4.45X_1^2$	$Y=656+8.50X_1+21.3X_2+43.0X_3+40.7X_4$

Table 6. Experiment Patterns for Model Validation

Expt ID	Pattern	PCC (%)	Starch (kg/t)	Flocculant (kg/t)	Silica (kg/t)
1	-0++	30	10	0.4	0.5
2	--0+	30	11	0.3	0.5
3	00++	35	10	0.4	0.5
4	0+0+	35	11	0.3	0.5
5	+0++	40	10	0.4	0.5
6	++0+	40	11	0.3	0.5

Starch Adsorption and Partition

The results for starch adsorption on washed hydrogen peroxide bleached pulp show that S880 gave the highest adsorption amount (29.6 mg/g fiber) on fiber surface, followed by the S304 (13.0 mg/g fiber) and S858 (6.5 mg/g fiber). For S304 and S858, the starch adsorption amount was inversely proportional to its nitrogen content. This is in accordance with previous work (Wågberg and Kolar 1996). The theoretical adsorption amount of cationic S880 starch on the pulp surface should be at about 3.2 mg/g pulp based on the charge neutralization theory (Wågberg and Kolar 1996). The experimental result shows the actual adsorption amount of S880 on the pulp surface reached 29.6 mg/g, which was much higher than the theoretical value. This is probably because in the other two cases (starches S858 and S304) the interaction of cationic groups with the hydroxyl groups of the fiber surface was too weak and the starch was desorbed very easily. The higher adsorption amount may also be explained by the higher tendency of starch S880 to form clusters because of hydrogen bonding between hydroxyl group and polymer entanglement (Shirazi et al. 2003b).

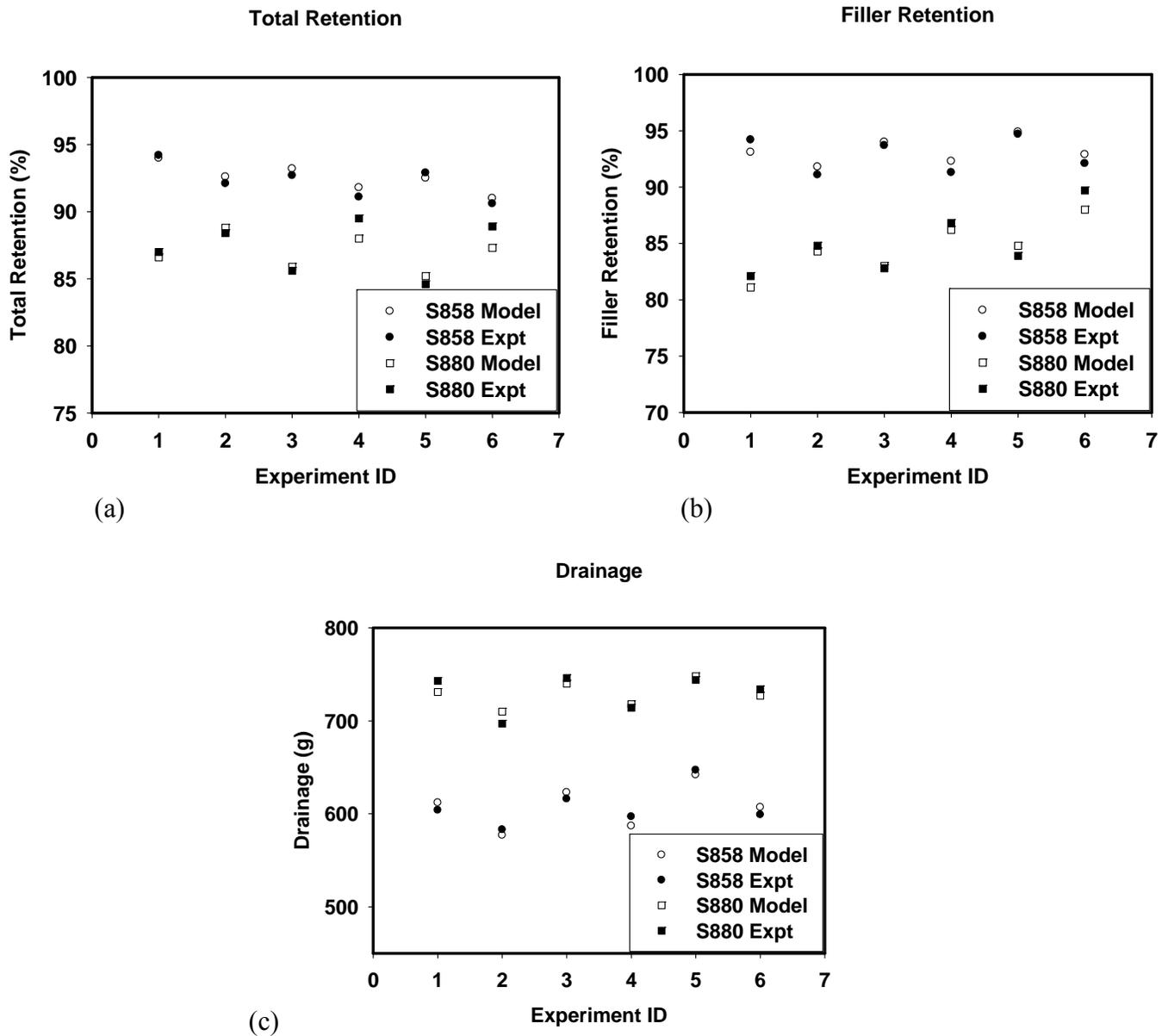


Fig. 4. Experiment and predicted values for (a) Total Retention, (b) Filler Retention, (c) Drainage

The pulp zeta potential after starch adsorption is shown in Fig. 5. As seen, The higher the starch charge density, the less negative the pulp zeta potential, indicating more charge was introduced to the pulp suspension for high charge density starch and its high affinity to the pulp.

Fig. 6 shows the starch partition behavior between fiber and fines. The adsorbed amount of these three starches was found to increase linearly with the increase of fines ratio in the pulp. This is due to the higher surface area of fines than that of fiber. The very high affinity of starch S880 with fiber and fines can improve the permeability of the pulp. This is supported by the fact that the best drainage performance was achieved with the retention system using S880, as shown in Table 2.

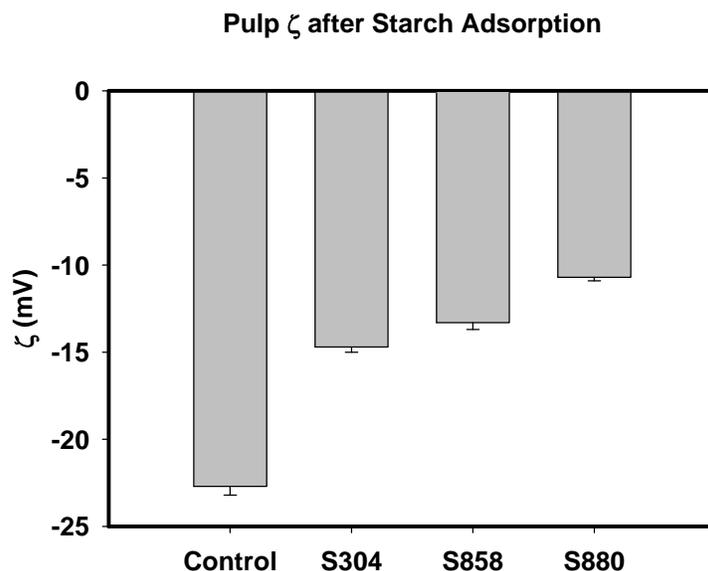


Fig. 5. Pulp zeta potential after starch adsorption

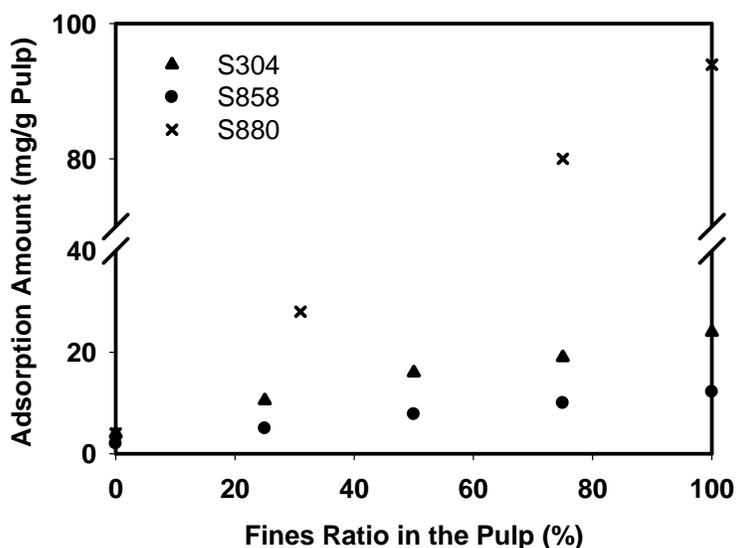


Fig. 6. Starch partition on fiber and fines

Handsheet Properties

The handsheets were prepared using a modified handsheet former with vacuum suction based on the PCC content and chemical dosage as shown in Table 2. The ash content, breaking length, and burst indices of the handsheets are shown in Figs. 7 and 8. The sample IDs in Figs. 7 and 8 correspond to those in Table 2. With the help of the retention chemicals, the ash content of the handsheet could be pushed up to 40% for S858 and S880 retention systems. The S858 retention system always gave slight higher ash content than the S880 retention system. This is in accordance with the Mutek DFR-04 retention results, as shown in Table 2. The S880 resulted in higher breaking length and

burst indices. One possible reason is the slightly lower ash content of the handsheet obtained with the S880 retention system. The other one, which is maybe more important, is the different adsorption behaviors of these two starches. S880 had a much higher affinity to fibers and fines than S858, as shown in Fig. 6. The high starch affinity with fibers will directly promote interfiber bonding (Stratton 1989) and thus the paper strength. This is supported by the paper physical properties as shown here.

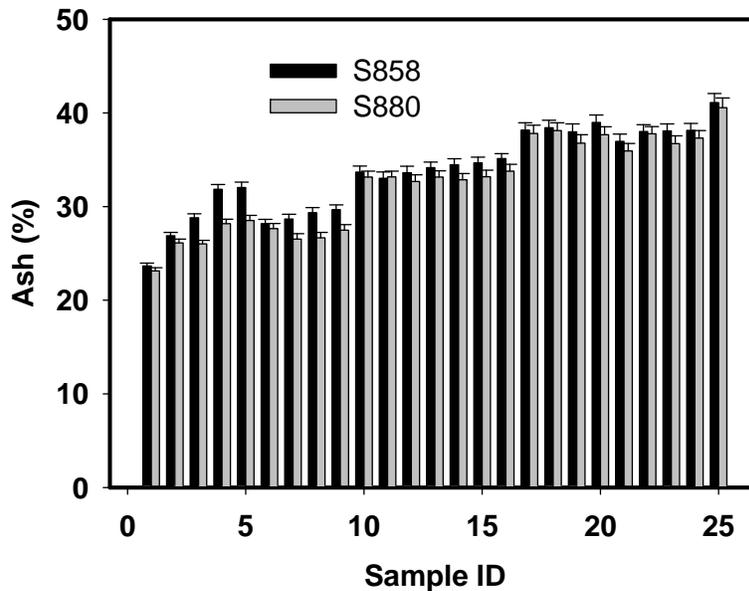


Fig. 7. Ash content of the handsheet made from S858 and S880

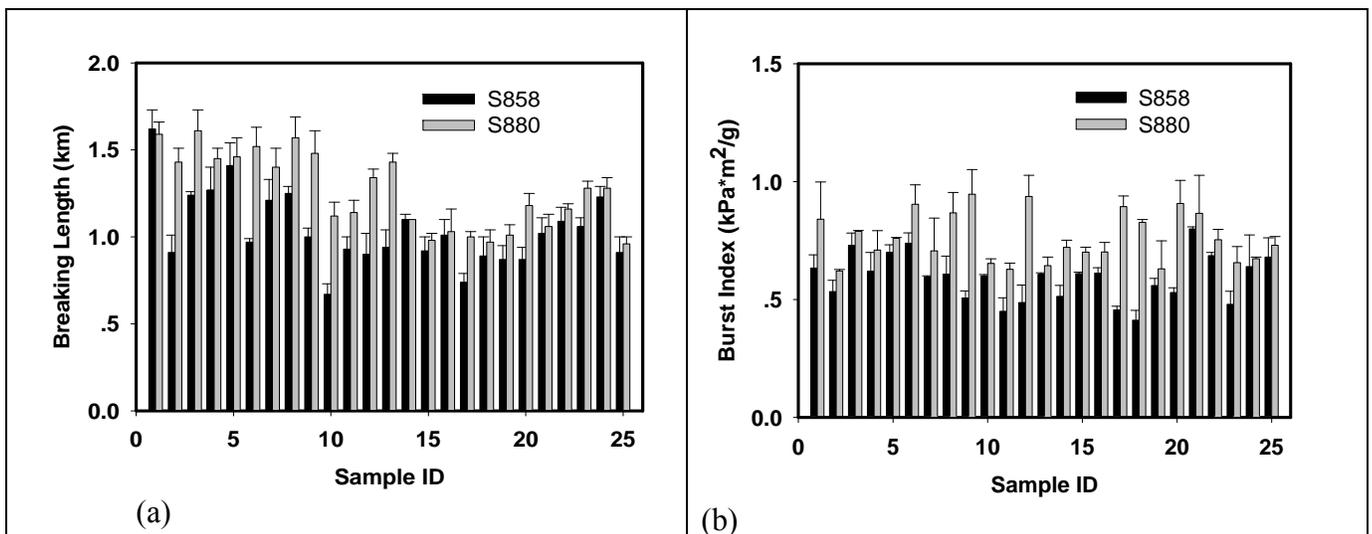


Fig. 8. Comparison of (a) breaking length (b) burst index of S858 and S880 retention system

CONCLUSIONS

The retention aid program using medium-charge starch (S858) gave the highest retention, and high-charge starch (S880) resulted in the fastest drainage. A significant synergism was found between starch (S858 and S880) and silica, which improves the retention. Empirical models constructed in this work can accurately predict the retention and drainage under various conditions. The starch adsorption amount was inversely proportional to its nitrogen content for S304 and S858. The S858 retention system always gave slightly higher ash content than the S880 system. The S880 retention system resulted in the higher breaking length and burst indices, possibly because it has a higher affinity for fibers and fines than the S858 system.

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