Research paper

Synergy of Bentonite and Starch Enhances the Physical Properties of Handsheets from Recycled Pulp

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【Summary】

In this study, we investigated the feasibility of applying bentonite to the papermaking wet end to retain raw starch in paper sheets. The results indicated that an increased starch dosage reduced the first-pass retention (FPR), while a polymer and starch showed an interaction and was helpful for increasing the FPR. However, the interaction of starch and bentonite, and the triple interaction among polymer, starch, and bentonite were detrimental to the FPR. The interaction of a polymer and bentonite hampered the decrease in the white water chemical oxygen demand. The main effect of the polymer and bentonite application was to improve static drainage. On average, the ring-crush strength of the resulting paper increased 31%, with a maximum gain of 53%. With respect to the main effects, increasing starch and bentonite dosages were both helpful for the ring-crush strength; conversely, the polymer tended to decrease the ring-crush strength. As for interactions, all were detrimental to gains in the ring-crush strength. On average, the burst index increased 25%, and the maximum gain was 61%. For the main effects, an increase in the starch dosage enhanced the burst index, while polymer and bentonite combination reduced the burst index. All interactions were found to detract from increasing the burst index.

Key words: starch, bentonite, recycled pulp, ring-crush strength, bursting strength.

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研究報告

膨皂土及澱粉對於提升回收紙漿物理性質的協同效應

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摘 要

本研究主要探討在造紙濕端添加膨皂土來留存生澱粉在紙張中，以提升手抄紙的物理性質的可行性。實驗結果顯示提高澱粉添加量會不利於一次保留率，高分子助凝劑及澱粉的相互效應有助於提升一次保留率。但是澱粉及膨皂土的相互效應及高分子助凝劑、澱粉、膨皂土的三階相互效應則不利於一次保留率。高分子助凝劑及膨皂土的相互效應不利於降低白水中的COD。高分子助凝劑及膨皂土的主效應會改善靜態濾水度。手抄紙的平均環壓強度提升31%，最高可以提升到53%。對於主效應而言，提高澱粉及膨皂土的添加量，會提升環壓強度；但高分子助凝劑則會有負作用。對於相互效應而言，所有相互效應皆不利於環壓強度的提升。對於主效應而言，提高澱粉的添加量，會提升破裂強度；但高分子助凝劑及膨皂土則會有負作用。對於相互效應而言，所有相互效應皆不利於破裂強度的提升。

關鍵詞：澱粉、膨皂土、回收紙漿、環壓強度、破裂強度。

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INTRODUCTION

After fibers, starch is the second largest raw material used in papermaking. The main domains of its applications according to the volume are surface sizing (60~68%), wet end additives (16~20%), coating binders (11~15%), sprays to increase ply-bonds (5%) etc. For industrial papers (liner and medium), cationic starch is often used in the wet end, and oxidized starch is often used at the size press or as a ply-bond spray to increase the physical properties of the paper (Mishra 2005). When used in the wet end, starch not only needs to be cationized (Deters 1990, Glittenberg 1993, Vihervaara 1994, Wang et al. 2011), anionized (Schneider 1992, Brouwer et al. 2002), or amphoterized (Nester and Maliczyszyn 2001) to enhance retention, but also requires cooking to gelatinize it, which allows proper curing online. At present, if raw starch is used, it has to be depolymerized to a substantial degree by hydrolysis before application. This step is costly and also hinders the starch from developing its full potential.

Bentonite, a clay mineral with a platy structure possesses the capacity for swelling delamination in a water medium. It is widely used in the papermaking wet end as a microparticle dual agent with polyacrylamide retention aids to enhance the first-pass retention (FRP) and to reduce the chemical oxygen demand (COD) loading of white water (Kundson 1993, Xu and Deng 1999, Asselman and Garnier 2001). Cationic modified bentonite, such as by primary or quaternary amino groups, and polyaminoamide-modified montmorillonite have proven to be effective in enhancing the flocculation of clay fillers (Liu et al. 2003).

Darvishzadh et al. (2014) used cationic starch and bentonite as retention aids to increase the drainage and tensile, tear, and burst indices of printing and writing paper. Their results indicated that a 0.4% dose of bentonite and a 1.5% dose of cationic starch could achieve the highest drainage; whereas 0.2% bentonite and 1.0% cationic starch produced the best strength properties.

At present, most industrial paper mills use a size press or coater to effect the surface application of starch, and to increase the physical properties of the resulting paper. However, due to operational considerations and drying cylinder temperature constraints, machine speeds often cannot be increased, causing increasing bottlenecks to production. The traditional mode of internally adding cationic starch at 1.5~2.0%, however, proved ineffective at increasing paper physical properties, and allowing total substitution of surface applications (Janson 1991). In recent years, there was a report of the development of using high dose of raw starch (10~15%), increased retention by bentonite, and gelatinization and curing the starch at the group I and II drying cylinders, which allowed total substitution for the size press, while the products achieved similar property. There is no research on the scenario reported so far, however.

This study focused on wet end applications of starch and by taking advantage of the retention effect of bentonite, retaining the starch granules on paper sheets, then through simulation of the group I and II drying cylinders, gelatinizing and curing the starch so that the physical properties of industrial paper handsheets were improved. The experimental parameters included dosages of a cationic retention aid (polymer), tapioca starch, and bentonite. Through the main and interactive effects of the 3 parameters, the influences on the FPR, the COD of white water, static drainage time, and handsheet properties of the ring-crush strength and burst index were delineated.

MATERIALS AND METHODS

Effects of the polymer, starch, and bentonite on the wet end and handsheet properties were investigated with a 2^3 factorial experimental design. The 2 levels of the parameters were the polymer at 100 and 500 ppm (midpoint at 300 ppm), starch at 10 and 15% to dry pulp (midpoint at 12.5%), and bentonite at 3000 and 10,000 ppm (midpoint at 6500 ppm). The experimental runs are shown in Table 1.

Each experimental set was replicated once more to allow an estimate of the standard deviation (SD). In total, there were 18 experimental sets. Handsheets were prepared using a standard handsheet mold, but in order to simulate typical corrugating medium, the grammage was 130 g m^{-2}. To simulate the heating effect of mill drying cylinders, a handsheet was placed between 2 copper plates (as shown in Fig. 1) which were preheated to 130℃, and pressed for 1 min by the weight of the plate to allow complete gelatinization of the starch contained in the sheet.

Materials

Wastepaper pulp was directly collected from the machine chest of a central Taiwan paper mill. It was comprised of 100% domestic collected old corrugated carton (OCC), 400 mL Canadian Standard Freeness (CSF). After the pulp was dewatered, it was kept in a freezer until use. The cationic retention aid polymer was polyacrylamide of the dry powder type, Percol 182, with a solids content of 90.4% from Taiwan Ciba Co. (now a part of BASF, Germany). Bentonite was AP1, Taiwan Ciba Co. (now a part of BASF, Germany),

Table 1. The 2^3 factorial table of experimental conditions

Run	Polymer (X_1) (ppm)	Starch (X_2) (%)	Bentonite (X_3) (ppm)
1	100	10	3,000
2	500	10	3,000
3	100	15	3,000
4	500	15	3,000
5	100	10	10,000
6	500	10	10,000
7	100	15	10,000
8	500	15	10,000
9	300	12.5	6,500

Fig. 1. A set of self-made copper heating plates.

with a moisture content of 9%, a surface area of 348 m^2 g^{-1}, and a cationic exchange capacity of 57.6 meq (100 g)$^{-1}$. The tapioca starch was from SMS corporation, Pathum Thani, Thailand, with a moisture content of 13%, ash of 0.20%, and 1% residue was retained on a 150-μm sieve.

Apparatus

The electronic balance to 4-digits was from Mettler Toledo aB204-S, with a precision of±0.1 mg (Taipei, Taiwan). The 306-2 disintegrator, the 306-A handsheet mold, the 306-B dryer, the 306-C press, the 3740-D ring crush tester, and the 3720-AD-BD bursting strength tester were from Lesson Instruments (New Taipei City, Taiwan). The CVD-452 oven was from Shang-Mei Instruments (Taichung, Taiwan), and the COD automatic reflux digestor was from Galaxy Instruments (Jiangsu Province, China).

Methods

Wastepaper pulp was diluted to a consistency of 1%, and in a randomly selected order, the starch (with a solids content of 87%), bentonite (with a solids content of 91%) and polymer (prepared as a solution with a 15% solids content) in designated amounts were added sequentially while stirring. The homogenized pulp was formed into handsheets of 130 g m^{-2} grammage, and the FPR of the drained water was determined (which was calculated from 2 consistency measurements:

the wastepaper pulp consistency and the white water consistency). COD loading of the white water was determined. The handsheets were pressed between 2 copper plates preheated to 130℃ for 1 min to gelatinize and age the starch. After conditioning in a constant temperature and humidity (CTH) room overnight, the grammage, ring-crush, and burst indices of the handsheets were determined.

Standards used in the procedure were as follows: handsheet, TAPPI standard T205 sp-02; grammage, TAPPI standard T410 om-93; ring-crush strength: TAPPI standard T818 cm-07; burst index: TAPPI standard T810 om-06; and COD: Taiwan National Institute of Environmental Analysis (NIEA), standard W517.50B.

RESULTS

Analytic results of the wet end and physical properties of the 2^3 factorial design are shown in Tables 2 and 3, respectively. Each experimental set was replicated twice for calculating SDs. In Table 2, wet-end properties of the FPR, white-water COD, and drainage time are presented. In Table 3 physical properties of the resulting paper of the ring-crush strength and burst index are presented, After a factorial analysis, the main and interactive effects of the response variables are summarized in Table 4.

DISCUSSION

With respect to the effects on the wet end properties, Table 4 shows that for the FPR results, the main effect of the polymer (-0.054) and interactions of the polymer and starch (0.028) and starch and bentonite (-0.020), and triple interactions of the polymer, starch, and bentonite (-0.017) were statistically significant. The interaction of the polymer and starch (18.0) for COD, and the interaction of the polymer (-2.25) and bentonite (-2.30) for the static drainage time were also singificant. Thus, for the FPRs, an increasing starch dose strongly contributed to poorer retention, which is reasonable, as starch granules are not likely to be well retained onto fibers. The interaction of the polymer and starch was helpful at increasing the FPR, meaning that when both doses increased, there was a synergistic effect. However, the interaction of starch and

Table 2. Wet-end results of the 2^3 factorial design

Run	FPR		COD		Drainage time	
	(%)	SD	(ppm)	SD	(s)	SD
1	98.5	0.42	57.6	20.4	13.1	0.14
2	95.6	1.56	36.0	10.2	11.2	0.28
3	91.4	1.13	57.6	0	13.2	0.21
4	95.7	1.41	36.0	10.2	11.0	0.00
5	99.1	0.42	43.2	0	10.8	0.28
6	96.9	1.13	72.0	20.4	8.3	0.35
7	90.4	2.12	43.2	10.2	11.3	0.35
8	90.6	1.56	43.2	0	8.9	0.14
9	94.4	1.84	57.6	0	7.8	0.13

Note: The blank condition (with no addition of chemical) of the first pass retenetion (FPR), chemical oxygen demand (COD), and drainage time were 83.4%, 39.6 ppm, and 14.3 s, respectively.

SD, standard deviation.

Table 3. Physical properties of the 2^3 factorial design

Run	Ring-crush strength ($kN\ m^{-1}$)	SD	Burst index ($kPa \cdot m^2\ g^{-1}$)	SD
1	15.6	0.57	1.50	0.059
2	15.8	0.86	1.81	0.021
3	18.0	0.18	2.03	0.051
4	15.7	0.73	1.52	0.011
5	16.2	0.16	1.25	0.021
6	17.0	0.28	1.31	0.046
7	19.6	0.57	2.17	0.049
8	14.5	0.14	1.68	0.095
9	17.5	1.28	1.92	0.080

Note: The blank condition (with no addition of chemical) handsheets had a ring-crush strength of 12.8 $kN\ m^{-1}$ and burst index of 1.35 $kPa \cdot m^2\ g^{-1}$.
SD, standard deviation.

Table 4. Main effects and interaction results of the 2^3 factorial design

Effect	Main effect: Criteria	X_1	X_2	X_3
FPR	±0.016	0.004	**-0.054**	-0.012
COD	±13.8	-3.6	-7.1	3.6
Drainage time	±0.32	**-2.25**	0.25	**-2.3**
Ring-crush strength	±0.51	**-0.81**	0.6	**0.54**
Burst index	±0.065	**-0.16**	0.38	**-0.11**

Effect	Interactions: Criteria	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$
FPR	±0.016	**0.028**	-0.012	**-0.020**	**-0.017**
COD	±13.8	-7.2	18.0	-7.2	-7.2
Drainage time	±0.32	-0.05	-0.20	0.3	0.10
Ring-crush strength	±0.51	**-1.76**	-0.25	-0.41	**-0.60**
Burst index	±0.065	**-0.34**	-0.058	**0.26**	**0.067**

Note: X_1, polymer; X_2, starch; X_3, bentonite; FPR, first pass retention; COD, chemical oxygen demand.

bentonite, as well as the interaction of all 3 parameters showed negative effects. We designated +1 as the high dose and -1 as the low dose conditions, and 0 as the midpoint. So a negative interaction suggests that when both parameters increased, their main effects tended to cancel each other out. The interaction of the polymer and bentonite significantly decreased the white-water COD. The main effects of the polymer and bentonite were helpful in reducing the static drainage time. In summary low doses of the polymer, starch, and bentonite, respectively at 100 ppm, 10%, and 3000 ppm, produced the best FPR, but at the cost of a higher drainage time.

Compared to the blank condition where

the OCC pulp was drained through the same wire without chemical addition, the FPR, COD, and drainage time were 83.4%, 39.6 ppm, and 14.3 s, respectively. Thus, it appears that the starch-bentonite strategy worked reasonably well, as the FPRs and drainage times of all experimental sets were better than the blank, and increases in the COD of the experimental sets were mostly marginally higher than the blank. A probable cause for the poor blank results might be the strong anionic conditions of the fibers.

As for the parameters' effects on the physical properties of the resulting handsheets, the main effects of the polymer (-0.81), starch (0.60), and bentonite (0.54) were all significant with a higher dose of the polymer reducing the ring-crush strength. Interactions of the polymer and starch strongly (-1.76) and all 3 parameters (-0.60) were also detrimental to the ring-crush strength development. Handsheets in the blank condition (with no addition of chemical) had a ring-crush strength of 12.8 kN m^{-1}, and the average of the experimental groups was 16.7 kN/m, a gain of 30%. The maximum value attained by an experimental set was 19.6 kN m^{-1}, which was an increase of 53% over the blank. From the main effects of the parameters, it was apparent that both starch and bentonite applications contributed to the increase, while increasing the polymer charge had an adverse effect on ring-crush strength development.

Results for the burst index suggested that the main effects of the polymer (-0.16), starch (0.38), and bentonite (-0.11) were all significant, and only the starch dose appeared to have a positive contribution to the bursting strength. The interactions of the polymer and starch (-0.34), starch and bentonite (0.26), and the triple interaction of the polymer, starch, and bentonite (0.067) were all significant as well. Thus, the synergistic effect of adding starch and bentonite produced a notable gain in the bursting strength. The burst index of the blank condition was 1.35 kPa·m^2 g^{-1}; whereas the average of all experimental sets was 1.69 kPa·m^2 g^{-1}, an increase of 25% over the blank. The maximum burst index attained by an experimental set was 2.17 kPa·m^2 g^{-1}, an increase of 61% above the blank value.

In summary, adding raw starch and retaining it with bentonite appeared to boost the ring-crush strength and burst index of the resulting paper, with optimal gains of 53% and 61%, respectively.

In the experimental scheme, starch granules are retained on the fiber surface when the surface is hydrated upon internal addition to the wet end. After being heated after they had formed, gelatinization took place and the polymeric chains of starch hydrated and flowed to the surrounding fibers, thus contributing to an increased bond strength that was reflected in gains in the ring-crush strength and burst index. However, the scheme required rather high doses of starch which due to the high particle number, would unlikely be fully retained by the microparticle system formed by the the interaction of polymer and bentonite. In view of the low COD loading in the filtrate, however, it appears that physical entrainment of starch particles by the fiber mat could be a contributing factor to its retention.

Other factors that were not examined were the pressure and time of pressing. In our preliminary experiments, it was demonstrated that the conditions chosen were adequate for the gelatinization and curing of starch.

CONCLUSIONS

This study mainly examined the effects of adding raw starch internally while using bentonite to help retain it on the fiber mat. The experimental results indicated that adding the

3 chemicals helped improve the FPR overall. However, an increase in the starch dose hinder the FPR. The interaction of the polymer and starch tended to improve the FPR; however, interactions of starch and bentonite and of polymer, starch, and bentonite were detrimental to the FPR. As a result, when all chemicals were applied at lower levels of 100 ppm polymer, 10% starch, and 3000 ppm bentonite, the best FPR was achieved. These conditions resulted in a longer static drainage time though.

Based on the experimental results, raw starch appeared to be well retained in the paper web, and upon post-forming gelatinization and curing, the ring-crush and bursting strengths of the resulting handsheets were effectively increased. Under optimal conditions, the gains in the ring-crush strength and the burst index reached as high as 53% and 61%, respectively, over those achieved by the blank OCC pulp.

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