

Research paper

## Effects of Adding Polyelectrolyte Complexes to the Papermaking Wet End on Paper Strength and Functionality

Eugene I-Chen Wang,<sup>1)</sup> Yuan-Shing Perng,<sup>2)</sup>  
Jiann-Gwo Shyu,<sup>1)</sup> Ching-Ming Hsieh<sup>1,3)</sup>

### 【 Summary 】

The main purpose of the study was to find ways of strengthening paper made from old corrugated containerboard (OCC) using the addition of cationic polyacrylamide (cPAM) and starch (CS) in conjunction with anionic PAM (aPAM) and starch (AS). Through modifying the wet-end conditions and modes of addition, we searched for optimal conditions to enhance paper strength, while in the meantime considering estimates of the drainage performance, production cost, and machine runnability. The results indicated that Percol 182, a cPAM, had the best enhancing efficacies on the tensile, burst, and folding strengths of the resulting paper. The amphoteric PAMs, Hercobond 6350 and PS 1280, had slightly inferior performances. While the aPAM, Percol 155, contributed to the tensile strength that was only better than an anionic starch, which had the worst burst strength. The tearing strength was highest when PS 1280 was used. Drainage effects of the additives differed according to the type and dose of the polyelectrolyte. Percol 182 significantly increased the freeness of the pulp, allowing water to drain faster. Hercobond 6350 was next, while Percol 155 significantly decreased the freeness of the pulp. When applying a fixed cPAM and CS to moderate the doses of an amphoteric PAM or aPAM, paper strengths varied with the polyelectrolyte complex used. For paper tensile strength, a pulp concentration of 1.00% and a tensile index Percol 182 dose of 1.00% were optimal, and the tensile indices of the resulting handsheets were optimized. However, when the cost factor was considered, then sequential CS/Percol 155 addition at a 0.75/0.25% dose was effective in elevating the tensile performance. For tearing strength, the sequential addition of CS with PS 1280 at doses of 0.25/0.75% and 0.50/0.50% was better. When cost was considered, adding CS and AS sequentially at a 0.75/0.25% or 0.50/0.50% dose was optimal for strength enhancement.

**Key words:** recycled pulp, zeta potential, polyelectrolyte complex, retention, drainage.

**Wang IC, Perng YS, Shyu JG, Hsieh CM. 2012.** Effects of adding polyelectrolyte complexes to the papermaking wet end on paper strength and functionality. Taiwan J For Sci 27(2):163-75.

<sup>1)</sup> Division of Wood Cellulose, Taiwan Forestry Research Institute, 53 Nanhai Rd., Taipei 10066, Taiwan. 林業試驗所木材纖維組, 10066台北市南海路53號。

<sup>2)</sup> Department of Environmental Engineering, Dayeh University, 168 Xuefu Rd., Dasun Township, Changhua 51591, Taiwan. 大葉大學環工系, 51591彰化縣大村鄉學府路168號。

<sup>3)</sup> Corresponding author, e-mail:cmhsieh@tfri.gov.tw 通訊作者。

Received September 2011, Accepted March 2012. 2011年9月送審 2012年3月通過。

## 研究報告

## 濕端添加聚電解質複合物對紙張強度與功能開發之研究

王益真<sup>1)</sup> 彭元興<sup>2)</sup> 徐健國<sup>1)</sup> 謝靜敏<sup>1,3)</sup>

## 摘要

本試驗以改善回收漿(OCC)的強度性質為主要目標，主要以陽性聚丙烯醯胺(cPAM)、澱粉配合陰性(aPAM)及澱粉，藉由改變各種濕端條件及添加模式，以期達到顯著增加回收漿紙力強度的目的，同時考慮濾水性質、成本及操作的方便性。試驗結果顯示cPAM之Percol 182對紙張抗張強度、破裂強度、耐摺力有最佳促進效果，兩性PAM之Hercobond 6350及PS 1280次之，aPAM之Percol 155其抗張指數僅高於陰性澱粉，但破裂指數卻是最低；而撕裂指數又以PS 1280最高。對濾水性的影響隨聚電解質種類及添加量而異，Percol 182明顯提高游離度，Hercobond 6350次之，Percol 155明顯減低游離度。當固定陽性PAM及陽性澱粉而變化兩性或陰性PAM及澱粉添加量時，紙張強度依各聚電解質有所不同。漿濃度為1.00%時，抗張指數以Percol 182添加量為1.00%時為最佳，但在考慮經濟成本下，在陽性澱粉及Percol 155添加量為0.75/0.25%時亦可提升紙張之抗張指數。撕裂指數以陽性澱粉及PS 1280添加至0.25/0.75%及0.50/0.50%時為佳，但在考慮成本下，則以陽性澱粉及陰性澱粉添加至0.75/0.25%及0.50/0.50%為最適化添加。

關鍵詞：回收紙漿、界達電位、聚電解質複合物、留存與濾水。

王益真、彭元興、徐健國、謝靜敏。2012。濕端添加聚電解質複合物對紙張強度與功能開發之研究。

台灣林業科學27(2):163-75。

## INTRODUCTION

In order to deal with growing trends of using ever-increasing amounts secondary fiber and less water to meet ever-more stringent environmental demands and pressure, the paper industry has made substantial technological advances in the past few decades (Au et al. 1995, Carrasco et al. 1998). Paper-making systems are approaching closed-loop ones, wherein pulp stocks are injected and paper products removed, while the process elements, e.g., water, in particular, are continually recirculated with only minimal make-up. This new reality created tremendous demands on the runnability of paper machines and resulting paper properties. Large-scale utilization of secondary fibers means that paper strength often needs a boost from wet-

end chemical additives to achieve required specifications. And with developing knowledge, the traditional single chemical addition appeared unable to meet the faster, better mantra of the new age. At present, dual chemicals and microparticle retention/drainage aid systems are widely being adopted. Along with our grasp of colloidal chemistry and polymer behavior, newer, more-diverse and -effective chemical regimes are becoming more prevalent to counteract the weaker strengths of secondary fibers. Particle charge detector (PCD) and system zeta potential (SZP) readings of pulp suspensions provide clues as to whether the addition of various chemicals is effective or not. Effective addition suggests that the chemicals are largely adsorbed onto

fiber surfaces, causing fiber surface charges to increase, as indicated by the SZP. On the other hand, ineffective addition entails chemicals being adsorbed by colloidal anionic trash in the suspension, leading to increased PCD readings.

One of the newer concepts is to use polyelectrolyte complexes (PECs) formed by interactions of charged polymer particles which attach to fibers and create better reinforcing efficiencies (Oertel et al. 1991, Chen et al. 2004, Hubbe et al. 2005, Feng et al. 2007). Xiao et al. (2009) found that adding PECs often improves drainage of the stock. Vanerek and van de Ven (2006) noted that based on the chemical and physical properties of 2 oppositely charged polyelectrolytes, 3 types of PECs (soluble, colloidal, and coacervate complexes) are formed. The latter 2 types are more effective as papermaking retention and drainage aids. In a broader sense, cationic polymers can also form complexes with anionic micro- and nano-particles such as nano-silica, help to bond to fibers, and improve retention and drainage (Sennerfors and Tiberg 2001, Khosravani et al. 2010).

The paper industry in Taiwan extensively utilizes secondary fibers in packaging-grade papers. Domestic and imported old corrugated containerboard (OCC) are important raw materials for the industry. In recent years, the rapid expansion of the Chinese paper industry has caused the supply of fibers, including OCC, to be very tight in the global marketplace. Determining how to properly utilize recycled OCC from domestic collection is becoming an important issue for papermakers. In practice, recycled OCC has high anionic trash loading, which tends to overwhelm the charge balance in pulp suspensions, often causing additives to lose their function. OCC also commonly has degraded fibers which have been recycled multiple times and which

contain hornified fiber fragments (fines) and other unwanted carryon substances, making drainage slow and affecting machine runnability. In this study, we examined the effects of adding polyelectrolyte dry-strength agents together with starches to pulp suspensions without first using an anionic trash catcher to adjust the charge balance of the suspensions. The performance was evaluated based on varying the modes of addition, and wet-end conditions on the resulting handsheets were evaluated with the aim of achieving improvements in paper strength. The drainage characteristics of the chemical regimes, their cost, and ease of operation were also taken into account. The electrical charges of the pulp suspensions were monitored using an SZP meter and a PCD to understand the interactions between the polyelectrolytes and fibers, and ensure optimal modes of addition. Evaluation of the addition modes and doses on the establishment of paper functionality and the optimal economic ones were determined. Knowing their effects on the entire papermaking system and performance benefits should provide a significant reference and improvements to the domestic Taiwanese paper industry which relies heavily on secondary fiber supplies.

Papermaking stock is a suspension system consisting of pulp fibers, fines, microparticle additives, etc. Coarser particles and colloidal particles exist in a mixed dispersion system. The purpose of adding chemicals is to modify the electrical charge states of the constituent particles or their bridging conditions, thus enabling uniform dispersion of the stock. Furthermore, the addition of chemicals in pulp suspensions often entails competition with the anionic trash contained therein for the cationic charged additive. Therefore, in this study, we used both a PCD and a SZP meter to respectively measure the

electrical charge states of colloids in the pulp suspensions as might be present in the paper machine head box, and determine the zeta potentials of the pulp suspensions which often reflect charge modifications on fiber surfaces in papermaking systems.

## MATERIALS AND METHODS

### Materials

The OCC pulp was provided by Longcheng Paper, Erlin, Changhua, Taiwan. The wastepaper sample was disintegrated to produce a homogeneous lot. The lot was air-dried. The dried pulp was screened to remove contraries such as sand and plastics and stored. Prior to a set of experiments, specimens were obtained from the lot, and their moisture contents were determined. Each 30 g of oven-dried material was used to carry out the wet-end experiment. The polyelectrolytes examined included 4 polyacrylamides (PAMs): a cationic (c)PAM Percol 182 (BASF Chemicals, Ludwigshafen, Germany), 2 amphoteric PAMs of PS 1280 (Taiwan Arakawa Chemicals, Keelung, Taiwan) and Herculobond 6350 (Hercules Chemicals Co., Taipei, Taiwan), and an anionic (a)PAM, Percol 155 (BASF Chemicals, supplied by Shenyu, Taipei, Taiwan); and 2 modified starches: a cationic starch (CS), Zmcat-t305 (Zihmao, Pingtung, Taiwan) and an anionic starch (AS), Emcoat k-85 (Shenyu). The characteristics of these chemicals are given in Table 1. Auxiliary chemicals included anionic and cationic polyelectrolyte titration standard solutions of the anionic Pes-Na (sodium polyethensulphonate) and cationic PolyDADMAC (polydiallyldimethyl ammonium chloride) (Mütek, Herrsching, Germany).

bond 6350 (Hercules Chemicals Co., Taipei, Taiwan), and an anionic (a)PAM, Percol 155 (BASF Chemicals, supplied by Shenyu, Taipei, Taiwan); and 2 modified starches: a cationic starch (CS), Zmcat-t305 (Zihmao, Pingtung, Taiwan) and an anionic starch (AS), Emcoat k-85 (Shenyu). The characteristics of these chemicals are given in Table 1. Auxiliary chemicals included anionic and cationic polyelectrolyte titration standard solutions of the anionic Pes-Na (sodium polyethensulphonate) and cationic PolyDADMAC (polydiallyldimethyl ammonium chloride) (Mütek, Herrsching, Germany).

### Methods

#### Single chemical addition series

For each specimen, 30 g oven-dry weight of the OCC pulp was reslashed to a consistency of 1%, and then PS 1280, Herculobond 6350, Percol 182, Percol 155, Zmcat-T305, and Emcoatk-85 were individually added to the pulp suspensions at respective doses of 0.10, 0.20, 0.30, 0.40, and 1.00% (0.03, 0.06, 0.09, 0.12, and 0.30 g) and mixed for 5 min

**Table 1. Characterization of wet-end additives (based on the manufacturers' specifications)**

Item	Description
PS 1280 (CP)	An amphoteric polyacrylamide (PAM), in liquid form with a nonvolatile content of > 15%, a viscosity of 1500~4000 mPa·s, and pH of a 0.5% solution of 3.0~5.0
Herculobond 6350 (IV)	An amphoteric PAM used as a dry-strength agent, supplied as a liquid with a solids content of < 12%
Percol 182 (III)	A cationic PAM, white powder of high molecular weight and low cationic charge, 98% of the particles of < 1400 μm, good solubility
Percol 155 (I)	A medium-molecular-weight, moderately anionically charged PAM. It is supplied as microbeads.
Zmcat-T305 (CS)	A cationic denatured starch, with a degree of saturation of quat ammonium of 0.03, a nitrogen content of 0.17~0.26%; highly viscous, 2000 mPa·s at 50°C, pH 5~8
Emcoat K-85 (II)	An anionic starch made of the phosphate-ester of potato starch, a white powder, pH value (20% solution) ≤ 7

for homogeneity. The pulp suspensions were then diluted to 10 L, or a pulp consistency of 0.30%. They were allowed to stand for 30 min before preparation of the handsheets. The target handsheet basis weight was 60 g/m<sup>2</sup> in accordance with the standard.

#### Sequential dual chemical addition series

For each set of experiment, 30 g oven-dry weight of OCC pulp was thoroughly disintegrated. Then the 6 chemicals were added, with the cationic ones added first followed by the anionic ones in sequential pairs. The detailed chemical regimes are shown in Table 2 which includes sequences and proportions of individual sets of polyelectrolyte additions. Combined chemical doses of 1.00, 0.75, 0.50, and 0.25% to dry pulp were added (involving 0.30, 0.225, 0.15, and 0.075 g of dry chemicals), during the dosing sequences. After each chemical addition, the pulp was stirred for 1 min, then the second chemical was added. After the chemicals were added, the pulp was further stirred for 5 min to homogenize it. The suspension was then diluted to 10 L, to a consistency of 0.30%, and allowed to stand

for 30 min, before beginning handsheet formation as noted above.

#### Determination of the charge characteristics of the pulp suspensions

A 100-mesh filter cylinder was inserted into homogenized pulp suspension to take a 10-mL filtrate sample. The filtrate was placed in the cell of a Mütek PCD 03 unit (Herschling, Germany), and the plunger of the instrument was activated to read the net charge of the filtrate in millivolts (mV). Then an automatic titrator filled with a standard polyelectrolyte, mostly a cationic polyDADMAC, solution was used to establish the micro-equivalency ( $\mu\text{eq}$ ) of the filtrate.

For the SZP determination, after adding the chemicals, a 500-mL portion of the stirred pulp suspension was taken and measured with an SZP meter (Mütek SZP 06) to determine the zeta potential.

#### Pulp freeness determination

The freeness of the pulp was determined in accordance with TAPPI standard T227 om-09, the Canadian standard freeness.

**Table 2. Polyelectrolyte complexing schemes of the sequential addition of 2 wet-end chemicals as the dose to dry pulp ratios**

	PERCOL 155 (I)	EMCOATK-85 (II)	PS 1280 (III)	Hercobond 6350 (IV)
PERCOL 182 (CP)	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	1.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	0.75/0.25	0.75/0.25	0.75/0.25	0.75/0.25
	0.50/0.50	0.50/0.50	0.50/0.50	0.50/0.50
	0.25/0.75	0.25/0.75	0.25/0.75	0.25/0.75
	0.00/1.00	0.00/1.00	0.00/1.00	0.00/1.00
ZMCAT-T305 (CS)	0.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	1.00/0.00	0.00/0.00	0.00/0.00	0.00/0.00
	0.75/0.25	0.75/0.25	0.75/0.25	0.75/0.25
	0.50/0.50	0.50/0.50	0.50/0.50	0.50/0.50
	0.25/0.75	0.25/0.75	0.25/0.75	0.25/0.75
	0.00/1.00	0.00/1.00	0.00/1.00	0.00/1.00

### Determination of handsheet paper strength

Handsheets were prepared in accordance with TAPPI standard T205 sp-06. The physical and mechanical properties of the resulting handsheets were tested according to pertinent TAPPI standards: T220 sp-10 for the grammage and apparent specific gravity of the pulp handsheets; T411 om-10 for the thickness strength properties of the handsheets; T494 om-06 for the tensile index; T423 cm-07 for the folding endurance of the paper; T414 for the internal tearing resistance; and T403 om-10 for the bursting strength of the paper.

## RESULTS AND DISCUSSION

### Electrical charge properties of the pulp suspensions

Figure 1A shows PCD charge values of the pulp after the series of a single chemical addition. At a dose of 1.00% to the dry pulp in pulp supplemented with Percol 182, a cPAM single chemical, the streaming current signal of the PCD (in mV) shifted toward the

positive. The PCD value had no absolute correlation with the cationic demand of the pulp suspension; however, the value did provide a glimpse into the electrical charge balance of the papermaking system.

Figure 2 shows changes in the zeta potential (in mV) when different chemicals and dosages were added under prescribed conditions. In Fig. 2A, only with the addition of an aPAM did the zeta potential show negative values. The cationic material somewhat moved the charge toward the positive. Other chemicals did not appear to significantly modify the fiber surface charges. From Figs. 1A and 2A, with cPAM at a 1.00% dose added to the pulp, the charges were largely adsorbed by anionic trash in the suspension. When cationic starch pulp was added, however, it appeared that fiber surface charges were modified to some extent. The relatively low anionic charge of the anionic starch did not greatly affect the fiber surface charge, while the aPAM was able to modify both the suspension and fiber surface charges. The amphoteric PAMs also did not appear to sig-

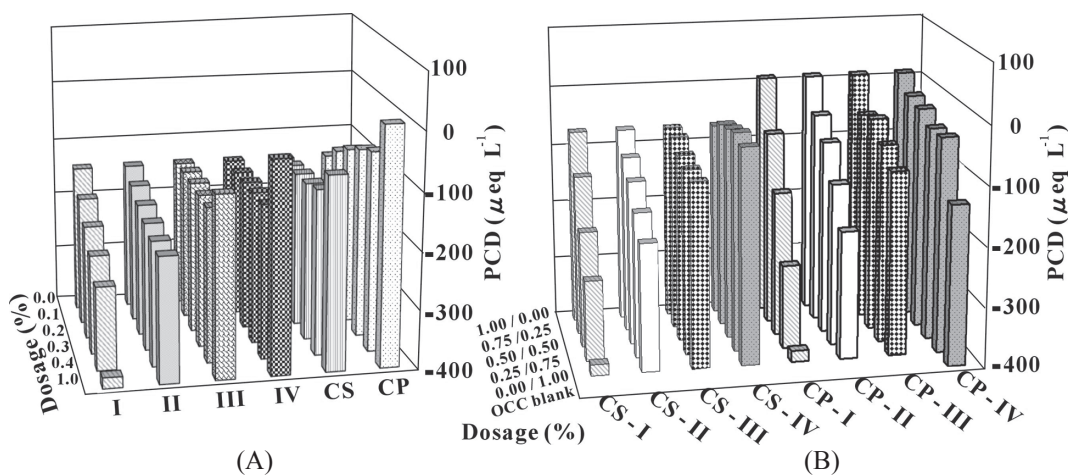
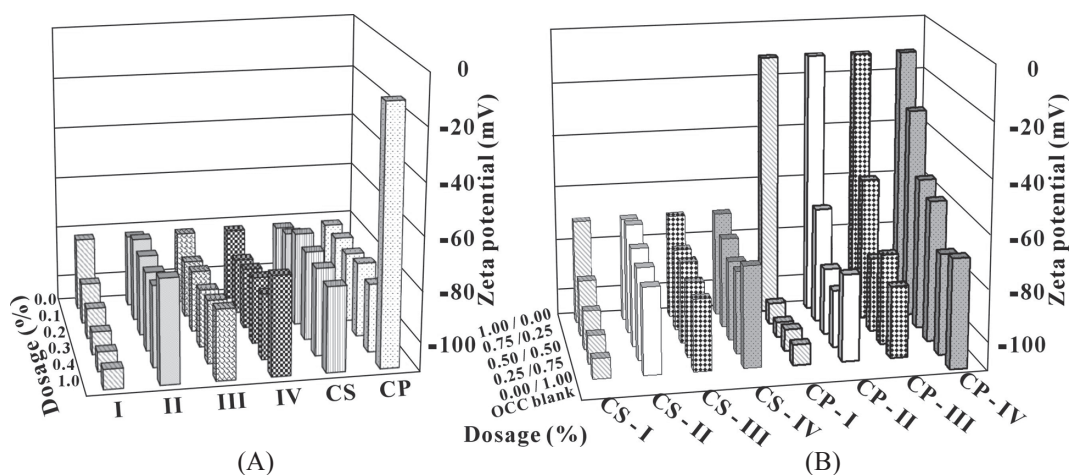


Fig. 1. Effects of single chemical (A) and dual chemical (B) sequential addition on changes in the pulp suspension charge balance ( $\mu\text{eq L}^{-1}$ ). CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 128; IV, Hercobond 6350.



**Fig. 2.** Effects of a single chemical (A) and the sequential addition of dual chemicals (B) on zeta-potential values of the pulp suspensions. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; IV, Hercobond 6350.

nificantly affect the charge of the suspension or on the fiber surfaces.

When a 1.00% dose of the cPAM was added, the OCC pulp showed increased electrical conductivity. The cPAM molecules were drawn to negatively charged fiber surfaces through static interactions, neutralizing the charge there and causing the zeta potential to be less negative. Along with increased adsorption, however, the fiber surface charge gradually decreased, shifting the zeta potential toward the positive. With decreased doses or with the sequential addition of a second chemical of either an amphoteric or anionic PAM or starch, the zeta potentials again shifted toward negative charges. After the sequential addition of a second chemical, Hercobond 6350 was less disruptive to the adsorption of cPAM onto fiber surfaces. The addition of an aPAM even at low doses notably affected the performance of the cPAM. However, with further addition of an aPAM even up to a dose of 1.00% to dry pulp, the zeta potential remained fairly constant at -100~110 mV. With the sequential addition of

a cationic starch, however, even at a 1% dose, there was insignificant modification of the fiber surface charge values. It was likely difficult for the bulkier molecule to be adsorbed onto the fiber surfaces, and it neutralized the negative charge there. Nicu et al. (2011) used cationic chitosan, a glucosamine derivative, with a great ability to form PECs with anionic polymers, and was better able to remove detrimental anionic trash. Li et al. (2004) also applied cationized chitosan to a chemical pulp suspension. They noted that adsorption of a CS onto fibers was weaker than quaternary chitosan. The primary amine on chitosan appeared to be more effective at being adsorbed onto the negatively charged cellulosic substrate than the bulkier quaternary ammonium of CS.

Comparisons of Figs. 1 and 2 indicate that adding a cPAM allowed the positive charge of the molecules to be adsorbed onto either fiber surfaces or anionic trash in the suspension, whereas the positive charges of the CS were largely adsorbed by anionic trash. There appeared to be discrepancies in

the charges of the 2 figures, as a portion of the charges was not detected. This was either due to a very low charge density, or to multiple interfering factors present in the suspension which made their detection difficult, or even that certain chemicals did not obey a strict static interaction rule of 1: 1 neutralization (Yoon and Chai 2006). Furthermore, when a polyelectrolyte molecule first attaches to the fiber surface, there are often free loops and ends with unbound cationic charges sticking out in the solution. These active sites can interact with particles or other fibers with an opposite charge. With the passage of time, however, the loops and ends are flattened onto the fiber and become inactivated. The figures also show that the streaming current signals change with different chemical additives and different doses as determined by the PCD instrument either as direct output (mV) or as polyelectrolyte titration results ( $\mu\text{eq L}^{-1}$ ), respectively. In Fig. 1, most notably, the aPAM, Percol 155, tended to increase the negative charge of the pulp suspension as the dose increased. Figure 2 shows that the overly anionic pulp suspension could be moderated with the cPAM, Percol 182, to a range almost adequate for most wet-end charge considerations (i.e., 0~50 mV) at the highest dose examined. As expected, the anionic chemical shifted the charge toward greater anionicity. The amphoteric Hercobond 6350 and PS 1280 produced little change to the charge condition.

### **Freeness and turbidity of the pulp suspensions**

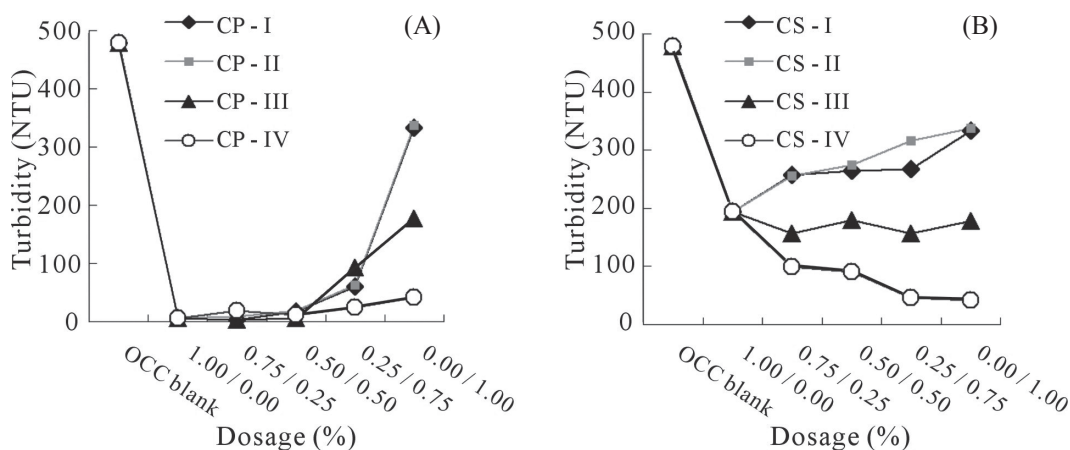
When cPAM was added to the OCC pulp at a 1.00% dose, the polymer facilitated bridging of particles, causing the pulp slurry to become thicker, and making stirring difficult. There appeared to be serious flocculation of the pulp and stratification of the liquid. The supernatant became quite clear as well.

As the SZP measurements of the fiber surface charges were conducted at 3-min intervals, along with the increasing time series, the zeta potential shifted from positive to negative. And as the SZP drew liquid for analysis, there was less of a tendency for the fibers to form a pad on the filter wire. The situation was moderated with lower doses of the cPAM and with the addition of the second chemicals, as the pulp slurry became more uniform. Figure 3 clearly shows that when the cPAM was added to the OCC pulp at a 1.00% dose, the turbidity of the white water decreased, as the fines, filler, stickies, and other dissolved organic substances were affixed to fibers along with the polyelectrolytes (Emerton 1980).

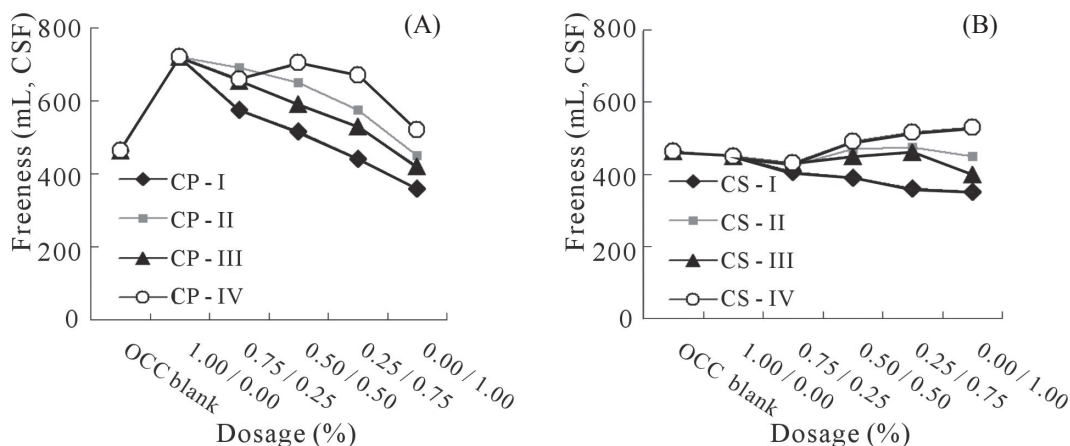
The pulp freeness of the suspension also increased with the addition of 1.00% cPAM, indicating an increased drainage rate (Fig. 4). These results were in agreement with the PCD and SZP charge observations.

The experimental results also suggested that adding the cPAM polymer alone could increase the drainage speed and enhance adsorption of fines and filler particles onto the paper web, thus saving water and steam consumption in the process, improve machine runnability, and reduce deposition in the recirculation system. However, based on cost considerations, the CS in conjunction with the aPAM at a 0.75/0.25% dose ratio might provide a better option. Xiao et al. (2009) studied the effects of adding polyelectrolyte complexes on pulp drainage. They determined the size and charge of cationic and anionic PAM polyelectrolyte complexes and found that properties of the complexes depended on the charge ratio, charge density, and molecular weights of the polymers. They noted that complexes with a low charge density and high molecular weight hastened drainage; while complexes formed by a high charge density and low-molecular-weight polyelectrolytes had no





**Fig. 3.** Effects of the sequential addition of dual chemicals of cPAM (A) or CS (B) followed by a second chemical on the turbidity of the pulp suspensions. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; IV, Hercobond 6350.



**Fig. 4.** Effects of the sequential addition of dual chemicals of cPAM (A) or cationic starch (B) followed by a second chemical on the pulp freeness. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; IV, Hercobond 6350.

clear effects on dewatering. Complexes of aPAM and cPAM as drainage and retention aids enhanced dewatering of the fiber suspensions compared to cPAM alone. The effective complexes had a broader optimal concentration range than that of a single cPAM. Modulating the amount and ratio of polyelectrolyte complexes provided a means to control the drainage efficiency. Our results were largely congruent with others.

### Handsheet strength properties

In addition to the drainage and retention objectives, wet-end chemicals are mostly intended to enhance interfiber bonding and the intrinsic strength of the fibers. The secondary OCC fibers we studied suffered strengths losses, as each cycle of fiber reuse entails irrecoverable shrinkage of the internal fiber pores, stiffening, and often shortening of the fibers as hornification of the chemical pulp

fiber takes place. These phenomena cause the fiber to lose surface fibrillation, and along with the disappearance of active surface hydroxyl groups, they become less prone to form interfiber bonds as well as losing the water retention capacity of the pulp (Phipps 1994). Paper physical and strength properties are precisely dictated by these factors. The sequential addition of dual polyelectrolytes exerted strengthening effects on the paper's mechanical properties to varying extents. The tensile strength, expressed as a tensile index, of the handsheets gained the most when the cPAM or CS was first added at a 0.1% dose; followed by 1% doses of PS 1280, Hercobond 6350, and aPAM. When the economics of the chemical costs were considered, a dual chemical polyelectrolyte complex entailing a cationic starch followed by aPAM at a 0.75/0.25% dose ratio appeared to be optimal (Fig. 5). In this study, the dual chemical systems had a total charge of 1.00%. However, at a dose of < 0.40% with a single polymer, such as Percol 182, the effects achieved were often comparable to the dual systems.

The internal tearing strength of paper is known to predominantly be influenced by the intrinsic fiber strength. Interfiber bonding is often less consequential. Test results of the handsheet tearing indices suggested that cPAM had no apparent benefit on enhancing the tearing strength (Fig. 6). Conversely, a PEC consisted of sequential addition of CS and AS at a 0.75/0.25 or 0.5/0.5 dose ratio produced the optimal strength gain. Probable reasons were hinted at by the respective SZP results which suggested that cPAM with its much higher cationic charge density, is an effective bridging agent and tended to preferentially clump together with colloidal particles and fines, while CS was more effective at modifying fiber surface charges, or was attached to the fiber surfaces and thus acted as an intrinsic fiber strength enhancer.

The effects of adding cPAM to the pulp suspensions on the performances of handsheet burst indices (Fig. 7) and folding endurance (Fig. 8) showed marked enhancements. However, with the addition of a second complexing chemical, the performance tended to

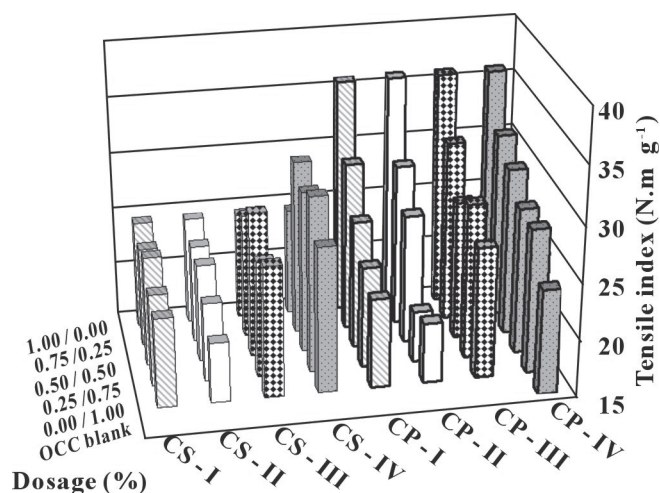


Fig. 5. Effects of the sequential addition of dual chemicals of cPAM or cationic starch followed by a second chemical on the resulting handsheet tensile strengths. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; and IV, Hercobond 6350.

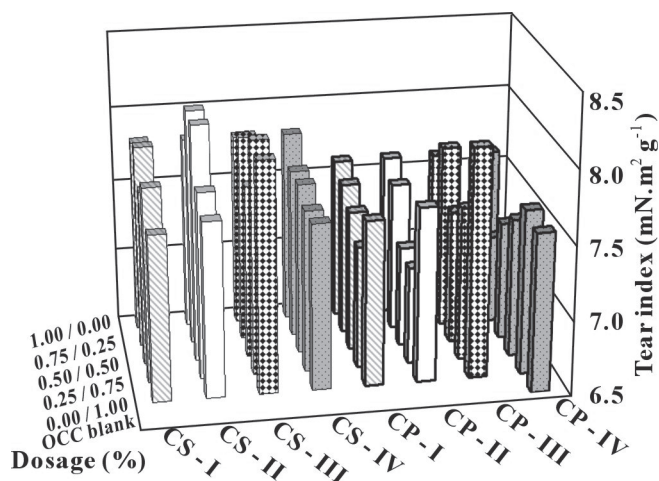


Fig. 6. Effects of the sequential addition of dual chemicals of cPAM or cationic starch followed by a second chemical on the resulting handsheet internal tearing strengths. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; IV, Hercobond 6350.

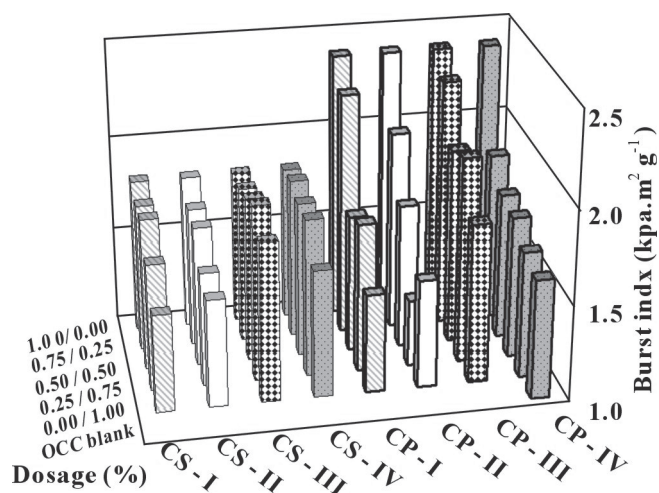
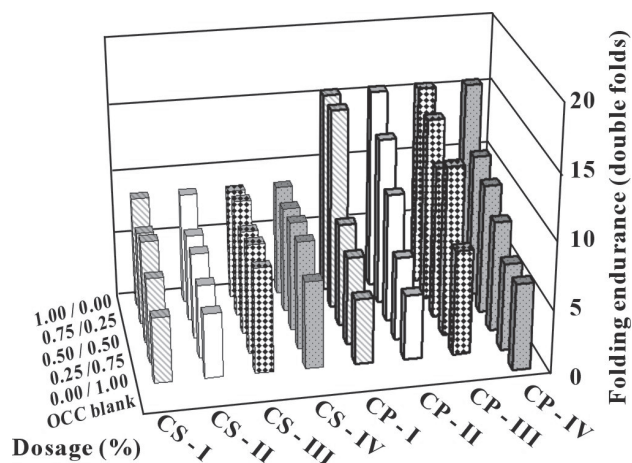


Fig. 7. Effects of the sequential addition of dual chemicals of cPAM or cationic starch followed by a second chemical on the resulting handsheet bursting strengths. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; and IV, Hercobond 6350.

abate somewhat. Compared to the internal tear resistance, it appeared that the modes of functioning of CS vs. cPAM exerted somewhat different functions on the fiber matrix, which could be traced to their different PCD and SZP curves at various doses.

Overall, the handsheet tensile, bursting, and folding endurance strengths appeared to change with shifts in the zeta potentials after chemical addition to the pulp suspensions. The exception included polyelectrolyte complexation of Percol 182 with Percol 155,



**Fig. 8.** Effects of the sequential addition of dual chemicals of cPAM or cationic starch followed by a second chemical on the resulting handsheet folding endurance performance. CP, Percol 182; CS, Zmcat-T305; I, Percol 155; II, Emcoat K-85; III, PS 1280; and IV, Hercobond 6350.

as this dual mode created a very negatively charged zeta potential series as there was a lack of 1:1 charge parity during the complexing process. Considering handsheet strength performances, adding cPAM appeared to effectively enhance interfiber bonding strength and led to better strength properties. However, the addition of a second chemical did not create further improvements but often detracted from the original performance achieved. Only the complexing of CS with AS at a 0.75/0.25 dose ratio appeared to boost the internal tear resistance of the handsheets.

In this study, the sequential mode of adding 2 chemicals of different charge characteristics was examined, and the expected boosting effect of the polyelectrolyte complex on the resulting handsheet strengths was largely unrealized. Another mode of polyelectrolyte complexing would be to premix the chemicals before adding them to the pulp suspensions. Our results (not shown) suggested that this mode provided no benefit over the sequential mode of addition. Judging by modifications of the zeta potential, suitable cationicity for

minimizing the negative charges of the system appeared to exert a predominant influence on the drainage and sheet strengths. This brings up our initiative for the next series of study in which a negative charged pulp suspension will be treated with an anionic trash catcher, poly aluminum chloride, to a nearly neutral charge level before the polyelectrolyte complexes are applied. In this way, we shall create a level field to examine whether complexing of polyelectrolytes brings any notable benefits.

## CONCLUSIONS

In this study, OCC pulp was supplied by a paper mill, and it was rather alkaline with a pH of 8.3 and a high anionicity of ca. -120 mV when made into a suspension with deionized water. Upon the addition of polyelectrolytes, the pH of the pulp suspensions remained between 7.9 and 8.3. We did not apply an anionic trash-catching agent to raise the pulp suspension to a nearly a 0 mV zeta potential state and added the wet-end polyelectrolytes to examine their effects on the ensuing charge

balances. Positive charges on the cPAM were adsorbed by fibers and the colloidal anionic trash alike. The strong flocculation effect it exerted on the pulp suspension led to an increase in freeness, i.e., improved drainage and machine runnability. However, the chemical is more expensive than CS which had an optimal strength-enhancing performance when sequentially applied with the aPAM at a 0.75/0.25 dose ratio, a pulp concentration of 1.00%, and a tensile index Percol 182 dose of 1.00% for optimal results. When PS 1280 was applied as a single agent, even at a 1% dose, the performance was inferior to the sequential addition of cPAM and PS 1280 at a 0.5/0.5 dose ratio, suggesting that polyelectrolyte complexing might contribute synergistically to the strength of the handsheets, such as the dry strength and damage rate improvement.

## LITERATURE CITED

- Au CO, Johansson KA, Thorn I. 1995.** The use of retention and drainage aids in the wet end. In: Au CO, Thorn I. editors. Application of wet end paper chemistry. London: Chapman Hall. p 13-7.
- Carrasco F, Mutje P, Pelach MA. 1998.** Control of retention in paper-making by colloid titration and zeta potential techniques. *Wood Sci Technol* 32(2):145-55.
- Chen JH, Hubbe MA, Heitmann JA, Argyropoulos DS, Rojas OJ. 2004.** Dependency of polyelectrolyte complex stoichiometry on the order of addition. 2. Aluminum chloride and poly-vinylsulfate. *Colloids Surfaces A-Physicochem Eng Aspects* 246(1-3):71-9.
- Emerton HW. 1980.** Handbook of paper science. Vol. 1. New York: Elsevier. p 149-64.
- Feng XH, Pouw K, Leung V, Pelton R. 2007.** Adhesion of colloidal polyelectrolyte complexes to wet cellulose. *Biomacromolecules* 8(7):2161-6.
- Hubbe MA, Moore SM, Lee SY. 2005.** Effects of charge ratios and cationic polymer nature on polyelectrolyte complex deposition onto cellulose. *Ind Eng Chem Res* 44(9):3068-74.
- Khosravani A, Latibari AJ, Mirshokraei SA, Rahmaninia M, Nazhad MM. 2010.** Studying the effect of cationic starch-anionic nanosilica system on retention and drainage. *Bioresources* 5(2):939-50.
- Li HB, Du YM, Xu YM, Zhan HY, Kennedy JF. 2004.** Interactions of cationized chitosan with components in a chemical pulp suspension. *Carbohydr Polymers* 58(2):205-14.
- Nicu R, Bohn E, Desbrieres J. 2011.** Chitosan as cationic polyelectrolyte in wet end papermaking systems. *Cell Chem Technol* 45(1-2):105-11.
- Oertel U, Petzold G, Buchhammer H, Geyer S, Schwarz S, Müller U, Rätzsch M. 1991.** Introduction of surface charge into Polymers by polyelectrolyte complexes. *Colloids Surf* 57(3-4):375-81.
- Phipps J. 1994.** The effects of recycling on the strength properties of paper. *Paper Technol* July/August:34-40.
- Sennerfors T, Tiberg F. 2001.** Adsorption of polyelectrolyte and nanoparticles at the silica-aqueous solution interface: influence of the history of additions of the two components. *J Colloid Interf Sci* 238(1):129-25.
- Vanerek A, van de Ven TGM. 2006.** Coacervate complex formation between cationic polyacrylamide and anionic sulfonated kraft lignin. *Colloids Surfaces A-Physicochem Eng Aspects* 273(1-3):55-62.
- Xiao LH, Salmi J, Laine J, Stenius P. 2009.** The effects of polyelectrolyte complexes on dewatering of cellulose suspension. *Nord Pulp Pap Res J* 24(2):148-57.
- Yoon SH, Chai XS. 2006.** Adsorption kinetics for polymeric additives in papermaking aqueous fibrous media by UV spectroscopic analysis. *B Kor Chem Soc* 27 (11):1819.

