Pretreatment to improve adsorption and effectiveness of wet end chemicals for a bleached chemithermomechanical pulp

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ABSTRACT: Bleached chemithermomechanical pulp (BCTMP) contains high amounts of anionic trashes that can seriously reduce the efficiency of many wet end functional and process chemicals. Fixing agents have been used to offset this negative effect, with varying success. In this study, we used a specially designed, starch-based fixing agent, namely, a low molecular weight, highly cationic starch (LHCS) to pretreat a BCTMP. We used ultraviolet (UV)-visible spectroscopic methods to investigate the effectiveness of LHCS use on the adsorption of some typical wet end chemicals, such as fluorescent whitening agent, tinting dye, wet strengthening agent, dry strengthening agent, neutral sizing agent, and retention agent onto the BCTMP. The results show that the adsorbed amounts and the adsorption efficiencies of these chemicals can be improved by LHCS pretreatment, variously resulting in higher brightness, better tinting, higher wet and dry strengths, better sizing, and higher retention and drainage.

Application: Pretreating BCTMP with a highly cationic starch with low molecular weight can increase the efficiencies of many paper additives used in a typical wet end system of the papermaking process, and UV-visible spectroscopic methods to measure the adsorptions of wet end chemicals can be effective in predicting the performance of these functional or performance chemicals.

Bleached chemithermomechanical pulp (BCTMP), a typical high-yield pulp (HYP), has been popular in the last two decades in the production of various paper grades [1-3]. HYP has a number of unique attributes; for example, high bulk and high scattering efficient [4]. However, it also has more highly anionic dissolved and colloidal substances (DCS), which may decrease the effect of various wet end chemicals used in the papermaking process, resulting in poor machine runnability and inferior product qualities [5,6]. Many fixing agents, also known as anionic trash catchers, including polyaluminum chloride, polyamine, polydiallyldimethylammonium chloride, polyethyleneimine, and starch-based polymers (specially designed highly cationic starches), have been used to offset the negative effect [7,8]. Among them, the starch-based fixing agent was effective, because it is capable of forming hydrogen bonds with cellulose fibers, and interacting with low molecular weight anionic carbohydrate compounds [9]. We also found that our laboratory-made starch-based fixing agent – a low molecular weight, highly cationic starch (LHCS) – showed excellent performance in reducing the DCS content in a deinked pulp, as well as improving strength [10].

In this study, the LHCS was applied to a BCTMP. The objective was to pretreat the BCTMP with the LHCS so that the negative effect of DCS on the subsequently added paper chemicals in stock preparation could be eliminated, their adsorption onto fibers increased, and their performance improved.

However, the adsorption of wet end chemicals onto cellulose fiber is not always easily determined. Often, the residual amount of a chemical in water phase is measured first, and the adsorbed amount onto fiber can be obtained by the difference of the added amount and the residual amount in the water phase. The colloidal titration method, which is based on the assumed stoichiometry between the charged chemical being measured in the sample and the oppositely charged standard titrant, often is used to determine the concentration of the highly charged polyelectrolyte-based chemicals [11]. However, such stoichiometric relationships might not work well, especially under the practical conditions of white water, which can have different pH and conductivity levels [12]. The task becomes even more challenging with additives having low charge densities, or those with high charge density but low concentration (low residual amount). Therefore, methods that improve on colloidal titration are desirable, and fluorescence labeling, chromatographic methods, and others have been reported [13-16].

In this project, ultraviolet (UV)-visible spectroscopy, which is readily available and simple to operate, was used to measure the adsorption amounts of some typical wet end chemicals in a BCTMP system. LHCS was used as the fixing agent to minimize the negative effect from the DCS carried from the BCTMP.

EXPERIMENTAL

Materials

Shandong Zhengda Papermaking Company supplied a mixed hardwood BCTMP for this study. The LHCS starch-based fixing agent was prepared in our own laboratory by reacting amylopectin starch with epoxypropyltrimethyl chloride, followed by acidic hydrolysis to decrease the molecular weight. The procedure is described in more detail elsewhere [10]. The cationic degree of substitution (DS) of the LHCS was as high as 0.65. The molecular weight or degree of polymerization (DP) of the LHCS was not analyzed by direct method, such as gel permeation chromatography (GPC); instead, we measured the time for a 0.1% LHCS solution flowing through a capillary viscometer at 30°C, maintained by a constant water bath, where the flow time for the undegraded highly cationic starch (HCS) was 172.9 s and that for the LHCS was 118.6 s, indicating that the DP of the amylopectin starch was decreased significantly.

Other wet end chemicals used in the study included a diaminostilbenesulfonate fluorescent whitening agent (FWA), a methyl violet (MV) tinting dye, a poly(amidoamine)epichlorohydrin wet strength agent (PAE), a dry strength agent-cationic starch (DSA-CS) made in our own laboratory [17], an alkyl ketene dimer (AKD) neutral sizing agent, and a cationic polyacrylamide (CPAM), a dry powder (average Mw around 4 million) retention agent. The PAE, DSA-CS, AKD, and CPAM had positive charges of 2.30, 0.43, 0.46, and 1.53 meq/g, respectively, based on dry solids.

Methods

Determination of residual concentrations in pulp water based on UV-visible spectroscopy

The calibrations of the UV-visible absorbance and chemical concentrations were established by using a 752 LabTech UV from LabTech Holdings, Holliston, MA, USA, under their corresponding maximum absorbance wavelengths of 620 nm for LHCS and DSA-CS, and 349.5 nm, 582.5 nm, 314 nm, 238 nm, and 470 nm, respectively, for FWA, MV, PAE, AKD, and CPAM, respectively (**Table I**) [18-22].

The BCTMP was disintegrated and then diluted to 1% in pulp consistency, followed by the addition of required amounts of 1g/L LHCS solutions, and gentle stirring for 30 s. Then one of the wet end chemicals (in diluted or dissolved form) was added into the pulp slurry, under the following fixed dosage: 0.67% FWA, 0.0002% MV, 0.4% PAE, 1.0% DSA-CS, 0.2% AKD, or 0.2% CPAM, all as the percentage of the solid effective chemical to the oven-dried mass of pulp. The pulp slurries were stirred for another 30 s, centrifuged at 2000 rpm for 5 min, and the supernatants were then taken to measure the UV-visible absorbance. Because the absorbance from the residual LHCS is negligible in relation to FWA, MV, PAE, AKD, and CPAM, the measured absorbance is mainly the result of the residual wet end chemical. In the case of DSA-CS, the absorbance resulting from residual LHCS must be deducted [23].

The difference between the added amount of an additive and its residual amount would be the amount of additive adsorbed on the fibers, and the ratio of the adsorption amount to the initial added amount was calculated as the adsorption ratio.

Comparison of pulp drainage, retention, and handsheet properties

Table II shows the experimental design methodology used in this study, with LHCS pretreatment followed by FWA addition as an example. Altogether there were four kinds of treatments and we prepared 12 pulp samples for them. For treatments II-IV, each has three pulp sample replicates. The run order of the 12 experiments was randomized deliberately to maximize uncontrollable experimental errors. Five handsheets were made from each pulp sample, and the data used for statistics (average, standard deviation, and t-test) are noted in Table II. T-test was a method to compare two sets of data; in this case, the difference between treatments II and III, and II and IV. The result of a t-test is a p-value that functions as the criterion to judge whether the difference is statistically significant ($p<0.05$ means the difference is statistically significant, otherwise not) [24]. The t-tests were calculated with Microsoft Excel 2003 software following its "Insert-Function-Statistics-TTEST" steps.

The LHCS pretreatment and the subsequent chemical additions were the same as those described previously. The pulp slurries pretreated with LHCS and followed by the addition of a wet end chemical were diluted, and handsheets (60 g/m^2) were made according to Chinese standard GB/T 7981-1987 "Preparation of laboratory sheets (conventional sheet-former method)." Brightness and L*a*b* values were measured according to GB/T 7974-2002 "Paper, board and pulp – Measurement of brightness – Diff / Geometry" and GB/T 17644-2008 "Test method for whiteness and chromaticity of textile fibers." Dry

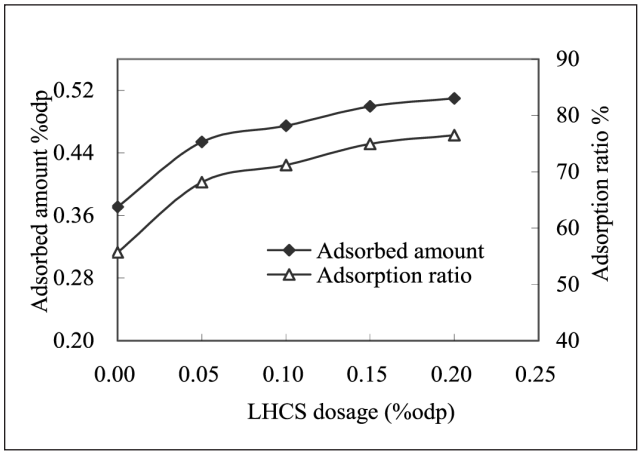
LHCS (620.0 nm)	FWA (349.5 nm)	MV (582.5 nm)	PAE (314.0 nm)	DSA-CS (620.0 nm)	AKD (238.0 nm)	CPAM (470.0 nm)
y = 0.0056x R^2 = 0.9964	y = 0.0088x - 0.021 R^2 = 0.997	y = 0.2469x + 0.0031 R^2 = 0.9984	y = 0.0012x - 0.0012 R^2 = 0.9983	y = 0.0069x R^2 = 0.9936	y=0.0044x R^2 =0.9968	y = 0.0016x - 0.0068 R^2 = 0.9936

I. Absorbance-concentration equations for low molecular weight, highly cationic starch (LHCS) and wet end chemicals under their respective maximum absorbance wavelengths. Note: x is concentration of chemicals (mg/L), y is absorbance, R^2 is the correlation coefficient.

Treatments	Experiments	Run Order	LHCS Dosage (% o.d. pulp)	FWA Dosage (% o.d. pulp)	Handsheet Numbers	Data for Statistics
I	N1	7	0	0	5	From 5 handsheets
	N2	1	0.05	0	5	From 5 handsheets
	N3	4	0.15	0	5	From 5 handsheets
II	N4	5	0	0.67	5	From 15 handsheets
	N5	2	0	0.67	5	
	N6	8	0	0.67	5	
III	N7	12	0.05	0.67	5	From 15 handsheets
	N8	11	0.05	0.67	5	
	N9	9	0.05	0.67	5	
IV	N10	3	0.15	0.67	5	From 15 handsheets
	N11	6	0.15	0.67	5	
	N12	10	0.15	0.67	5	

II. Experimental design taking LHCS pretreatment followed by fluorescent whitening agent (FWA) addition as an example. Treatments I-IV represent LHCS only, FWA only, LHCS dosage level at 0.05% o.d. pulp followed by FWA, and LHCS dosage level at 0.15% o.d. pulp followed by FWA, respectively.

tensile strength was measured according to GB/T 453-2002 "Paper and board – Determination of tensile properties (Constant rate of loading methods)" and wet tensile strength was measured according to GB/T 465.2-1989 "Paper and board – Determination of tensile strength after immersion in water." The sizing degree was measured according to GB/T 5405-2002 "Paper – Determination of the sizing value (Liquid permeance method)," which is based on the penetration of ferric chloride solution to ammonium thiocyanate solution. The drainage was measured on the LHCS pretreated, CPAM added, and diluted (0.3%) pulp samples by using a drainage freeness and retention. LHCS and CPAM treatments were the same for the retention test as for the drainage test, but with the addition of 20% GCC (based on o.d. pulp). The ash retention was measured according to GB/T 463 -1989 "Paper, board and pulp – Determination of ash."



1. Effect of LHCS on adsorption of FWA at a fixed dosage of 0.67%.

LHCS (% o.d. pulp)	Brightness (% ISO)	p-value
0	72.14 ± 0.52	—
0.05	75.06 ± 0.48	0.002
0.15	74.42 ± 0.37	0.003

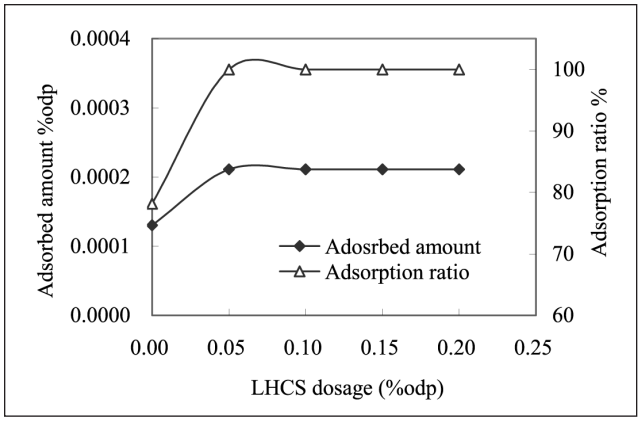
III. LHCS pretreatment on brightening performance of FWA (FWA dosage fixed at 0.67%).

RESULTS OF LHCS PRETREATMENT AND DISCUSSION

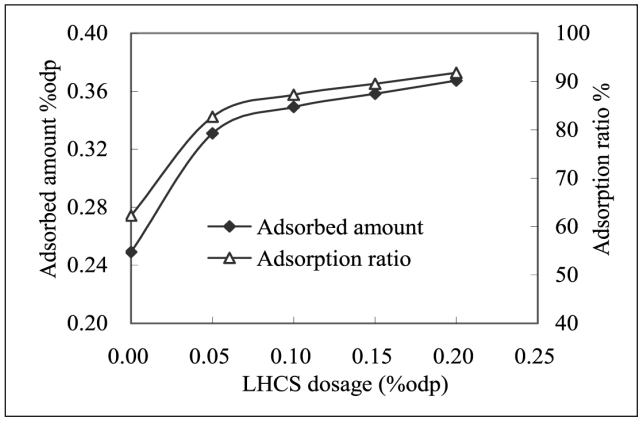
Adsorption of FWA and its brightening performance

FWA can absorb ultraviolet light and reflect blue or violet visible light, thus, improving paper brightness. FWA may not be as effective for the BCTMP as that for the chemical pulp, because BCTMP contains a high amount of lignin, which also strongly absorbs UV light and decreases the effect of FWA. However, many paper mills still use FWA. Some recent studies showed that the brightness stability of BCTMP could be improved by using FWA [25-27].

The adsorbed amount of FWA on fibers increased with the dosage of LHCS pretreatment (**Fig. 1**). The adsorption ratio was increased from 55.7% without LHCS pretreatment to 80.2% with the LHCS dosage of 0.20% o.d. pulp. We would expect the increase in FWA retention to lead to an increase in the brightening effect. On the other hand, the addition of cationic polyelectrolyte might lead to reduced intensity (quenching) or a "greening effect" caused by excessive self-agglomeration of FWA. **Table III** shows the measured brightness of the handsheets. Pretreament with 0.05% LHCS resulted in about three units gain in ISO brightness, compared with the control (no LHCS pretreatment). These results



2. Effect of LHCS on adsorption of methyl violet (MV) at a fixed dosage of 0.0002%.



3. Effect of LHCS on adsorption of poly(amidoamine) epichlorohydrin (PAE) at a fixed dosage of 0.40%.

indicated that a higher adsorption of FWA leads to higher brightness gain. When the LHCS dosage was increased to 0.15%, a slight drop in brightness was seen compared with that of 0.05% LHCS, because of the greening effect.

Adsorption of MV and its tinting performance

Violet or blue dyes often are used to tint paper so that it looks whiter. MV is a representative tinting dye for such purpose. It is a basic dye with weak cationic charge, and it may be influenced by the DCS. **Figure 2** shows the results of LHCS pretreatment. The adsorbed amount of MV on fiber increased as a result of the LHCS pretreatment; the adsorption ratio was increased from 78% with no LHCS pretreatment to almost 100% when treated using 0.2% LHCS.

LHCS (% o.d. pulp)	Wet Tensile Index (N.m/g)	p-value
0	2.33±0.19	—
0.05	2.43±0.27	0.026
0.15	2.58±0.17	0.024

V. LHCS pretreatment on wet-strength performance of PAE at a fixed dosage of 0.40%.

Table IV shows the effect of LHCS pretreatment on the tinting effectiveness of MV, based on the L*, a* and b* color space values. Statistical analysis showed that the differences in lightness (L*) were not significantly altered by LHCS pretreatment, but the a* value and the b* value were improved. These results indicated that the performance of MV was improved after the LHCS pretreatment. Table IV also shows that the standard deviation of L*, a*, b* values increased significantly after LHCS pretreatment. This phenomenon was ascribed to the slight deterioration of paper formation after LHCS pretreatment, because LHCS has some coagulation effect on fiber components. This will cause the subsequently added MV to be adsorbed onto the more unevenly distributed fiber materials, causing higher standard deviations in L*a*b* values.

Adsorption of PAE and its wet strength improvement

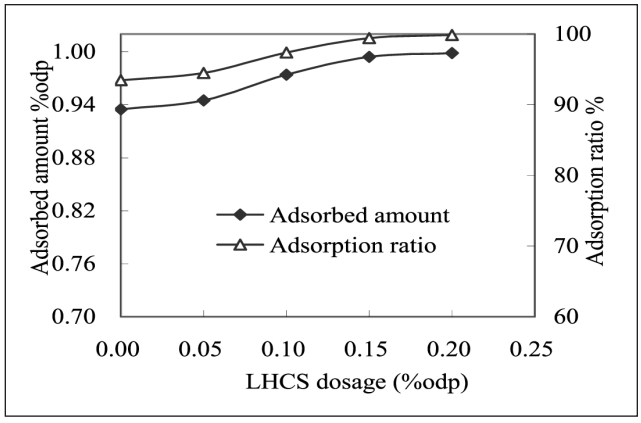
PAE is widely used as a wet strength agent in papermaking. It works through cross-linking reactions with the functional groups on the cellulosic fibers and self cross-linking [20]. Before curing, the molecular weight of PAE is low but its cationic charge density is high; therefore, PAE itself can act as a fixing agent. **Figure 3** shows that without LHCS pretreatment, the adsorption ratio of PAE was only 62%, but with LHCS pretreatment, the adsorbed amount of PAE increased significantly, and its adsorption ratio increased to about 92% at the dosage of LHCS of 0.20%. As for wet strengthening, **Table V** shows that with 0.05 or 0.15% LHCS, the increments of wet tensile strengths of the paper-sheets was 4.5% or 11.0%, respectively.

Adsorption of DSA-CS and its dry strength improvement

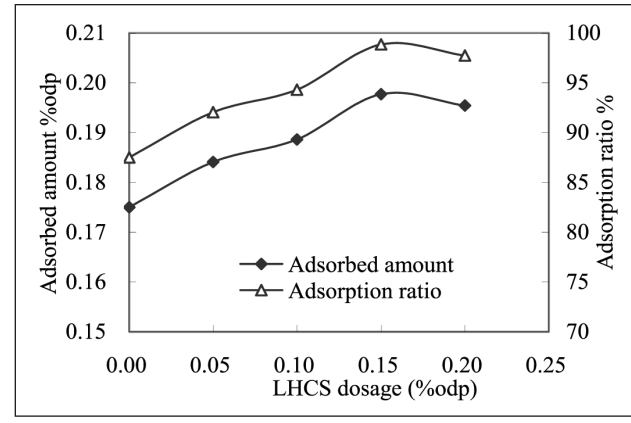
Cationic starch with a low degree of substitution (DS of 0.02-0.04) is widely used as a dry strength agent (DSA) in paper-

LHCS (% o.d. pulp)	L*	p-value	a*	p-value	b*	p-value
0	91.97±0.21	—	-1.50±0.06	—	9.24±0.26	—
0.05	92.29±0.68	0.055	-1.16±0.61	0.019	8.61±0.88	0.010
0.15	92.43±0.86	0.032	-0.76±0.47	2.98×10^{-7}	8.25±0.88	1.03×10^{-4}

IV. LHCS pretreatment on the tinting performance of MV at fixed dosage of 0.0002%.



4. Effect of LHCS on adsorption of a dry strength agent-cationic starch (DSA-CS) at a fixed dosage of 1.0%.



5. Effect of LHCS on adsorption of alkyl ketene dimer (AKD) at a fixed dosage of 0.20%.

LHCS (% o.d. pulp)	Tensile Index (N.m/g)	p-value
0	25.83±0.75	—
0.05	28.05±0.88	0.021
0.15	29.45±0.55	0.001

VI. Effect of LHCS pretreatment on performance of a DSA-CS at a fixed dosage of 1.0%; the tensile strengths for bleached chemithermomechanical pulp (BCTMP) itself, BCTMP treated with 0.05%, and 0.15% LHCS only, were 23.07±1.71, 25.04±0.89, and 25.26±2.43 N.m/g, respectively).

LHCS (% o.d. pulp)	Sizing Degree (s)	p-value
0	40.41 ± 1.26	—
0.05	47.29 ± 0.66	$1.09\acute{}10^{-10}$
0.15	51.77 ± 1.05	$1.85\acute{}10^{-18}$

VII. Effect of LHCS pretreatment on sizing performance of AKD at a fixed dosage of 0.20%.

making. However, the weakly charged starch can easily be neutralized by anionic DCS in BCTMP, so that the starch would be in white water, resulting in an increase in the chemical oxygen demand (COD), and even slime growth [28]. A special cationic starch-based dry strength agent (DSA-CS) with a higher degree of substitution (DS of 0.075) was developed to minimize the negative effect of DCS. As **Fig. 4** shows, the DSA-CS itself had a good adsorption to BCTMP fibers; its adsorption ratio was as high as 93% when its dosage was 1%. Despite that, the adsorbed amount and adsorption ratio of the DSA-CS can be increased further with the use of LHCS. At an LHCS dosage of 0.20%, the adsorption ratio of the DSA-CS reached almost 100%. **Table VI** shows that with LHCS pretreatment, the dry strength was improved from 25.83 (0% LHCS) to 28.05 (0.05% LHCS) and 29.45 N.m/g (0.15%).

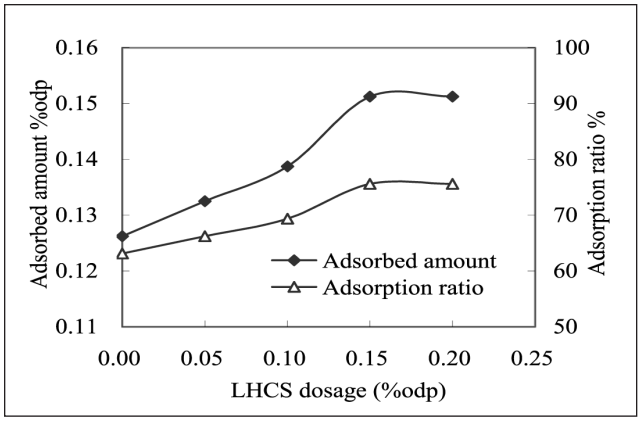
This strength increment might be caused by LHCS itself, at least partially. Our previous study revealed that LHCS had some strengthening effect on a recycled newsprint pulp [10]. In this study for the BCTMP being used, the tensile strengths for the BCTMP itself, BCTMP treated with 0.05%, and 0.15% LHCS only were found to be 23.07±1.71, 25.04±0.89, and 25.26±2.43 N.m/g, respectively, indicating that the strengthening effect of LHCS was around 9.5%. The strengthening effect of DSA-CS itself at 1.0% o.d. pulp dosage was around 12.0% (from 23.07±1.71 to 25.83±0.75 N.m/g). However, when the pulp was pretreated with LHCS at 0.15% o.d. pulp followed by DSA-CS addition at 1.0% o.d. pulp, the increment was around 27.7% (from 23.07±1.71 to 29.45±0.55), indicating that the LHCS and the DSA-CS had synergistic effects on strengthening, which also can be ascribed to the increased amount of DSA-CS adsorption.

Adsorption of AKD and its effect on sizing

AKD has been used widely in papermaking as a representative neutral sizing agent. Recently developed AKD emulsions have been designed to improve their self-retention onto fibers [29], but highly anionic DCS in a modern papermaking system can still hinder their adsorption onto fiber, causing lower sizing and potential deposit problems associated with the unretained and hydrolyzed AKD [30]. Therefore, improvement of AKD retention is of critical importance. **Figure 5** shows that, at 0.2% AKD, the adsorbed ratio of AKD on fiber increased from 88% to 98% with the LHCS pretreatment. **Table VII** shows that a much higher sizing degree was obtained when it was measured by following the ferric chloride-ammonium thiocyanate penetration method.

Adsorption of CPAM and its retention and drainage enhancing

Although many new retention and drainage systems, such as micro- and nanoparticle retention systems, have been developed in recent years, CPAM remains as one of the most wide-



6. Effect of LHCS on adsorption of cationic polyacrylamide (CPAM) at a fixed dosage of 0.20%.

LHCS (%)	Drainage Speed (mL/20 s)	p-value	Ash Retention (%)	p-value
0	676±9	-	60.8±6.2	—
0.05	723±7	0.002	63.4±6.6	0.488
0.15	753±6	2.85´10-4	71.1±4.9	0.009

VIII. Effect of LHCS on retention and drainage performance of CPAM at a fixed dosage of 0.05%. The drainage speed for the pulp treated by LHCS only were 456±10, 582±10, and 610±10 mL/20s, respectively, and the ash retentions were 39.5%±0.6%, 54.4%±2.6%, and 56.4%±0.2%, respectively, for LHCS dosages at 0%, 0.05%, and 0.15% o.d. pulp.

ly used retention agents. In this study, CPAM was chosen as the representative retention and drainage aid. The hypothesis was that the highly cationic starch with low molecular weight would neutralize the anionic DCS from BCTMP, and subsequently a bridging effect would be provided by CPAM, which has a high molecular weight and low cationic charge density. **Figure 6** shows that when the dosage of CPAM was fixed at 0.20% o.d. pulp, with no LHCS pretreatment, the adsorption of CPAM onto BCTMP fibers was only 63%, but it could be improved to about 75% when the BCTMP was pretreated by using 0.15% LHCS.

Table VIII shows the retention and drainage effects of CPAM, with or without LHCS pretreatment. As measured by the dewatering amount within 20 s in a dynamic drainage jar, the drainage speeds were increased from 676 mL to 753 mL when the dosages of LHCS and CPAM were 0.15% o.d. pulp and 0.05% o.d. pulp, respectively. Under the same dosages, the GCC retention was improved from 60.8% to 71.1%, which can bring significant economic benefits.

CONCLUSIONS

The presence of DCS in BCTMP can hinder the efficiency of many wet end chemicals. This study demonstrated that pretreating the BCTMP with a specially designed, highly cationic starch with low molecular weight, which functions as a fixing agent, can minimize the negative effect from the DCS of BCTMP. The experimental results showed that both the adsorptions and the specific function of a diaminostilbenesulfonate fluorescent whitening agent, a methyl violet tinting dye, a polyamidoamineepichlorohydrin wet strengthening agent, a cationic starch dry strengthening agent, an alkyl ketene dimmer sizing agent, and a cationic polyacrylamide retention agent, can be improved significantly. In addition, our results indicated that the UV-visible spectroscopic method is effective in measuring the adsorption behavior of these common wet end additives, so that their performance can be predicted. **TJ**

ACKNOWLEDGMENTS

Financial support from the Project of China-Canada International Joint Research (2008DFA91290), the Project of Tianjin Municipal Science & Technology Commission (09JCYBJC27100), and the Foundation for Excellent Doctoral Dissertations of Tianjin University of Science and Technology in 2010 (B201005) is greatly appreciated.

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High dissolved and colloidal substances (DCS) content in pulps is a well known problem for papermaking. In our previous study, a specially designed starch-based fixing agent (LHCS) was found to be effective in treating DCS in a recycled pulp. Therefore, in this study we wanted to extend its application to another typical pulp (BCTMP) with high DCS contents; however, we wanted to try different evaluation methods, because it is always laborious to test the performance of a wet end chemicals by measuring pulp and/or handsheet properties. Our thinking was to measure the adsorptions of the wet end chemicals. In most cases, the adsorption of a certain wet end chemical is difficult to measure by a common method such as colloidal titration, but UV-visible spectroscopy can be more universal and accurate. Therefore, we tried UV-visible spectroscopy to measure the adsorptions of some typical wet end chemicals onto a BCTMP, before and after LHCS pretreatment, and the relationship between the improved adsorptions of these chemicals and their functions were evaluated.

This study supported again that our specially designed starch-based fixing agent is very effective in treating DCS in pulp raw materials. It complemented that by measuring the adsorption of a wet end chemical by UV-visible spectroscopic method; its performance in improving pulp or paper property can be predicted to some extent. Previous studies have not shown so clearly that the adsorptions of various wet end chemicals can be improved by a fixing agent pretreatment, and that their adsorptions can be measured so successfully by UV-visible spectroscopy.

The most difficult aspect of this research was to determine the residual concentration of different wet end chemicals in the dual components system (LHCS fixing agent followed by another chemical). At first, we worried that their UV-visible spectra would overlap heavily; this was true. But when we determined the adsorption of the fixing agent itself, we found its adsorption was very high (and its residue in water was very little), so that its contribution of UV-visible absorbance to the other chemicals can be neglected, even for its most similar chemical – the cationic starch dry strength agent.

We discovered that for the wet end chemicals, the improvement of their adsorptions always led to improvement of their performances, and the adsorptions can be measured conveniently by UV-visible spectroscopic methods. This indicates that UV-visible spectroscopy can be used to predicate the performance of wet end chemicals; e.g., the best chemical from a group of chemicals with the same chemistry or the same application purpose can be screened easily without testing pulp or handsheet properties laboriously.

Mills can consider using starch-based fixing agents when they want to treat DCS in their pulp raw material. They also can use UV-visible spectroscopic methods to check if their chemicals are well adsorbed onto fibers, or to select the best chemical from a group of chemicals supplied by different chemical makers.

In the next step, we want to use the same UV-visible spectroscopic methods to investigate the adsorption or accumulation of wet end chemicals in papermaking systems under different times of whitewater recirculation.

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