Highly substituted cationic starch as an anionic trash catcher for high-yield pulp

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ABSTRACT: High-yield pulp (HYP) and recycled fibers containing anionic trash are being used increasingly in the manufacture of various paper grades. Traditionally, anionic trash catchers (ATCs), such as PEI, CPAM, and poly-DADMAC, are used to minimize the anionic trash problem. In this work, we studied an alternative ATC, highly substituted cationic starch (HS-CS). We determined the efficiency of HS-CS with different degrees of substitution of 0.57-0.97 in furnish containing dissolved colloidal substances (DCS). Flocculation behavior was also demonstrated in a dynamic drainage jar (DDJ). The results showed that HS-CS is a very good ATC. With the addition of HS-CS, the negative effects of DCS on the microparticle retention system can be minimized and the effectiveness of retention aids can be improved. The results from the dynamic flocculation experiments support the same conclusion.

Application: Modified starch with highly substituted cationic groups can be used as an effective anionic trash catcher for furnish containing high-yield pulp to minimize the negative effect of dissolved and colloidal substances.

In recent years, high-yield pulp has found increased application in the production of value-added paper grades [1-2]. The use of recycled fibers also has increased markedly due to the shortage of fiber resources and restrictive environmental regulations. Both high-yield pulp and recycled pulp contain more anionic trash than the virgin bleached chemical pulps. As whitewater closure becomes common practice in paper mills, there could be a build-up of anionic trash in the system, which can have negative consequences such as increased wet end chemical cost, reduced drainage, and decreased product quality [3-5].

The dissolved colloidal substances are primarily composed of anionic hemicellulose, oxidized lignin, resin, and fatty acids [6], and can form polyelectrolyte complexes with cationic papermaking additives, thus decreasing the effectiveness of these polymers. Usually, the DCS-containing furnishes are pretreated by highly cationic low molecular weight polymers, such as PEI, CPAM, poly-DADMAC. These additives are often referred to as anionic trash catchers (ATCs) or fixing agents [7-8]. ATCs decrease the cationic demand of anionic trash, thus reducing its negative interaction with polymers. Modified starches as dry strength agents, retention and drainage agents, and flocculants, are widely applied. Generally, the degree of substitution (DS) of cationic starch varies from 0.01 to 0.07, which is rather low [8]. The modification and application of highly substituted cationic starch (HS-CS with its DS of higher than 0.1) have been a research subject in recent years. For example, Nyström and Rosenholm [9] studied the modified cationic starch with DS of 0.2 and 0.5 as strength additives and fixing agents, respectively. They found that the combination of highly cationic starch and anionic sodium polyacrylate (NaPA) provided excellent performance.

In our laboratory we have made significant efforts in improving the peroxide bleaching process of high-yield pulps/mechanical pulps and the results were summarized in a recent publication [10]. Most recently, we started a comprehensive project on using HYP as part of the pulp furnish to produce printing/writing paper grades, and the effect on wet-end operation.

The objectives of this study were 1) to determine the efficiency of highly substituted cationic starch (HS-CS) with DS of 0.57-0.97 to be used as ATC to neutralize the anionic trash in the HYP containing furnish; 2) to optimize the application of HYP in the traditional dual retention system, CPAM/bentonite; and 3) to demonstrate the flocculation behavior via a dynamic drainage jar.

EXPERIMENTAL

Materials

The softwood and hardwood bleached kraft pulp (SWBKP, HWBKP) and aspen high-yield pulps (250/80, 325/83 and 325/85) were obtained from a Canadian pulp mill. The SWBKP and HWBKP were further refined in a PFI to 470 and 490 ml CSF, respectively, while the high-yield pulps were used as they were received. Cationic polyacrylamide (CPAM, Percol 292) and anionic bentonite (Hydrocol 0) came from Ciba. The precipitated calcium carbonate sample (PCC, ALBACAR HO) was obtained from Specialty Minerals Inc. PEI with molecular weight of 25,000 and poly-DADMAC with a molecular weight of 200,000 were obtained from Aldrich Chemical Company Inc. Three HS-CS samples with DS of 0.57, 0.74, and 0.97 were prepared in the laboratory.

Preparation of HS-CS

First, we added cooked starch into a flask, followed by the addition of alkali. We then added the cationic 3-chloro-2-hydroxypropylthrmethylammonium chloride. Subsequently, we moved the sample into an oven with a temperature of

80°C for four hours. The reaction product was filtered and then washed with ethanol, vacuum dried, and refined into a white powder [11,12].

Measurement of cationic demand (CD)

We soaked the pulp samples overnight and dispersed them into a 1% pulp suspension with deionized water. We then filtered them through a 500ml Büchner funnel with a 200-mesh Teflon screen and recycled the filtrate to go through a fiber mat to retain the fines. Finally, we used a Mütek PCD 03 equipped with a PCD-titrator to measure the cationic demand (CD) of the filtrate and 0.001N poly-DADMAC with its molecular weight of 200,000, was used as the titrant.

Pre-treatment of HYP with ATCs

We dispersed five grams of HYP into a 5% pulp suspension with deionized water. We added the ATCs directly into the pulp suspension, mixed them for 10 minutes, and then filtered them in a 500 ml Büchner funnel with a 200-mesh Teflon screen. We then recycled the filtrate through a fiber mat to retain the fines. We collected the filtrate samples and determined their cationic demand.

Preparation of DCS-free HYP samples

Washing is an effective way to remove anionic trash from high-yield pulp [13]. To prepare the DCS free pulp sample, HYP was dispersed into 1% pulp suspension with deionized water and filtered in a Büchner funnel with a 200-mesh Teflon screen. The filtrate was recycled to go through a fiber mat to collect the fines, and the pulp pad was then washed twice in the funnel.

First-pass retention and ash retention

We evaluated filler retention performance by following the first pass retention (FPR) and first pass ash retention (FPAR), as determined in a dynamic drainage jar (DDJ). First, the pulp samples (30% SWBKP and varied amount of HYP and HWBKP) were mixed well in a 0.5% pulp consistency. A 500 ml 0.5% pulp suspension was put into the DDJ, which was set at 500 rpm. Subsequently, 30% PCC was added, followed by the addition of chemicals at a controlled time. For the single retention system, only CPAM was added at 500 rpm. After 10 seconds the first 100 ml of filtrate was collected. For the dual retention system, first CPAM was added at 500 rpm for 10 seconds, then DDJ was speeded up to 750 rpm for 15 seconds, and then decreased to 500 rpm, bentonite was added, and the first 100 ml of filtrate was then collected. For the multi-component retention system, the difference was the use of the fixing agents (PEI, poly-DADMAC, or HS-CS) at 500 rpm for 10 seconds before the addition of CPAM.

We then filtered the DDJ filtrate using pre-dried and weighed ashless filter papers. The residues were dried at 105°C and reweighed to determine the solids content. We determined the PCC filler content in the filtrate with the titration method. First, the filter papers used for retaining PCC filler in the filtrate were cut into pieces and put into a flask, to which 25 ml of deionized water and 10 ml of 0.5N H_2SO_4 were added. We then heated this mixture to boiling and kept it boiling for 10 minutes to ensure a complete reaction between PCC and H_2SO_4. Finally, the flask was cooled down, 3-4 drops of indicator were added and 0.5N NaOH was used to titrate the suspension in flask. We calculated the PCC content in the DDJ filtrate as:

$$m = \frac{C_1 \times 10 - C_2 \times V}{1000} \times \frac{100}{2} \quad (1)$$

Where: m = the mass of PCC in filtrate, g
C_1 = the concentration of H_2SO_4, N
C_2 = the concentration of NaOH, N
V = the consumed volume of NaOH, ml
10 = the total volume of H_2SO_4, ml
100 = the molecular weight of calcium carbonate

The FPR was defined as the proportion of total solids in the stock suspension retained in the sheet, as in equation (2). The consistency of the stock was known from the pulp and filler input, and the consistency of the filtrate was determined by the solids content of the oven-dried filter pad.

$$\text{FPR}(\%) = \frac{\text{Consistency of Stock} - \text{Cons of DDJ Filtrate}}{\text{Consistency of Stock}} \times 100 \quad (2)$$

The FPAR was determined from equation (3). The filler content of the stock was known from the amount added, and the filler content in the filtrate was determined from equation (1).

$$\text{FPAR}(\%) = \frac{\text{Fillers in Stock}(\%) - \text{Fillers in DDJ Filtrate}(\%)}{\text{Fillers in Stock}(\%)} \times 100 \quad (3)$$

Dynamic flocculation behavior

We used a DDJ, equipped with a photometric dispersion analyser (PDA), which was designed to provide the changes in the state of aggregation (or flocculation) of a suspension [14-15].

We added 500 ml of 0.5% pulp suspension into the DDJ and allowed it to circulate to ensure a steady flow and the absence of bubbles. The filtrate from the DDJ was passed through 3 mm tubing to the PDA via a peristaltic pump set at a speed to give a fixed flow of 120 ml/min. The mechanical stirrer was set at 500 rpm. The gain on the DC signal was adjusted to give a constant reading of 10.0 voltages. All the experimental procedures, including the addition of PCC and chemicals, were the same as those for the measurement of FPR and FPAR.

RESULTS AND DISCUSSION

Cationic demand of commercial high-yield pulps

Alkaline peroxide bleaching of high-yield pulp releases dissolved and colloidal substance (DCS) into the water phase

[16] and the important components of DCS include anionic hemicellulose, oxidized lignin, resin, and fatty acids [6, 17]. Their charge properties derive from the dissociation of their carboxylic groups. The dissociation constants (pKa) vary from 3.8 to 6.5.

Figure 1 shows the cationic demand of three commercial HYP with brightness levels of 80%, 83%, and 85% ISO. Evidently, the cationic demand of the HYP is significantly affected by the pulp brightness: the higher the brightness of HYP, the higher its cationic demand. The explanation is that a higher brightness was obtained via the addition of more hydrogen peroxide and caustic soda, thus, more hemicellulose, resin, and fatty acids are dissolved. Also, more lignin is oxidized and dissolved.

Figure 1 shows that the increase in cationic demand is relatively small when the brightness of HYP increases from 80% ISO to 83% ISO; while for the 85% ISO brightness HYP grade (325/85), the cationic demand is much higher (jumping from Point D to Point B at pH 7.0). These results may reflect the difference in peroxide bleaching conditions: for aspen HYP at a brightness of less than 83% ISO, brightness increase is easily achieved; therefore, only mild bleaching conditions (less chemicals) are needed. For a brightness target above 83% ISO, bleaching becomes progressively more difficult, more chemicals are needed, and more anionic trash is generated.

Based on the same consideration, there may be an economic reason to bleach aspen HYP to a brightness of 83% ISO via the conventional peroxide bleaching technology. A further increase in brightness may be obtained from the addition of an optical brightening agent (OBA).

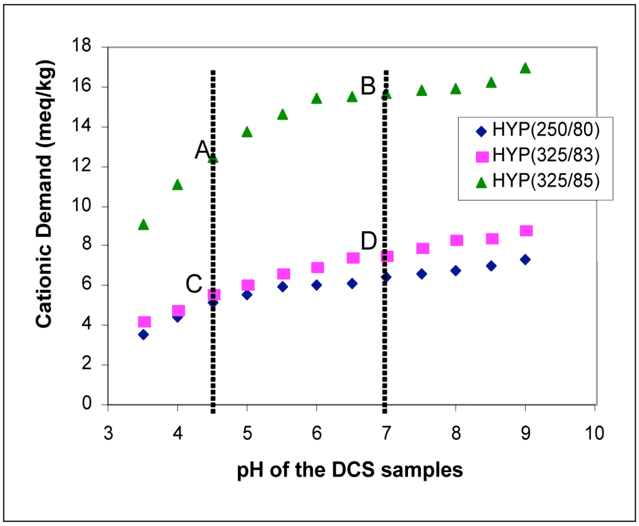
Figure 1 also shows that the cationic demand of DCS increased significantly with the increase of pH, especially for the very high brightness grade HYP (325/85). At pH 4.5, the cationic demand is relatively lower and mainly comes from the hemicelluloses, such as polygalacturonic acids (Point A or Point C). As pH further rises from 4.5, the increase in cationic demand is due to fatty and resin acids, and oxidized lignin [6]. Evidently, for the very high brightness HYP (325/85), much more oxidized lignin, fatty and resin acids are produced than for the other two grades, 250/80 and 325/83. Again, these results can be explained by the difference in peroxide bleaching conditions in producing these three HYPs.

Detrimental effects of DCS on the filler retention

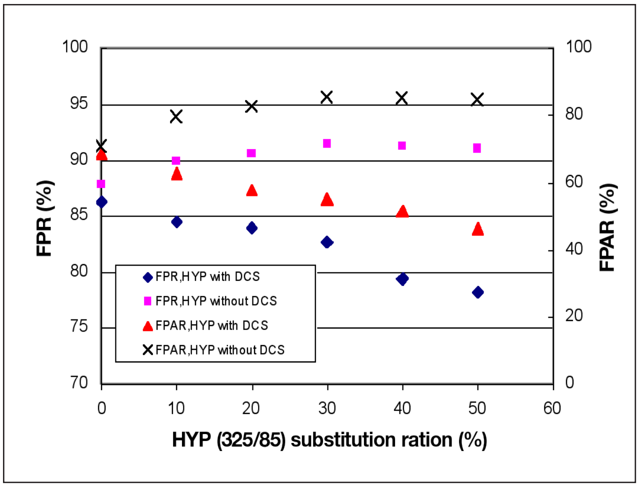
Figure 2 shows the effect of DCS in HYP on the filler retention in a single cationic polymer retention system. Two samples were studied: one was a regular HYP (identified as HYP with DCS) and the other was a DCS-free HYP (identified as HYP without DCS). For the regular HYP, the filler retention (both FPR and FPAR) decreases as the HYP substitution increases, while for the DCS-free HYP, the filler retention increases as the HYP substitution is increased up to 20%. For the DCS-free HYP, due to the high carboxylic group content and the unique presence of sulfonic group [18], HYP fibers have a positive effect on filler retention, which is then responsible for the increased filler retention as the HYP substitution increases. The decreased filler retention for the regular HYP is due to the presence of DCS, which negatively affects the filler retention. In reality, market HYP always contains DCS, which can impart negative consequences to the filler retention.

Effect of ATCs on minimizing the negative effect of DCS

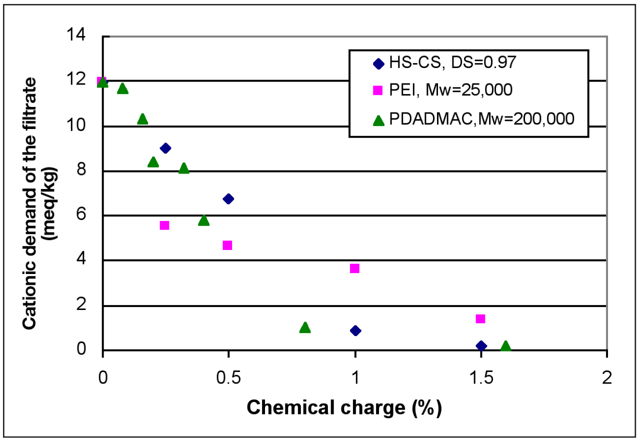
The most effective and the simplest way to minimize the negative effect of DCS is to apply ATCs (PEI, PDADMAC, and HS-CS) to pre-treat the DCS containing furnish. **Figure 3** shows the effect of some ATCs on decreasing the cationic demand of anionic trash. With the increase of ATCs dosage, the cationic demand decreases significantly. At the lower dosage



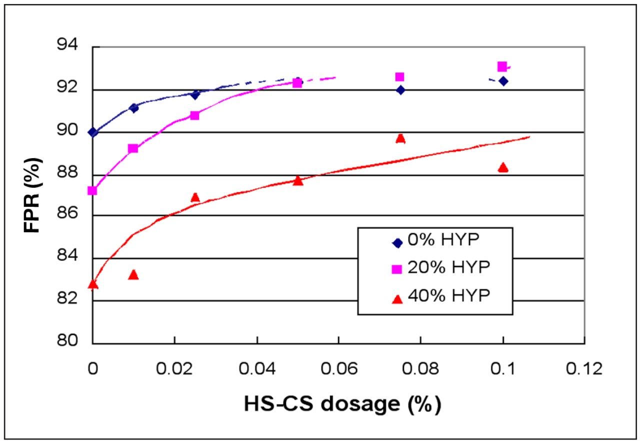
1. Effect of pH on the cationic demand of filtrate samples.



2. Effect of DCS on the filler retention in single retention system. *(30%PCC; 0.05% Percol 292)*



3. Effect of ATCs dosage on the cationic demand of filtrate samples. *(100% HYP (325/85); 5% pulp consistency; 0.5% chemical dosage)*



4. Effect of HS-CS dosage on first pass retention in multi-component retention system.
(30% PCC; HS-CS with DS 0.97; 0.05% Percol 292; 0.3% bentonite)

(less than 0.5%), PEI with Mw=25,000 is more effective than PDADMAC and HS-CS. At the dosage of more than 1.0%, almost all of the anionic trash could be neutralized by PDADMAC or HS-CS. HS-CS performs as well as PEI and PDADMAC.

Effect of HS-CS with different DS levels

The conventional single-component retention system suffers from a number of shortcomings. For example, it is susceptible to the shear force normally experienced on a paper machine. The dual or multi-component retention aid systems were designed to overcome such weaknesses [19]. Their resistance to shear force is increased and hence they are more suitable for high-speed paper machines. Today, microparticle systems are widely used in fine paper manufacture, as they provide superior retention, drainage, and formation characteristics [20-21].

Table I presents the application of HS-CS with three DS levels in the conventional microparticle retention system (CPAM/bentonite). At the same HS-CS dosage, the filler retention (FPR and FPAR) was improved significantly as the DS increased from 0.57 to 0.74 or 0.97, indicating that the effectiveness of HS-CS increased at a higher DS. Compared with the control, the HS-CS sample with DS of 0.97 performs best. At the dosage of 0.01%, the FPR and FPAR can increase from 85.77% and 69.44% to 90.20% and 78.93%, respectively. Also, for the HS-CS with the same DS, filler retention increased with the increase of the HS-CS dosage.

Effect of HS-CS charge on filler retention

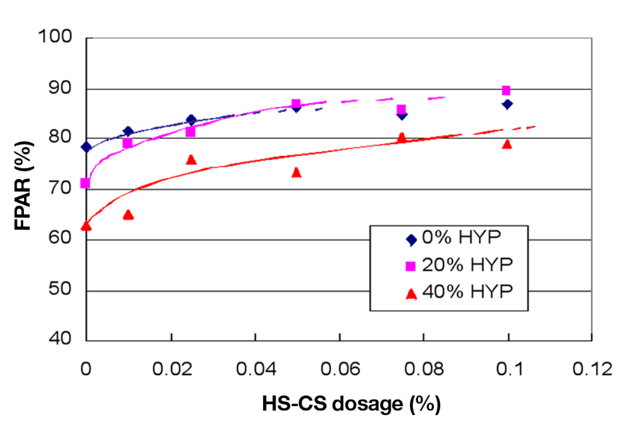
Figure 4 shows the effect of HYP substitution in a multi-component retention system (HS-CS with DS of 0.97 + 0.05% CPAM + 0.3% bentonite). With the increased HS-CS dosage, the FPR increased significantly, especially for the 40% HYP substitution furnish. These results support the conclusion that HS-CS reduces the negative effect of DCS, resulting in a higher efficiency of retention aids.

Figure 4 also shows an interesting phenomenon for the furnish with 20% HYP substitution. With the addition of 0.08% HS-CS, or even more, the FPR of furnish was higher than that of furnish without HYP. This can be explained by the high carboxylic group content and presence of sulfonic groups in HYP fibers and fines [18]. In other words, HYP fiber and fines have a positive effect on filler retention, if the negative effect of DCS can be eliminated by the addition of ATCs.

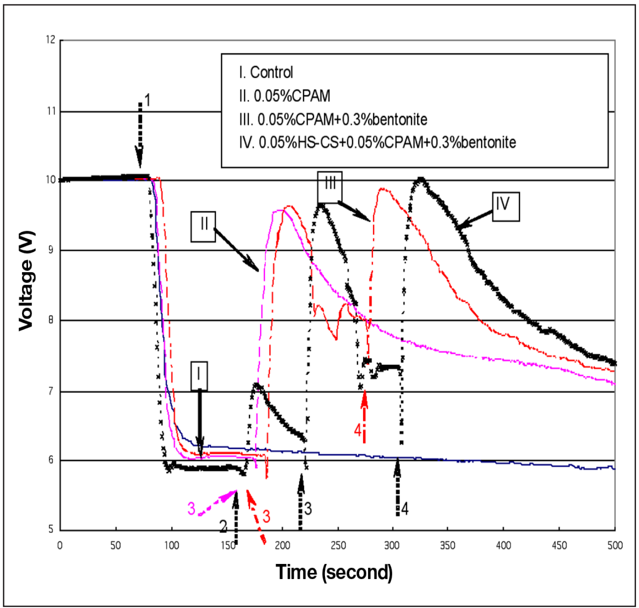
Figure 5 presents the FPAR results of furnishes with three HYP substitution levels, and they are in agreement with those in Fig. 4. Likewise, the furnish at 20% HYP substitution has a positive effect on the FPAR with the addition of 0.08% or more HS-CS.

HS-CS with different DS		DS 0.57		DS 0.74		DS 0.97	
HS-CS dosage (%)	0	0.01	0.075	0.01	0.075	0.01	0.075
FPR (%)	85.77	86.68	90.86	88.40	91.02	90.20	92.56
FPAR (%)	69.44	75.73	81.87	76.00	86.53	78.93	85.73

I. Effect of HS-CS with different DS on filler retention in multi-component retention system.
(20 %HYP (325/85); 30% PCC; 0.05% Percol 292; 0.3% bentonite)



5. Effect of HS-CS dosage on first pass ash retention in multi-component retention system.
(30% PCC; HS-CS with DS 0.97; 0.05% Percol 292; 0.3% bentonite)



6. Filler retention of 20% HYP containing furnish in different retention systems. *(30%SWBKP+50%HWBKP+20%HYP; adding point: 1-PCC, 2-HS-CS, 3-CPAM, 4-bentonite)*

Dynamic flocculation behavior

Figure 6 shows the filler retention of 20% HYP substitution pulp furnish in different retention systems. Theoretically, a higher voltage means lower turbidity and better flocculation. For the control, only 30% PCC was added at Point 1. For the single retention system, CPAM was added at Point 3. For the dual retention system, CPAM and bentonite were added at Points 3 and 4, respectively. For the multi-component retention system, HS-CS was added at Point 2, CPAM and bentonite were added at Points 3 and 4, respectively. When bentonite was used, we induced a high shear force to break down the flocs before it was added.

It is evident that the multi-component retention system is the best. With the addition of HS-CS, the negative effect of DCS in HYP can be minimized and the efficiency of retention aids can be improved.

The results in Fig. 6 support the conclusion that HS-CS behaves similarly to the traditional ATCs, such as PEI and poly-DADMAC. It can substitute for PEI or poly-DADMAC to serve as an ATC in DCS-containing furnishes. This is a new option for papermakers to find some cost-effective ways for the papermaking wet-end operation.

CONCLUSIONS

The higher the brightness, the higher the DCS content in HYP. This is due to a strong bleaching condition (more hydrogen peroxide and caustic soda required) during the HYP bleaching process, resulting in more hemicellulose, resin and fatty acids, and oxidized lignin dissolved into the water phase. The DCS in HYP has a detrimental effect on filler retention (FPR and FPAR). The results from furnishes with or without DCS showed that due to the presence of DCS, the typical market HYP has a negative effect on filler retention in furnish containing HYP. However, at a low HYP substitution (less than 20%), with the addition of anionic trash catchers (ATCs), such as highly substituted cationic starch (HS-CS), higher filler retention can be achieved because more carboxyl groups and unique sulfonic group are present in HYP fibers or fines.

HS-CS is a very good ATC, especially the HS-CS sample with DS of 0.97. With the addition of HS-CS, the negative effects of DCS on the traditional microparticle retention system can be minimized and the effectiveness of retention aids can be improved. HS-CS can be substituted for PEI, or CPAM or poly-DADMAC, the commonly used ATCs in papermaking wet-end operation. The results from the dynamic flocculation study support the same conclusion. **TJ**

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INSIGHTS FROM THE AUTHORS

We chose this topic because, while high-yield pulp can provide papermakers with the benefits of lower production costs and improved product qualities such as bulk and opacity, HYP also contains more dissolved and colloidal substances than bleached kraft pulp. These substances can have a negative effect on wet-end chemistry and in our research we sought to develop a way to minimize those effects.

Our previous research results had shown that the DCS from HYP can be largely neutralized by the addition of conventional anionic trash catchers such as PEI and poly-DADMAC. In this study we identified a novel biodegradable highly substituted cationic starch as a more cost-effective ATC for furnish containing HYP. The most difficult aspect of the research, which involved a large amount of laboratory work, was screening out the less-effective substances.

We found the highly substituted cationic starch to be very effective. With the addition of a small amount of HS-CS, the negative effects of DCS on a micro particle retention system can essentially be eliminated. We were surprised by finding that a 10%-20% HYP substitution for bleached kraft could lead to higher first-pass filler retention when an effective ATC is added.

Our findings show that paper mills can use up to 20% HYP as a substitute for bleached kraft to reduce costs and improve paper bulk and opacity without losing efficiency in filler retention. The extra amount of DCS in the HYP can be controlled with an effective ATC like HS-CS. Future studies will include the interaction of HS-CS with DCS under more complex wet-end conditions.

Hu

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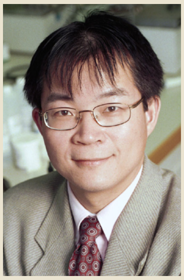

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