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Starch in wet-end of papermaking as retention & strength aid

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ABSTRACT

Papermakers use mainly two forms of starch for addition at the wet-end section of papermaking process viz., cationic and amphoteric starch. The starch added in the thick pulp stock mainly increases the strength properties, whereas it increases the filler retention when added in the thin pulp stock. With modern retention aid polymers and techniques, use of starch as retention aid chemical is almost discarded with time. This study was devised to see the effect of dosage and dosing point of three different starches on filler retention and paper properties. Out of three starch samples two were cationic having different degrees of substitution and one was amphoteric. All the starches were added into pulp stock in two different manners; in thin stock as retention aid and in thick stock as strength aid. The comparison of all the three starches added in thin stock was done with a typical polymeric retention aid. The amphoteric starch gave better retention as compared with cationic starch. The use of any of the starches in thin pulp stock as retention aid was not economical. The effect of amphoteric starch and cationic starches added in thick pulp stock as strength aid was also compared. Optimized dose and dosing point of some starches may improve the strength properties even at increased filler level in paper sheets.

KEYWORDS

Cationic starch;
Amphoteric starch;
Paper strength;
Filler retention;
Papermaking;
Ash.

INTRODUCTION

Like cellulose, starch is comprised of glucose units linked together by oxygen bridges called glycosides. The main difference in starch comparing cellulose is the orientation of the molecules in that linkage (alpha rather than beta). In starch, all the glucose repeat units are oriented in the same direction. But in cellulose, each successive glucose unit is rotated 180 degrees around the axis of the polymer backbone chain, relative to the last repeat unit[1].

This subtle difference means that starch is more readily soluble in water and more easily digested by bacteria and other living things. Mainly two forms of starch are used in wet-end of papermaking process viz. cationic and amphotieric starch. Cationic starch is derivatized with a quaternary ammonium compound. The degree of substitution is usually about 0.02 to 0.03 on the basis of glucose units (0.20-0.35% nitrogen). Amphoteric starch contains phosphate groups in addition to the cationic quaternary amine groups.

Starch contributes to the stiffness and bonding within a sheet of paper. Cationic starch is mainly used to improve internal bond, tensile strength, and as part of certain retention and drainage programs. The main point to bear in mind when using starch at wet-end section of papermaking process is the fact that each papermaking furnish has a limitation on its ability to retain the starch efficiently. In some cases, the critical factor is the surface area of papermaking furnishes and in other, the limited amount of anionic colloidal charge at the fiber surfaces. Cationic starch is expected to contribute to inter-fiber bonding strength by increasing the effective area of bonding between the fibers. It is mainly used to improve the dry strength of paper, to emulsify the sizing agents and as a part of many retention & drainage programs[2].

The word "amphoteric" implies that a chemical product has both positive and negative ion groups when it is dissolved in solution. When papermakers refer to amphoteric starches they are usually referring to products derived from corn starches. Amphoteric starches also are prepared from waxy maize, a variety of corn that produces only the branched type of starch, amylopectin. The cationic group is the same quaternary ammonium substituent used in preparation of cationic starches. The anionic groups usually are phosphates. Strictly speaking all cationic potato starches are really amphoteric starches since potato starch contains about 0.08% phosphorous. The cationic content of amphoteric starches is typically 0.2-0.3% nitrogen. The main use of amphoteric starch is also same like cationic starch i.e. enhancement of dry strength, improving drainage and retention[3].

Starch has to be dissolved in water and cooked prior to use. The performance of starch as a dry strength agent is only moderately affected by its point of addition. In the stock preparation section, starch is generally added in two points; one before any chemical dosing in thick stock and another after all the chemical dosing in the thin stock. When the starch is added to the thick stock, the main aim is to increase the strength properties, whereas when it is added to the thin stock, the purpose is to increase the filler retention. Addition to the thick stock has both potential advantages, and disadvantages. If strength improvements are the key requirement, the cooked starch is added as far back in the system as possible, typically into the thick stock. Advantages include getting a higher proportion onto long fibers, ensuring good retention and a relatively high effect on overall dry-strength. Also, addition to the thick stock ensures that any flocculation caused by the starch has been completely reversed before the head box making it possible to get a very uniform sheet. Disadvantages of early addition include breakdown of starch by hydrodynamic shear and possible disappearance of some of the starch into the interior of pores in the fiber cell walls. For these reasons, it is common to add at least part of the starch to the thin stock with only a few seconds of exposure to furnish before it is made into paper. If retention improvements are desired, the cooked starch is added into the thin stock loop, close to the flow box. Starch induced flocs are very sensitive to hydraulic shear forces. Sometimes split addition of starch is also used in an attempt to maximize both strength improvement and retention. Excess cationic starch can result in the overall charge of the wet-end system crossing over from anionic to cationic. If this happens, drainage and formation of stock on the wire is severely disrupted. The batch procedure takes about 20 to 30 minutes at about 95 °C at atmospheric pressure. The performance of amphoteric starch can be enhanced if alum or polyaluminum chloride (PAC) is also being used. Amphoteric starches have a reputation for performing well under conditions of high electrical conductivity. Also, they can be an effective strength agent for systems that would tend to become overly cationic if a straight cationic starch was used[4].

When the lower amount of gelatinized solution of the cationic starch is added to the pulp stock, it provides high bonding strength by the electrostatic attraction, and drastically increases the retention of starch. However, when the dose of the cationic starch was more than the negative charge of the pulp, the retention of starch decreased. Accordingly, high retention of starch was accomplished when the cationic starch was added less than about 1% of pulp, but retention was lowered when the starch was added more than 1%[5].

Overuse of cationic starch in a machine system can negatively impact wet-end chemistry and forming section drainage. The anionic charge on amphoteric starch molecules can help in retaining cationic fines and fillers. Thus, higher addition rates of amphoteric starch can be employed to improve dry strength response versus traditional wet-end cationic starch applications[6].

In this communication, we have tried to optimize the point of addition of cationic and amphoteric starches of different degree of substitution into the pulp slurry through evaluating the retention of filler and properties of paper.

EXPERIMENTAL

Materials

The pulp used in this study was a mixture of 80% mixed hardwood and 20% bamboo. It was taken from an integrated pulp and paper industry in north India. The pulp was beaten to 30 °SR in PFI mill (Hamjern Maskin as, Norway) under standard beating conditions as per Tappi test method T 248 sp-00.

The ground calcium carbonate (GCC) was used as filler. The particle size of GCC less than 2 microns was 60%. It was used at a fixed dosage of 300 kg/t pulp. Three different starch samples; two cationic starches (CS-1 and CS-2) and one amphoteric starch (AS) were procured from different chemical suppliers in India and used both as strength and retention aid. A typical polymeric retention aid (RA) was also used to compare the retention mechanism with different starches. The studies were carried out in neutral sizing.

Typical 70 g/m^2 paper handsheets were prepared in British handsheet former and conditioned at 23±1 °C in 50±2% relative humidity for one day and used for further testing.

Methodology

Four dose levels viz. 2.5, 5.0, 7.5 and 10.0 kg/t pulp of each starch sample was used both as strength and retention aid as per sequence given in Figure 1. The Dissolved charge of pulp slurries was measured on Particle charge detector (model: PCD 03 pH, made by Műtek Wet Lab, Germany). Ash content in paper handsheets was determined as per Tappi T-211 om-93. The ash and first pass ash retention were calculated using the following formulas:

$$\text{Ash Content in paper, \%} = \frac{\text{Weight of ash in paper (g o.d.)}}{\text{Weight of handsheet (g o.d.)}} \times 100$$

$$\text{FPAR, \%} = \frac{\text{Ash in paper (\%)}}{\text{Filler added based on pulp and filler (\%)}} \times 100$$

Opacity of paper handsheets was tested on Datacolor (Datacolor, USA; model: Spectraflash 300 UV) brightness tester as per Tappi test method T-425 om-01. Strength properties of paper handsheets were determined as per relevant Tappi test methods.

RESULTS AND DISCUSSION

General characteristics of various starches

The general characteristics of different starches are given in TABLE 1. The source of all starches was potato. The pH of the starch slurries was ranging from 6.4 to 7.4. Streaming potential and anionic demand values show that cationic starch-1 (CS-1) was less cationic than cationic starch-2 (CS-2). The degree of substitution of CS-1, CS-2 and AS was 0.025, 0.03 and 0.04 (0.02 each for cationic and anionic) respectively.

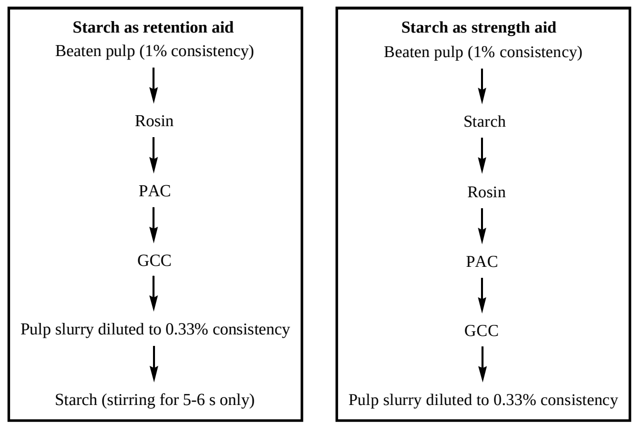

Figure 1 : Sequential addition of chemicals

TABLE 1 : General characteristics of different starches

Sample	CS-1	CS-2	AS
Source	Potato	Potato	Potato
pH (1% w/v)	6.4	7.4	7.1
Streaming potential, mV	+165	+737	+1436
Anionic charge demand, μeq/l	1201	1939	3245
Degree of substitution, mol/mol	0.025	0.035	0.04

The particle size distribution of CS-2 was lower than that of CS-1. The percentage of particles of CS-2 less than 1.0 micron was 68% whereas it was only 25% in case of CS-1. The particle size distribution of AS was comparable to that of CS-2 (TABLE 2).

TABLE 2 : Particle size distribution of different starches

Particle size, μm	Abundance, %		
	CS-1	CS-2	AS
< 0.5	8	33	26
0.5-1.0	17	35	39
1.0-2.0	29	23	21
2.0-3.0	32	3	14
> 3.0	14	6	0

Use of starch as retention aid

In order to understand the effect of starch on retention of filler, it was added in the thin pulp stock (0.33% consistency). As expected, with increasing starch dosage, the ash in the paper was increased. As shown in Figure 2, the highest ash content was achieved with AS followed by CS-2 and CS-1 respectively. It was in the order of decreasing cationic charge and degree of substitution. The highest ash in paper was achieved with the highest used dosage of cationic starch i.e. 10 kg/t. In case of CS-1, the highest ash in paper was 10.1%, whereas it was 12.5 and 13.0% in case of CS-2 and AS respectively. The first pass ash retention (FPAR) was 42.2, 50.8 and 54.6% with CS-1, CS-2 and AS respectively.

The starches added as retention aid reduced the physical strength of paper. As shown in Figure 3, the breaking length of paper was reduced with increase in dosage of CS-2 and AS. There were two reasons of this reduction in paper strength. The first one was that the starch added in the thin stock could not be used to make the bonds between fibers rather it was totally consumed in the formation of filler and fiber fines flocs due their opposite charge chemistry. The second reason was the increase in ash in paper which was also responsible for lesser fibers and fiber bond in a constant weight/volume of paper. The breaking length of paper with increasing dosage of CS-1 was almost unchanged probably due to lesser ash content in paper and it low molecular weight. The latter was responsible to make smaller and softer flocs, and some portion of the starch might have been used in developing the fiber-fiber bonds

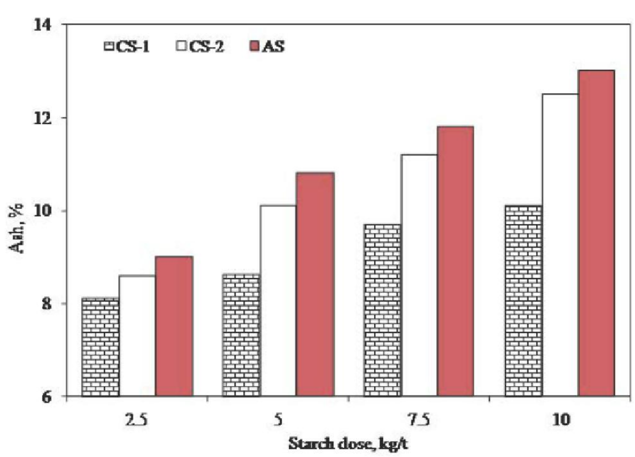

Figure 2 : Effect of starches on ash content of paper when added in thin pulp stock as retention aid

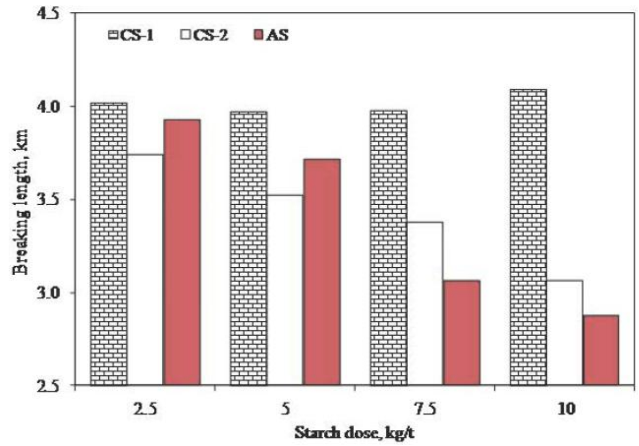

Figure 3 : Effect of starches on breaking length of paper when added in thin pulp stock as retention aid

to some extent. It was also noticed that initially at 2.5 and 5.0 kg/t dose levels, the breaking length of paper was higher in case of AS as compared with CS-2 but with further increase in starch dose this trend turned out to opposite; in case of higher dosage of AS, the decrement in breaking length was very fast.

Similar to the case of breaking length, the burst index of paper was reduced with increasing dosage of CS-2 and AS whereas it was slightly increased with increasing dosage of CS-1. The higher drop in burst index was observed with CS-2 as compared that with AS (Figure 4). Initially at lower dosage of starch (2.5 kg/t), the burst index of paper was slightly higher with CS-2 as compared with other two starches but on increasing dosage from 2.5 to 10 kg/t, the burst index dropped rapidly with CS-2. Due to higher cationicity and molecular weight, CS-2 was benefitial for increasing burst index of paper at lower dosage only, beyond which it might have provided high cationicity to pulp stock and caused bigger flocs which in turn reduced the paper formation and inter-fiber bonding.

In addition to the physical strength of paper, the opacity of the sheets was also compared with all the starches. As shown in Figure 5, the opacity of paper sheets was increased with increasing dosage of starch. This was true for all starches certainly due to increase in ash content of paper with increase in dosage of starch. The highest opacity was achieved in case of CS-2 followed by AS and CS-1. CS-2 was certainly responsible of making denser flocs as compared with AS. Due to the both cationic and anionic groups in AS, it was possibly used in coagulation and flocculation and made larger flocs.

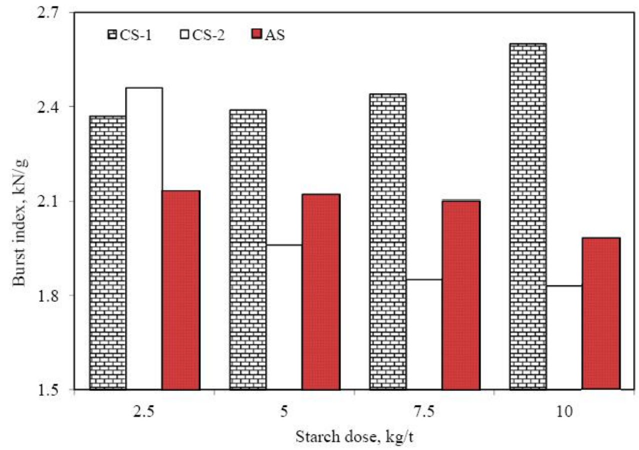

Figure 4 : Effect of starches on burst index of paper when added in thin pulp stock as retention aid

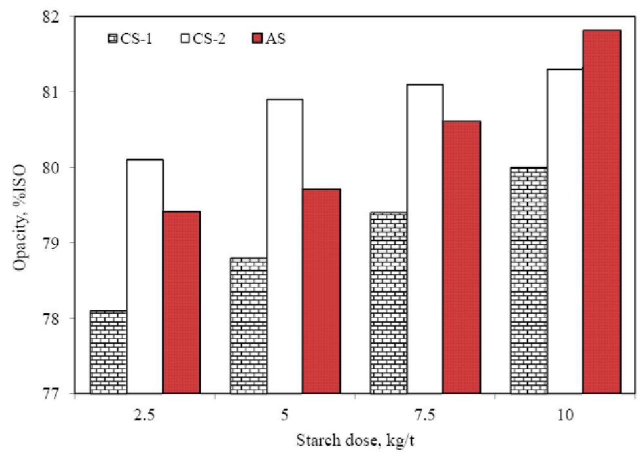

Figure 5 : Effect of starches on opacity of paper when added in thin pulp stock as retention aid

Comparison of starch and retention aid polymer

The all three starches used as retention aid in thin pulp stock were compared with a typical polymeric retention aid chemical which is used commercially in the paper industry. The paper sheets were prepared with the ash content of 10% with all the chemicals. It was observed that in order to get around 10% ash in paper sheets the dosage of CS-1, CS-2 and AS was 10, 5 and 5 kg/t respectively whereas it was only 50 g/t in case of typical retention aid (RA). As shown in Figure 6, the breaking length of paper sheets was different for different retention aid chemicals at same ash level. In case of CS-1, it was the highest i.e. 4.09 km followed by 3.71, 3.52 and 3.48 km in case of AS, CS-2 and RA respectively. The reason of higher breaking length with CS-1 was possibly due to its higher dosage required to attain 10% ash level in the sheet. It seems that the higher dosage of CS-1 was contributing to both retention of filler and paper strength. However, its contribution towards retention was not very good as it required higher dosage. Thus it reflected that most of the CS-1 might be consumed in inter-fiber bonding due to which breaking length of paper was higher. The burst index of paper sheets was also highest with CS-1 followed by RA, AS and CS-2. The burst indices of paper with CS-2 and AS were much lower as compared those with CS-1. The ISO opacity was the highest in case of RA followed by CS-2, CS-1 and AS respectively.

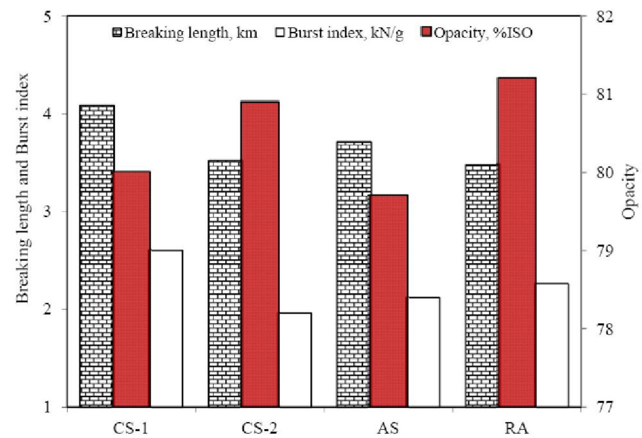

Figure 6 : Paper properties with different starches and typical retention aid at 10% ash level

Use of starch as strength aid

When starches were added in the thick stock (1% consistency) as strength aid it was observed that with increasing dose of starch, the ash in paper increased but the increment was much lower as compared when the starches were used as retention aid. The highest ash content was achieved in case of AS. Whereas, it was almost similar in case of both CS-1 and CS-2 at all dose levels. As shown in Figure 7, the ash content increased from 7.8 to 8.6% in case of both CS-1 and CS-2, whereas it increased to 9.5% in case of AS. The FPAR increased from 33.3 to 35.8, 34.7 and 37.5% with increasing the dosage of CS-1, CS-2 and AS from 2.5 to 10 kg/t respectively.

At different dose levels, the breaking length was different with different starches. In case of CS-1, the breaking length of paper sheets was increased, whereas in case of both CS-2 and AS, it was decreased with increase in dosage of starch. As shown in Figure 8, initially at 2.5 and 5.0 kg/t dose levels, the breaking length of paper was higher in case of CS-2 as compared to CS-1 but with further increase in starch dose this trend became opposite. In case of AS, a rapid decrement in breaking length was seen with increasing starch dose.

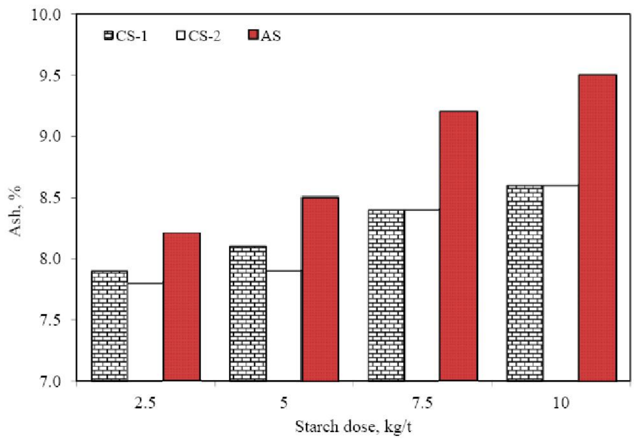

Figure 7 : Effect of starches on ash content of paper when added in thick pulp stock as strength aid

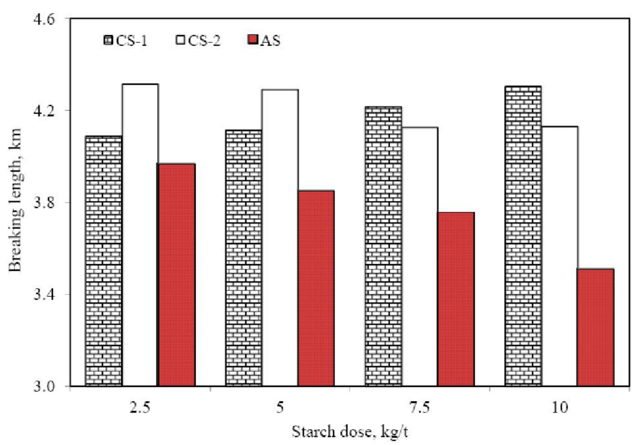

Figure 8 : Effect of starches on breaking length of paper when added in thick pulp stock as strength aid

As shown in Figure 9, the effect of different starches as strength aid on burst index was also different. At 2.5 kg/t dose level, the burst indices with all the starches were comparable. The burst index of paper was comparable with both CS-1 and AS at all dosage levels. In case of both CS-1 and AS, the burst index of paper was increased with increasing starch dose whereas in case of CS-2 it remained almost constant on increasing its dosage from 2.5 to 10 kg/t. At 10 kg/t dose level, the burst indices were 2.70, 2.34 and 2.69 kN/g with CS-1, CS-2 and AS respectively.

As shown in Figure 10, the opacity of paper sheets was increased with increasing dosage of starch except with CS-1. In case of CS-1, the opacity of paper was increased on increasing the dosage from 2.5 to 5 kg/t and then remained unchanged on further increasing its dosage to 7.5 and 10 kg/t. This trend was similar to the trend observed when starches were used as retention aid. It was again due to the increase in ash content of paper with increase in starch dose. The highest opacity was achieved with AS followed by CS-1 and CS-2 respectively. At 2.5 and 10 kg/t dose levels, the opacity of paper was comparable for CS-1 and CS-2 but at 5.0 and 7.5 kg/t dose levels, it was higher in case of CS-1 as compared to CS-2.

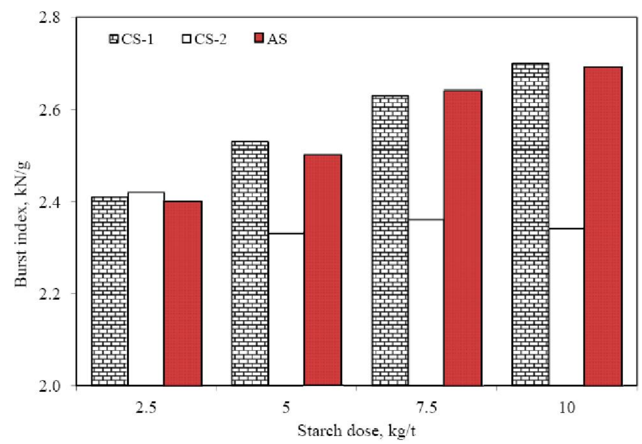

Figure 9 : Effect of starches on burst index of paper when added in thick pulp stock as strength aid

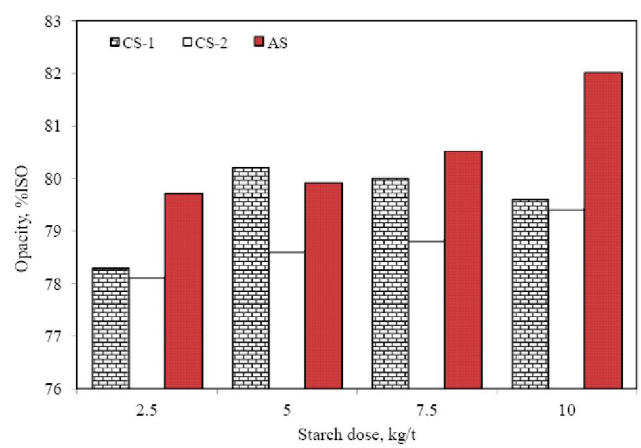

Figure 10 : Effect of starches on opacity of paper when added in thick pulp stock as strength aid

Comparison of starches as strength aids

All the three starches were compared for various properties of paper at 8.5% ash level. In order to achieve 8.5% ash in paper, the dose of CS-1 and CS-2 were 10 kg/t pulp whereas it was only 5 kg/t in case of AS.

As shown in Figure 11, the breaking length of paper was different for different strength additives at same ash level. In case of CS-1, it was the highest i.e. 4.30 km followed by 4.13 and 3.85 km with CS-2 and AS respectively. The higher breaking length with CS-1 and Cs-2 was due to their higher dosage required to get the same ash in paper which ultimately helped in inter-fiber bonds and increased the paper strength. The burst indices of paper with CS-1 and AS were almost comparable i.e. 2.70 and 2.64 kN/g whereas it was lower in case of CS-2 i.e. 2.34 kN/g. At the same ash level, the ISO opacity was the highest in case of AS (80.5%). The ISO opacity was almost comparable with CS-1 and CS-2 i.e. 79.6 and 79.4% respectively.

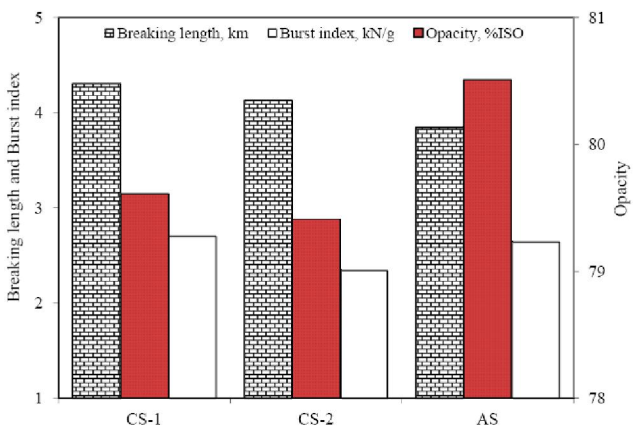

Figure 11 : Paper properties with different starches at 8.5% ash level when used as strength aid

CONCLUSIONS

The amphoteric starch was a better retention aid chemical when used in the thin pulp stock as compared with cationic starches. The strength properties were higher with cationic starches. It was possibly due to the lesser ash content with cationic starches. Filler retention was the highest with typical retention aid polymers as compared with starches when used as retention aid. None of the starches was found good alternate to use as a retention aid chemical in terms of their commercial application due to higher dosage of starch as compared to typical retention aids. All the starch chemicals were helpful in increasing the paper strength. Cationic starch-1 provided higher strength to paper even though it had lesser degree of substitution than cationic starch-2. The opacity was the highest with amphoteric starch at same ash levels. The cationic starch was found as a good strength aid chemical whereas amphoteric starch can be used for getting better opacity in paper due to its good retention aid properties; with little compromise of strength properties in case of latter.

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