INFLUENCE OF PULP SUSPENSION PH ON THE PERFORMANCE OF CHITOSAN AS A STRENGTH AGENT FOR HARDWOOD CMP PAPER

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Chitosan – a well-known carbohydrate – has found new applications in the papermaking industry. Although the effect of pH on the properties of chemical pulps has been investigated in a number of studies, it has not been reported related to hardwood mechanical pulp, to our knowledge. In the present research, the effect of different pH levels (5.5, 7 and 8.5) on the performance of chitosan as a dry strength additive in paper produced from chemi-mechanical hardwood pulp was studied. The results indicated that the effect of chitosan on the properties of chemi-mechanical paper depended strongly on the pH of the furnish. The addition of chitosan to the stock at acidic pH did not have any specific effect on the strength properties. In contrast, neutral and alkaline pH resulted in improvements in the dry strength properties of paper sheets. The maximum apparent density was observed at pH 8.5, which was attributed to the precipitation of the chitosan on the fiber surface. The results showed that chitosan would be more effective in low dosages. The dependence of chitosan performance on pH in chemi-mechanical pulp was similar to that reported for chemical pulps.

Keywords: chitosan, dry strength, chemi-mechanical pulp, fiber, wet end, pH

INTRODUCTION

An improvement in the mechanical properties of paper sheets can be achieved by increasing the bonding between cellulose fibers.[1,2,3,4] To improve both wet and dry strengths of paper, a number of polymeric materials have been used, including cationic starch, polyvinyl alcohol, urea, cationic polyacrylamide, poly-vinyl amine, phenol- and melamine-formaldehyde resins, and so forth. When wet strength is required, the polymers must reinforce the interfiber bonding areas, so that the fibers can remain chemically linked in the presence of water.[5] It has been proposed that a dry-strength additive should have the following specifications:[1,3,4,6]

- it should be soluble in water-based environments for easy application with conventional paper making systems;
- it should be substantive to cellulose, so that retention is efficient;
- it should be compatible with the cellulose surface, so as not to disrupt conventional hydrogen bonding;
- it should contain a functional group capable of ionic, covalent or hydrogen bonding with the paper fiber surface within the paper making process;

- it should be non-toxic and perfectly natural to conform to environmental regulations with minimum problems in paper recycling.

Such requirements are met by chitosan. Chitosan is a high molecular weight linear carbohydrate composed of ß(1→4)-linked 2-amino-2-deoxy-ß-D-glucose units, prepared by the hydrolysis of the N-acetyl groups from the natural polymer chitin (Fig. 1). Chitin is easily obtained from crab or shrimp shells and fungal mycelia.[7]

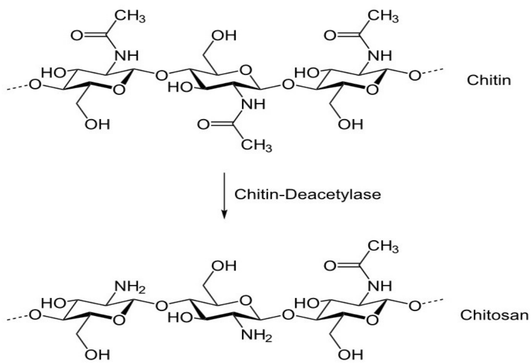

Figure 1: Chitosan formation from chitin

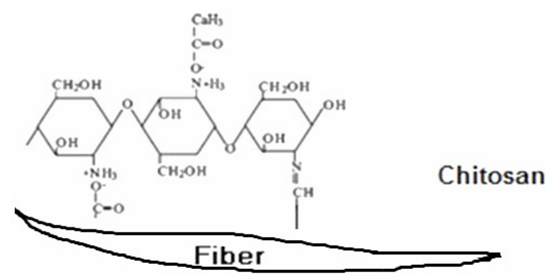

Figure 2: Formation of ionic and/or amino bonds between chitosan and pulp fibers (Ashori *et al.*[1])

Chitosan has basic amino groups, which under acid conditions are protonated and act as a cationic polyelectrolyte.[1,4,8,9,10,11] Figure 2 presents the formation of ionic and amino bonds between chitosan and cellulosic fibers, which is believed to happen upon drying of paper.[12] It is expected that the usage of chitosan can improve both product properties and machine runnability. In papermaking, chitosan has been found to be effective as a dry and wet strength agent,[4,9,12,13,14,15] as well as in sizing[1,15] and retention.[5,15]

The pH is an important variable in the electrostatic relations of fiber suspensions. Many authors have stated that chitosan has shown clear pH-dependent behavior when applied as paper strength additive.[9,14] There are many controversial justifications for the reasons to use chitosan at different pH levels. Some researchers carried out experiments on chitosan addition to kraft kenaf fibers and stated that since the pKa value of carboxyl groups in these fibers was in the range of 4-4.5, and that of the ionized amino groups in chitosan was about 6, the application of chitosan at pH 5 was selected to maximize the number of ionized functional groups available for chitosan retention and ionic bond formation.[1] They named this application method "equilibrium adsorption". Also, they stated that since chitosan salts revert to the insoluble free amino form under alkaline conditions, chitosan was not ionized in the water phase and therefore a much smaller randomly coiled configuration upon precipitation into the solid phase was assumed. They named the application of chitosan under alkaline conditions "precipitation". Based on these considerations, it can be expected that under acidic pH conditions, chitosan can be more involved in paper strength improvement. By contrast, it was indicated that chitosan adsorbed at pH 5 did not affect the sheet strength at all.[16] Other results indicated that dry and wet strengths of the paper network were best improved by chitosan addition at pH 10, and such results were explained to have been caused by the optimized retention of chitosan on the fibers, as well as by a better interaction between the anionic groups of the pulp suspension and the cationic groups of the chitosan.[4]

Depending on the manufacturing method and the lignocellulosic raw materials used, pulps can have very different surface charge content. It has been recognized for years that the charged groups of cellulosic fibers have a key impact on the wet-end chemistry, especially with respect to dry strength additive performance. High lignin, hemicelluloses and fines content results in a higher anionic charge in a mechanical pulp suspension, compared to a chemical pulp one.[17] Chitosan has been widely studied in chemical pulps, but no research has been dedicated to the effect of chitosan as a dry strength agent in mechanical pulps.[1,3,4,10,12]

In view of the foregoing discussion, the objective of this study was to investigate the effect of varying dosages of chitosan as a dry strength additive in chemi-mechanical pulp (CMP) and its interaction with different pH levels of the suspension, representative for acid, neutral and alkali conditions.

EXPERIMENTAL

Materials

CMP pulp produced from mixed hardwood at Mazandaran Wood and Paper Industries Company (located in the northern part of Iran) was used. Valley beating was applied to reach the target freeness of 300 ml CSF. Table 1 summarizes the specifications of the CMP hardwood pulp as first supplied by the company.

Chemicals

Medium molecular weight chitosan (relative molecular weight of 270 kDa) was acquired from Sea Fresh Company (Thailand). The degree of deacetylation of the chitosan was approximately 93%. Some general specifications of the utilized chitosan are shown in Table 2.

The conductivity of the tap water used in this study was measured between 500 and 760 µS/cm. To prepare the chitosan solution, 1 g of dry material of chitosan was solubilized in 200 ml 1% aqueous acetic acid and the solution was stirred for 2 hours at room temperature.[1,4]

To ensure the acidic pH condition of the pulp slurry (pH 5.5), 0.1 N sulfuric acid was added to the pulp suspension. For satisfying the alkali conditions (pH 8.5), 1% w/v NaOH was applied to the suspension. As Table 1 shows, the initial pH of the CMP pulp ranged between 7.7 and 8.3. Therefore, a neutral condition at pH 7 was also fulfilled by the addition of 0.1 N sulfuric acid. Other literature has suggested different acids and acid concentrations, as well as an alkali source, *i.e.* 1% acetic acid and 3% NaOH, respectively,[1,18] but in the current study, we failed to reach to a desirable pH level using the recommended concentrations.

Sheet preparation and testing

Solutions of chitosan were added in dosages of 0, 0.75, 1.25 and 2 percent based on oven-dry weight of pulp at pH levels of 5.5, 7 and 8.5. The mixture was stirred at 220 rpm for 30 s at room temperature. The suspension was then diluted with tap water to 0.5% consistency. The handsheets with 60 GSM were made in a TAPPI Sheet Making Machine. The prepared papers were dried using the ring and plate method, according to standard TAPPI Test Method T 205 sp-02. The sheets were tested for tensile (TAPPI T494OM-01), burst (TAPPI T403OM-02), and tear (TAPPI T414OM-04) strengths. Also, apparent density was determined by dividing basis weight by the measured thickness of the paper. To decrease the effect of local roughness of the papers, the thickness of five handsheets was measured in each measurement as a stack. All the experiments were carried out in 5 replicates and the statistical analysis was performed using Statistical Analysis Software (SAS) and SPSS.

Visual ranking of formation uniformity

Considering the effect of flocculation on some physical properties of paper, including smoothness and caliper, a special procedure was adapted for estimating the effect of chitosan addition on floc formation in paper.

Table 1
Specifications of CMP hardwood pulp

Primary CSF	Yield (%)	pH	Fines content (%)
480	86.2	7.7-8.3	26.7

Table 2
Specifications of shrimp chitosan

Property	Mode or value
Raw material	Shrimp
Powder color	Cream
Particle size (mesh size)	60
Ash content (%)	0.51
Moisture content (%)	9
Solution appearance	Transparent
Degree of acetylation (%)	93
Insoluble material (%)	0.40
Viscosity at 24-25 °C	55
Molecular weight	270000
Amount of heavy metals (ppm)	0

A visual assessment of the samples was made to choose three out of four samples, which looked more different from each other in terms of uniformity or flocciness. The three standard samples were labeled as "2", "4" and "6", ranking from the lowest formation to the highest one in terms of flocculation. Then, several people acquainted with the definition of flocculation were asked to rank the samples on a scale from 1 to 7, based on comparison with the standards.

RESULTS AND DISCUSSION

Visual ranking of formation uniformity

As it is well accepted, the addition of flocculating agents, especially long chain cationic additives, will tend to deteriorate the uniformity of formation of a paper sheet prepared in the laboratory. As shown in Figure 3, the results have a proper correlation with this concept, however, the explanation is not so obvious. According to these results, the best formation was achieved by the treatments with no chitosan addition in all pH ranges, although the difference between the control treatments and the others was not large. The addition of chitosan appeared to deteriorate the formation, but no significant difference was observed (group "c" in Duncan grouping test), except in two of the treatments (pH 5.5/2% chitosan and pH 8.5/0.75% chitosan level).

The obtained data indicate that the addition of different chitosan dosages at different pH (except the above mentioned treatments) had no considerable effect on the formation. Under acidic conditions, although the chitosan resulted in a positive charge, the anionic charge of the fibers was also reduced, which caused a reduction of the electrostatic interaction and lower fiber flocculation, thus deterioration of paper formation was observed. Mechanical pulp suspensions usually have higher anionic charge, compared to chemical pulps,[17] but this difference had no obvious effects on formation. It seems that the treatment at pH 5.5 and 2% chitosan, the highest dosage of chitosan considered, probably changed the zeta potential to higher than zero and therefore the formation uniformity was deteriorated. Moreover, at neutral and especially alkali pH, the chitosan precipitates on fibers and contributes to inter-fiber bonding by more hydrogen and probably covalent bonding.[10] Because of these differences, the electrostatic interactions in the suspension, which would lead to flocculation, tend to be restricted.

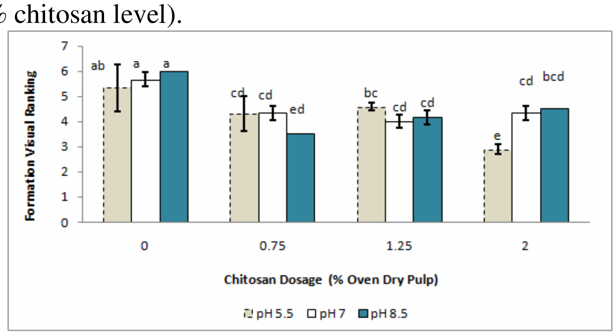

Figure 3: Effects of chitosan addition levels on visual ranking of handsheet formation at different pH levels

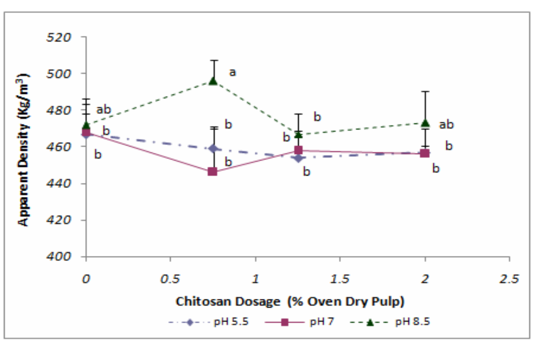

Figure 4: Effects of chitosan addition levels on apparent density of handsheets at different pH levels

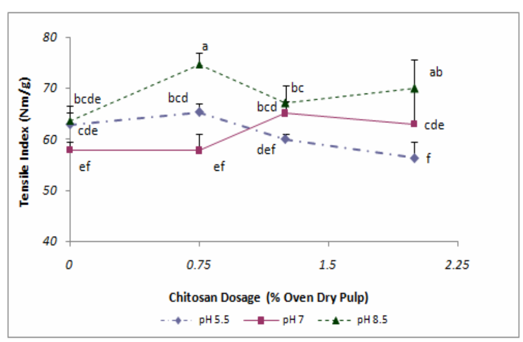

Figure 5: Effects of chitosan addition on tensile index of handsheets at different pH levels

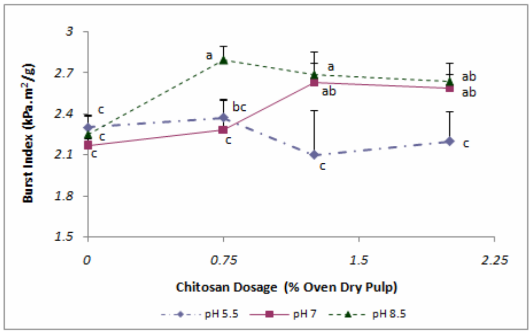

Figure 6: Effects of chitosan addition levels on burst index of handsheets at different pH levels

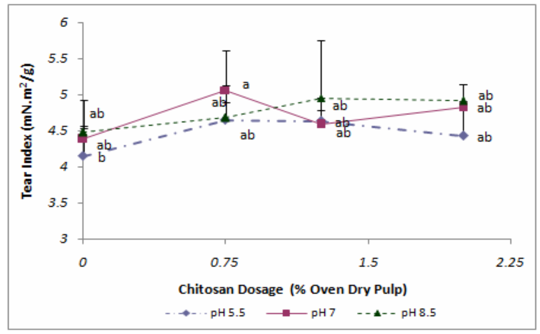

Figure 7: Effect of chitosan addition levels on tear index of handsheets at different pH levels

Apparent density

The effect of adding different dosages of the chitosan solution at pH levels of 5.5, 7 and 8.5 on the apparent density of CMP hardwood pulp is shown in Figure 4. According to Figure 4, there were not any statistical differences among the treatments, except for the treatment involving pH 8.5 and 0.75% chitosan dosage. These results were comparable with the formation uniformity results. As it is well accepted, the formation can have a considerable effect on apparent density by flocculation and fines retention. The maximum apparent density was observed at pH 8.5, compared to the acidic and neutral conditions, probably due to the precipitation of chitosan on the fiber surface. It seems that highly efficient precipitation of chitosan on the fiber surfaces and low flocculation gave rise to good strength results (increased fiber-fiber and fiber-fine bonding, and subsequent fiber and especially fines retention) at higher pH. Other researchers also concluded that chitosan had better performance at higher pH levels, and this was attributed to an increase in chitosan absorption onto the surface of the fibers and a decrease in the repulsion among chitosan-coated fibers.[9] The positive effect of higher pH levels on the performance of chitosan was emphasized elsewhere.[10] The results also showed that, at acid and neutral pH, there was not any statistical difference among different chitosan dosages, but under alkaline conditions, using more than 0.75% chitosan decreased the apparent density obviously.

Tensile index

The effects of chitosan addition levels on the tensile index of the handsheets at different pH levels, of 5.5, 7 and 8.5, are shown in Figure 5. This figure also indicates a significant difference among the treatments as revealed by the analysis of variance for tensile strength. As can be noted, the trends are very similar with those of apparent density, and the highest tensile index was achieved at pH 8.5. As mentioned before, probably the improvement in the performance of precipitated chitosan in the fiber-fiber and fine-fiber bonding, as well as in fines retention, is a key factor in this respect.

These results are in disagreement with those of A. Ashori *et al.*,[1] but in accord with the results of a number of other researchers.[4,10,14,16] It was also concluded that chitosan had better performance at higher pH levels, and this was attributed to an increase in chitosan absorption onto the surface of the fibers and a decrease in the repulsion among chitosan-coated fibers.[9]These results also confirmed the findings of another study, where it was found that the influence of chitosan on paper properties mainly depends on the pH of the suspension and the best effect on the dry and wet-web strength was reached at higher pH.[10]

The results shown in Figure 4 also indicated that at pH 5.5, different chitosan dosages did not exhibit any statistically significant effects related to the tensile index increase, which is in contrast with the results of Ashori *et al.*[1] The results at pH levels of 7 and 8.5 convey a different story. At pH 7, the addition of 1.25% chitosan led to a tensile index enhancement, as compared to the control and to the addition of 0.75% chitosan dosage. However, the addition of more chitosan did not have any effect on the tensile index. In alkaline conditions, the best result was observed at 0.75% chitosan addition. As mentioned before, the results were compatible with those for apparent density.

Burst index

The effect of chitosan addition levels on the burst index of the handsheets at different pH levels, of 5.5, 7 and 8.5, are shown in Figure 6, which indicates significant differences among the treatments, as revealed by the analysis of variance for tensile strength. As expected, the burst index showed a similar behavior to that of the tensile index. The reaction of the burst index to the process variables can be justified by the same reasons utilized for the tensile index variations. However, another research[6] showed that chitosan was almost completely adsorbed onto the surfaces of cellulose fibers, especially onto the surfaces of particles of fines and colloidal carbohydrates, possibly by hydrogen bonding, electrostatic neutralization, van der Waals forces, and so forth. It was suggested that these phenomena were probably related to an increase in the retention of fines, thus accounting for the fact that the burst index of paper could be affected.

Tear index

As might be expected, chitosan did not have a specific effect in enhancing the tear index, except in the case of the treatment at pH 7 with 0.75% chitosan dosage. According to Figure 7, although the treatments showed some differences compared to each other, different chitosan addition did not have significant effects when comparing the results for the same pH level. Also, at a constant level of chitosan, the variation of pH level did not cause any specific change in tear strength. Dry strength additives, which usually increase tensile and burst strength by improving inter-fiber bonding, do not have a direct positive effect on the tearing strength of paper. These results are in contrast with what was explained by Lertsutthiwong *et al*.,[12] in terms of the specific action of chitosan on beaten cellulose fibers.

CONCLUSION

The present study allowed drawing the conclusions listed below.

- The effect of chitosan on the properties of chemi-mechanical paper strongly depended on the pH of the furnish.
- The addition of chitosan to the stock at acidic pH did not have any specific effect on the strength properties. In contrast, neutral and alkaline pH resulted in an improvement in the dry strength properties of the paper sheets.
- The maximum apparent density was observed at pH 8.5, compared to the acidic and neutral conditions, probably due to the precipitation of chitosan on the fiber surface. It seems that highly efficient precipitation of chitosan on the fiber surfaces and low flocculation gave rise to the good strength results at higher pH. This improved performance may cause increases of fiber-fiber and fiber-fine bonding and subsequent retention of fines.
- The results showed that chitosan would tend to be more effective at low dosages, relative to the range considered in the present work.
- The dependence of chitosan performance on the pH of the CMP pulp (a variation of mechanical pulp) was similar to what has been reported for chemical pulps.

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