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The Effect of the Utilization of Chitosan on Properties of Paper

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Abstract

The aim of this study is to investigate the effect of chitosan on mechanical and resistance properties of paper produced from beaten eucalyptus pulp. The effects of the utilization of chitosan in different dosages (0%, 0.25%, 0.5% and 1% based on oven dry pulp) and pH (5.5, 7 and 8.5) on handsheet formation were determined. The results show that chitosan improves the mechanical properties by increasing tensile index, tear index and burst index. Moreover, chitosan makes paper more water resistant. The optimal dosage of chitosan was 0.5%, so that the effect of pH has been investigated at this concentration. It was found that chitosan can be used in both acid and neutral condition but pH 7 is the best, because at this pH the highest values are attained regarding strength and water resistance properties of the paper. Therefore, chitosan may be used as a multi-additive in wet-end application, as adhesive and sizing agent.

Introduction

In the past, natural polymers like guar and locust bean gums and the native and modified starches have been the most commonly used dry strength additives. The performance of these natural polymers is difficult to control and the use of starches involves lengthy preparations and further additives are required for adhesion to the fibers (Muzzzarelli and Jeuniaux, 1977).

The marine cationic biopolymer called "chitosan" or "polyglucosamine" can be produced from crustacean chitin by deacetylation with concentrated alkali (Roberts, 1992; Englewood and Fort Lee, 1989; and Muzzarelli, *et al.* 1977). It may be used as an new additive to improve paper quality because chitosan is high density of positive charge, low toxicity, biodegradable, biocompatable and antimicrobial and antifungal properties (Englewood and Fort Lee, 1989; and Chandrkrachang, 1996).

From previous research, the author has concluded that chitosan which was applied on the surface of handsheet could improve the mechanical properties of handsheets in terms of tensile index, tear index, surface strength and burst index. When chitosan concentration was increased, the strength of paper also increased. Moreover, the reduction of beating on fiber could be done by using chitosan (Lertsutthiwong, 1997).

The objective of this study was to investigate the effect of the utilization of chitosan in wet-end by varying dosage of chitosan and pH of handsheet.

Materials and Methods

Pulp

In this study, eucalyptus pulp (Leave Bleach Kraft Pulp, LBKP) from Thailand was used after beating in a PFI mill to 308 ml of Canadian Standard Freeness.

Chitosan preparation

Fresh shrimp shell was washed with water once before deproteination with 4% NaOH (ratio = 1:3.2 (w/v)), room temperature for 24 hours. After washing several times, it was decalcified with 4% HCl (ratio = 1:3.2 (w/v)), room temperature for 12 hours and washed until neutralization. Chitin was dry under sunlight and then it was deacetylated 2 times with 50% NaOH (ratio = 1:15 (w/v)); the first time was done at room temperature for 3 days and the second time was done at 40°C for 3 days.

The properties of chitosan were determined in the following parameters: moisture content was determined using an oven at 105°C for 24 hours and ash content was done using a muffer furnace at 650°C for 3 hours. Degree of deacetylation was analyzed using HPLC (Ng, *et al.* 1996), protein content was analyzed using microbiuret method (Hein, 1999) and the average molecular weight is determined by following Wang method (1991). Viscosity of 1.5% chitosan solution in 1% acetic acid was investigated using Brookfield viscometer, Model DV-VII+ (Wanichpongpan, 1999).

Chitosan solution

Chitosan solution was prepared by adding 100 ml of 1% acetic acid into 1.5 g of oven dry (o.d.) chitosan and shaking at 150 rpm for 24 hours.

Chitosan-paper preparation

Chitosan-paper was prepared by using standard equipment following Tappi Test Method T 205 om-88 (Tappi Press, 1999). Beaten o.d. eucalyptus pulp of 30 g was disintegrated at 10,000 revolution and made volume upto 4 liters. After stirring at 500 rpm for 5 minutes, chitosan was added in the dosage of 0, 0.25, 0.5 and 1% based on o.d. pulp and continue stirring for 10 minutes. Before making the volume upto 12 liters, it was adjusted pH to 5.5, 7 and 8.5 with 1% acetic acid or 3% NaOH solution. After mixing this pulp suspension for 20 min, 80 g/m^2-chitosan-paper was prepared. Chitosan-paper was kept in a condition room at 27°C, 65% RH for 24 hours, before testing the following parameters:

- Tensile index (Following Tappi Test Method T 494 om-88)
- Tear index (Following Tappi Test Method T 414 om-88)
- Burst index (Following Tappi Test Method T 403 om-91)
- Water drop test (Following Tappi Test Method T 432 om-87)

- Retention of chitosan

Results and Discussion

Chitosan preparation

At the beginning of the process, shrimp waste was washed with water for removal of some protein and fat. Then protein and pigment could be removed by soaking in diluted NaOH solution and HCl solution was used to remove mineral especially calcium carbonate from shrimp shell. Finally, chitin was deacetylated using concentrated NaOH solution 2 times caused to get high degree of deacetylation without using high temperature.

According to low temperature in the process, the chain of chitosan was not much destroyed which caused high molecular weight and automatically gave high viscosity as shown in Table 1. Degree of deacetylation was 88.7% and the solubility of this chitosan in 1% acetic acid was 100%. The other properties such as moisture, ash and protein contents were shown in Table 1.

Table 1 The properties of chitosan

Parameter	Value
Moisture content (%)	4.83
Ash content (%)	0.84
Apparent viscosity of 1.5% chitosan (cps.) (60 rpm., spinder no. S63, 25°C)	1472
Solubility (%)	100
Molecular weight	$1.1173 * 10^6$
Protein content (%)	1.55
%DD	88.7

The effect of chitosan on paper properties at pH 5.5

This experiment was done by adding different amounts of chitosan solution (based on o.d. pulp) into beaten eucalyptus fibers and final pH of pulp suspension was 5.5. It was found that chitosan could improve mechanical properties by increasing the strength of paper as shown in Figure 1. Higher dosage of chitosan (upto 1%) was added in pulp suspension gave higher strength in terms of tensile index, tear index and burst index. When beaten eucalyptus pulp was treated with 0.5% chitosan, tensile index was increased about 48%, tear index was 59% and burst index was 91% over the pulp untreated with chitosan as shown in Table 1. Moreover, 1% chitosan also increased 76% of tensile index, 88% of tear index and 142% of burst index. Due to chitosan has a strong positive charge, it can form films on negatively charged surfaces and it can also bind to negatively charged materials (Englewood and Fort Lee, 1989). Figure 2 shows the effect of chitosan to help paper resist to water. The addition of 0.5% chitosan gave higher water resistance than without adding chitosan (control) approximately 10 times and 1% chitosan solution could help paper to resist water approximately 13 times of control as shown in Table 2. The optimal dosage of chitosan based on the trend of the increasing of mechanical and water resistance properties was 0.5%.

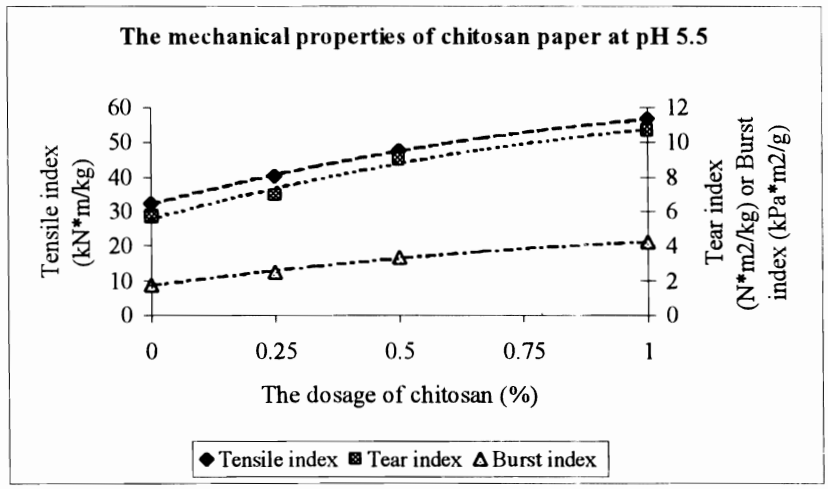

Figure 1 The effect of chitosan on the mechanical properties of paper at pH 5.5

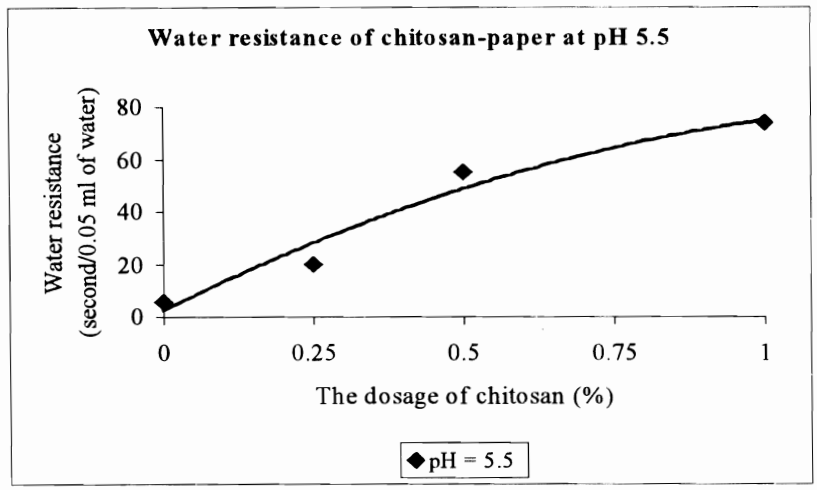

Figure 2 The effect of chitosan on water resistance properties at pH 5.5

Table 2 The effects of chitosan on properties of handsheet at pH 5.5

Properties	Untreated handsheet (control)	Handsheet treated with 0.5% chitosan	Handsheet treated with 1% chitosan
Tensile index (kN*m/kg)	32.2±1.3	47.7±2.5	56.6±2.9
Tear index ($N*m^2/kg$)	5.70±0.63	9.05±0.68	10.7±0.3
Burst index ($kPa*m^2/g$)	1.75±0.05	3.35±0.13	4.23±0.25
Water resistance (second/0.05 ml of water)	5.66±0.53	55.1±3.8	73.8±13.1

The effect of chitosan on paper properties at pH 7

When different percentages of chitosan were applied into the pulp suspension at pH 7, the strength of paper could be improved by increase tensile index, tear index and burst index with increasing the dosage of chitosan as shown in Figure 3. The optimal dosage of chitosan was 0.5% (based on o.d. pulp) because it could give high strength of chitosan-paper. The trend of strength of chitosan-paper was decreased when chitosan was applied more than 0.5%. That meant 0.5% chitosan

solution gave the highest bonding force. When 1% chitosan solution was applied at pH 7, the excess chitosan may precipitate on pulp. That means the strength of paper depended on individual fiber strength, interfiber bond strength, number of interfiber bonds (bonding area) and distribution of fiber (sheet formation) (Scott, 1996).

Commercial pulp has some anionic character due to the presence of carboxyl groups originating from the hemicellulosic uronic acid residues or from oxidation associated with the bleaching process. Ionized chitosan is probably retained by the formation of ionic bonds between the amino group in chitosan and anionic functions present on the fiber surface. Chitosan is very efficient in neutralizing all the anionic sites on the fiber and it should be capable of forming hydrogen bonds with non ionic areas of the fiber surface as well (As cited by Jeuniaux and Muzzarelli (1977).

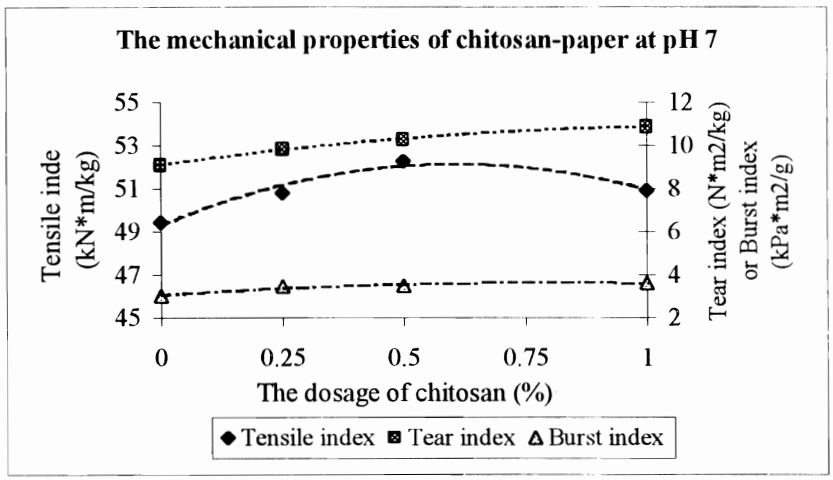

Figure 3 The effect of chitosan on mechanical properties of chitosan-paper at pH 7

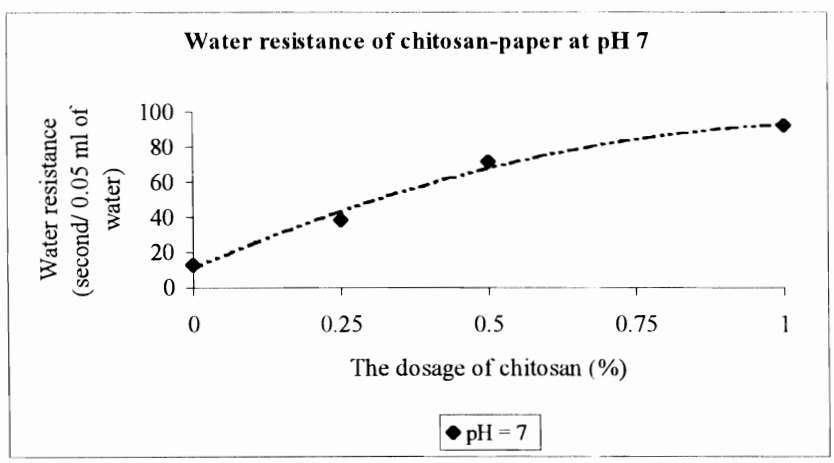

Figure 4 The effect of chitosan on water resistance properties at pH 7

Moreover, chitosan could improve water resistance as shown in Figure 4. The increasing of the dosage of chitosan was increasing water resistance. The optimal dosage of chitosan solution based on the increasing of mechanical and water resistance properties was 0.5%.

The effect of chitosan on paper properties at pH 8.5

Figure 5 and Figure 6 show the mechanical properties and water resistance of chitosan –paper at pH 8.5. The results show the same effects as pH 7 but the values of tensile index, tear index, burst index and water resistance at pH 8.5 were less than pH 7. When chitosan was added more than 0.5%, the mechanical properties and water resistance of paper decreased slowly. It could say that the optimal dosage of chitosan at pH 8.5 was 0.5%.

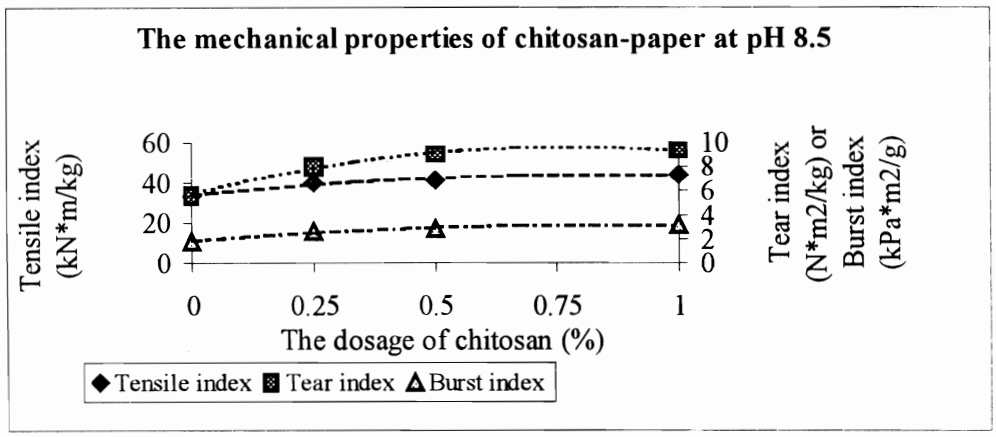

Figure 5 The mechanical properties of chitosan-paper at pH 8.5

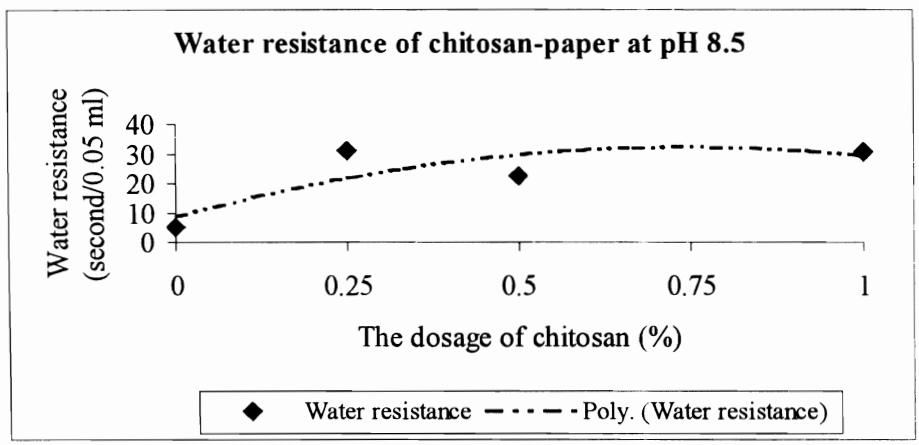

Figure 6 The effect of chitosan on water resistance properties at pH 8.5

The comparison of the effect of pH

From the previous results, they concluded that the optimal dosage of chitosan might be used in wet end was 0.5%. Therefore, this experiment was investigated the effect of pH by adding 0.5% chitosan in beaten eucalyptus pulp suspension and adjust pH to 5.5, 7 and 8.5 before making handsheets. The results showed that pH 7 could give highest value of water resistance, tensile index and burst index. That means chitosan is suitable to use in neutral condition. On the other hand, at pH 8.5 some amount of chitosan might precipitate instead of interaction with fibers and caused low strength and water resistance. However, chitosan could also be used in acidic condition as shown in Table 3.

Table 3 The effect of pH on properties of chitosan-paper

pH	Water resistance (second/ 0.05 ml of water)	Tensile index (kN*m/kg)	Tear index ($N*m^2/kg$)	Burst index ($kPa*m^2/g$)
5.5	55.1	47.7	11.1	3.35
7	71.4	52.3	10.3	3.48
8.5	22.6	41.5	9.01	2.86

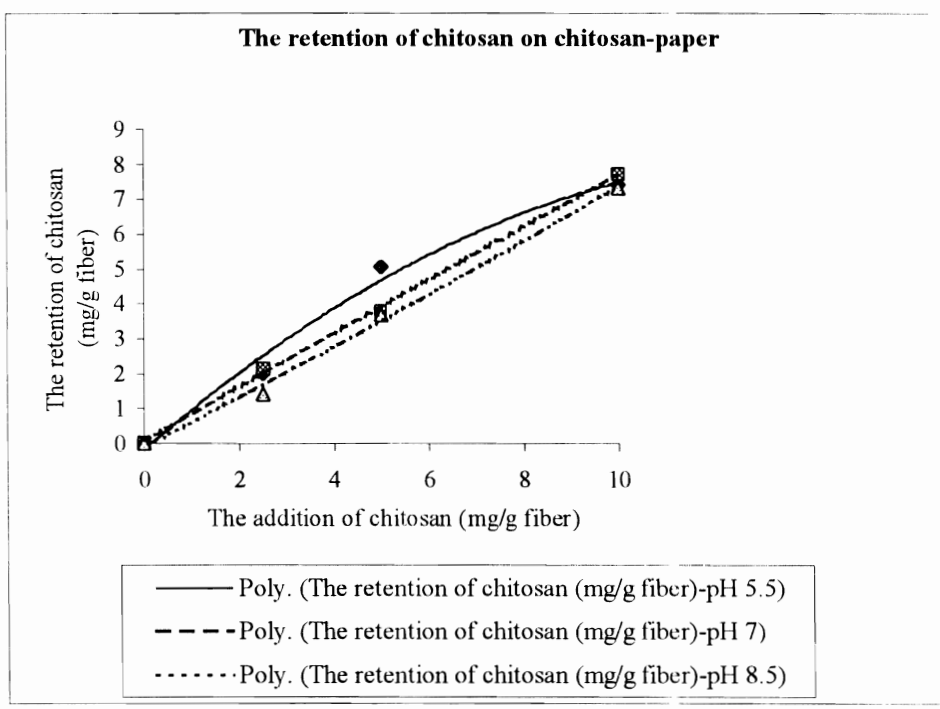

Figure 7 The effect of pH on the retention of chitosan

The retention of chitosan in different pH was shown in Figure 7. It was found that the retention of chitosan at pH 5.5 was higher than pH 7 and 8.5 when the utilization of chitosan was less than 10 mg/g fiber. That means pH effected to the retention of chitosan and in alkaline condition chitosan could pass through the mesh during preparing handsheet easier than acidic condition but it was not much different between pH 7 and pH 8.5. At 10 mg/g fiber, the retention of chitosan in different condition was nearly the same approximately 75%.

Conclusion

Chitosan could improve to the mechanical, barrier and resistance properties of paper in both acidic and neutral condition, so that chitosan may be used as a multi-additive in wet-end, as adhesive and internal sizing agent in wet-end. and the optimal dosage of chitosan was 0.5%, respectively.

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