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Mechanical Properties of Paper from Oil Palm Pulp Treated With Chitosan from Horseshoe Crab

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ABSTRACT

The application of chitosan as an additive in papermaking to improve the strength and water resistant properties is described. Unbleached sulphate pulp from oil palm stem was treated with chitosan. The chitosan was prepared in the laboratory using the chitin obtained from horseshoe crab shells. The optimum condition for the addition of chitosan to the sulphate pulp was found to be 0.4% chitosan of medium molecular weight at pH 10. Substantial improvement in strength properties, particularly tear and stretch was observed for the paper treated with chitosan. The freeness of the pulp increased with decreasing viscosity of chitosan.

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INTRODUCTION

The large hectare of oil palm plantations in Province of North Sumatera, amounting about 2.0 million ha, generates a massive amount of residues in the form of trunk, fronds and empty fruit bunches. These residues are expected to be the source of fibrous raw material for various products including for pulp and paper in the future. Pulp properties of oil palm residues have been reported by Khoo& Lee [4] and Mohd Nor *et al.* [6]. Sulphate and semi chemical pulp of acceptable strength and moderate yield were produced.Huge quantities of chitosan can be produced annually, mainly from sea animals, the organic skeletal component of these invertebrates. The application of chitosan and its derivatives as a wet strength additive in paper making has been studied. Laleg found that chitosan could increase the strength of never-dried webs, dry paper, and wetted paper [5]. A study on the adsorption of chitosan on cellulose was conducted by Domszy *et al.* [2]. They found that the amount of chitosan adsorbed increases with decrease in molecular weight and increase in the degree of N-acetylation of the chitosan. The objective of this study was to examine the effect of chitosan on the strength and water resistance properties of the paper from oil palm pulp.

MATERIAL AND METHODS

Preparation of Chitin:

Chitin was prepared according to the method of Hackman [3]. About 3.5 kg of wet horseshoe crab shells was added into a pail containing 30 litres of 2 M NaOH solution. The mixture was .kept for 24 h with occasional stirring. The mixture was then filtered. The solid material obtained was washed until the pH of the washing became neutral. The cleaned solid material was then added into a pail containing 30 litres of 2 M HC1 and left for 24 h with occasional stirring. The mixture was filtered and the solid material obtained was washed several times until the pH of the washing became neutral. Finally, chitin was obtained and air dried at room conditions. The dried chitin was bleached with hydrogen peroxide, sulphuric acid and distilled water at a ratio of 1:10:100.

Preparation of Chitosan:

Chitosan was prepared according to Arisol& Md. Radzi [1]. About 500 g of chitin powder were added to 50% NaOH solution and kept for 6 days with occasional stirring every day. The chitosan obtained in the alkaline

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form was washed with water until the pH of the washing was neutral. The chitosan was dried at room temperature.

Determination of Viscosity:

The viscosity of chitosan in acetic acid solution prepared at different conditions was measured using a digital viscometer (Brookfield Model DV-I) at 25 °C. The readings were taken daily to determine the changes in viscosity of the chitosan solution with time.

Preparation of Pulp from Oil Palm Stem:

Oil palm stems in disc form were shredded and hammer-milled. The fibrous strands obtained were pulped in a MK digester. Sulphate pulping was conducted at 14% active alkali and 170 °C. The time taken to reach the maximum temperature was 1.5 h and this temperature was maintained for 2 h. The pulp obtained was washed and screened in the fractionator to remove the shivy material. The screened pulp was stored in a refrigerator before being used for paper-making.

Papermaking and Addition of Chitosan:

Hand sheets were prepared from the oil palm stem unbleached pulp, added with or without chitosan according to APPITA P203-M75. The hand sheets were air-dried and conditioned for 24 h in a room controlled at 23 °C and 50% relative humidity. The hand sheets were tested for their physical strength properties according to APPITA P208-75.

RESULTS AND DISCUSSION

Preparation of Chitin and Chitosan:

During the preparation of chitin, HCl solution was used to dissolve the calcium carbonate from the horseshoe crab shell. This reaction occurred as shown by the released of carbon dioxide gas. The precipitation process was completed when there was no more bubbling of carbon dioxide gas.The purpose of soaking the horseshoe crab shells in NaOH solution was to remove the protein (deproteination). The resulting chitin was immediately washed with water to avoid deacetylation of chitin by the alkali into papery material.The bleach chemicals consisting of hydrogen peroxide and sulphuric acid were found to be effective as within a short time all the chitin became white but did not dissolve. If the hydrogen peroxide concentration is increased and the bleaching time is prolonged the mixture will form a slurry. This is due to the dissociation of chitin's polymer chain. The yield of chitin was found to be 30.2 %. The chitosan prepared dissolved easily in 1 % acetic acid. The amount of chitosan produced was 68.6%. Muzzarelli [7] obtained about 70 % yield of chitosan.

Viscosity of Chitosan Solution:

The changes in the viscosity of the chitosan in acetic acid with time are given in Table 1. The viscosity decreased with increasing time. This is due to the hydrolysis process which occur in acidic solution. The rate of hydrolysis is dependent on the molecular weight of chitosan. The concentration of acid used greatly influences the rate of hydrolysis of chitosan whereby the rate of hydrolysis is proportional to the concentration of acid used.All the chitosan samples (low, medium and high molecular weights) exhibited a similar trend, *i.e.*, the viscosity of chitosan solution decreased with an increase in time (Table 1). This is expected since the chitosan will hydrolyse in the acidic solution resulting in the shortening of its polymer chain, thus lowering the viscosity. The different trend as seen among the different samples of chitosan indicate the different rates of hydrolysis.The viscosity of the solution is proportional to the degree of polymerisation (DP). As chitosan is being hydrolysed in the acidic solution, its DP decreases. The DP will decrease rapidly until the hydrolysis gives certain molecular size which has no effect on viscosity.

Properties of Oil Palm Pulp Treated with Chitosan:

Oil palm pulp beaten at 3000 rpm was treated with 0.4% chitosan (low m.w.) at pH 10. Different viscosities of chitosan for a period of 5 days were used. The paper made was tested for its strength properties. Chitosan of low molecular weight showed decreasing trend in strength properties of paper and an increasing trend in pulp freeness with decreasing viscosity of chitosan (Table 2).

Table 1: Viscosity of chitosan solutions.

Day	Viscosity (cps)														
	0.2%			0.4%			0.6%			0.8%			1.0%		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
1	290	380	470	325	480	640	410	540	670	550	680	810	590	720	890
2	190	270	350	220	370	510	280	390	500	400	540	660	470	590	760
3	120	190	260	150	280	410	210	300	390	300	430	550	380	500	660
4	90	ISO	210	100	220	330	160	240	320	220	350	460	300	410	580
5	70	120	170	80	180	270	110	190	270	150	280	390	220	340	510

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Note: A = low m.w., B = medium m.w., C = high m.w

Table 2: Properties of oil palm pulp treated with 0.4% chitosan (low m.w.).

Day	Freeness (csf, ml)	Tear index (mN m^2/g)	Burst index (kPa m^2 g)	Tensile index (Nm/g)
1	485	7.6	4.0	60.9
2	505	7.0	3.5	57.9
3	525	5.7	3.2	55.9
4	560	5.0	2.7	52.7
5	590	3.7	2.0	48.6

Table 3: Properties of oil palm pulp treated with 0.4% chitosan (medium m.w.).

Day	Freeness (ml, csf)	Tear index (mN m^2/g)	Burst index (kPa m^2 g)	Tensile index (Nm/g)	Stretch (%)
1	450	12.1	6.54	73.4	5.1
2	455	11.4	6.24	71.4	4.8
3	470	11.2	5.94	69.5	4.6
4	480	9.9	5.46	67.5	4.5
5	495	8.9	5.15	65.5	4.3

One-day-old chitosan solution having higher viscosity gave higher strength properties than those pulp treated with a 5-day-old chitosan solution having lower viscosity. At low viscosity of chitosan the bonding of fibers are greatly affected resulting in low strength properties.Table 3 gives the properties of pulp beaten at 3000 rpm and treated with 0.4% chitosan solution of medium molecular weight at pH 10. It is interesting to note that there were increment in pulp freeness and reduction in the pulp strength when the same chitosan prepared was added from the first day up to the fifth day. This phenomenon is similar to what was exhibited by low molecular weight chitosan (Table 2). Pulp when treated with a 5-days-old chitosan solution had about 26% reduction in tear index. 11% reduction in tensile index, 16% reduction in stretch and 10% increment in freeness over the pulp treated with 1day-old chitosan solution This was expected since the fresh chitosan with its high viscosity will give rise to lower pulp freeness. By comparing the results between low m.w chitosan and medium m.w chitosan, apparently the medium m.w chitosan indicated overall higher paper strength properties.

Table 4: Physical properties of wet handsheets treated with 0.4% chitosan.

Day	Freeness (ml, csf)	Tear index (mN m^2 /g)	Tensile index (Nm/g)	Stretch (%)
1	450	6.8	44.5	4.5
2	455	6.2	42.4	4.3
3	470	5.2	40.4	4.6
4	480	4.6	39.1	3.7
5	495	3.6	36.1	3.4

Table 5: Properties of pulp treated chitosan of different concentration.

Chitosan addition	Freeness (ml, csf)	Tear index (mN m^2/g)	Burst index	Tensile index	Stretch (%)
(%)			(kPa m^2g)	(Nm/g)	
0	525	7.9	4.3	646	30
0.2	465	9.3	54	70.4	4.7
0.4	450	12.1	6.5	73.4	5.1
0,6	410	5,7	5.5	678	4.4
0.3	380	38	4.4	GU	3.8
1.0	260	-	-	-	-

The paper made from pulp treated with 0.4% chitosan (medium m.w) was also tested for its strength properties. The paper was soaked in distilled water for 30 min before being tested. The results are shown in Table4.The effect of pulp freeness and strength properties with increasing concentration of chitosan is shown in Table 5. The optimum strength properties in terms of tear index, tensile index and stretch were obtained at 450 ml when the chitosan solution was at 04% concentration and pH 7. At 1-0 % chitosan, hand sheets could not be produced because of the high viscosity of the solution.The strength properties increased with increasing pH but the properties were optimum when the chitosan solution was at pH 10 (Table 6). Beyond this pH.thestrength properties of the pulp apparently started to decrease. Further increase in alkalinity, above pH 10, it would convert all the amino groups to their neutral form and would then at the same lime assume the coiled configuration, which would further reduce the ionic interaction between chitosan and cellulose.

Table 6: Properties of oil palmpulp treated with 0.4% chitosan at various pH.

pH	Tear index (mN m^2/g)	Burst index (kPa m^2g)	Tensile index (Nm/g)	Stretch (%)
4.5	9.9	5.4	67.3	4.5
8.0	10.8	6.1	70.4	4.8
10.0	12.1	6.5	73.4	5.1
12.0	11.5	6.2	72.7	4.9
14.0	9.9	6.1	70,7	4.7

Conclusion:

Chitosan prepared from chitin of the horseshoe crab shells can be used to improve the strength properties of paper made from unbleached pulp obtained from oil palm stem. The strength properties of paper were influenced by the molecular weight, concentration and pH of the chitosan in acetic acid solution. Both the high pH beyond 10 and high concentration of 1.0% of chitosan were detrimental to the bonding of the paper produced as indicated by the reduction in strength properties.

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