Evaluation of Chitosan as Additive in Paper Making

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Abstract

The effect of adding chitosan as natural polymer on the strength and optical properties of paper sheets loaded with kaolin was studied. The pulp furnish used in this work was mixture from bleached rice straw and wood pulp in ratio 60%:40%. Different parameters were examined namely: the percentage of chitosan, in presence or absence of kaolin, and pH-value. Evaluation of using the chitosan as retention aid was investigated by comparing the obtained paper properties with those obtained from using conventional retention agents such as: cationic starch and polyacrylamide.

INTRODUCTION

Filler pigments are used to increase the opacity, brightness, smoothness and printability of papers. A large number of fillers are available, ranging from cheap low-grade clays, calcium carbonate and talc to the expensive titanium dioxide (1). Cellulose fibres normally are negatively charged. This has a strong bearing on properties of a paper stock, which predominately consists of anionic species like pulp fibres, fillers, and additives. Repelling interactions between such negatively charged particles hamper the process of flock formation, which may cause problems for water drainage and particle retention. The literature reveals that the increase of filler retention is usually achieved by wet end addition of poly-electrolytes to the paper stock as retention aids, in the presence of which the filler particles tend to agglomerate. The large filler particles are retained more efficiently than the fine filler (2). Many substances are reported as retention aids, such as acrylamide-dextrane graft copolymer, blends of non-ionic and cationic surfactants, cationic starch, oxidized starch, Accostrength 86, and polysilicate microgels (3-7). Functional additives like cationic starch and polyacrylamide are also able to behave as dry strength additives (8). Chitosan (poly-2-aminodeoxy-1, 4 glucoside) has also reported to impart wet strength to paper (9). The literatures for using chitosan to improve the strength properties of paper produced from short fibres furnish are scarce (9,10).

The present work represents a trial to improve sheet properties produced from Egyptian pulp furnish (rice straw & wood pulps mixture) through addition of chitosan. This work also represents an attempt to increase the filler (kaolin) retention in pulp fibres by using chitosan as retention aid additive and compare the properties of produced loaded sheets with those obtained in case of conventional retention aid additives, e.g., cationic starch and polyacrylamide, as well as rosin-alum addition.

EXPERIMENTAL

The pulp furnishes used in this study were a mixture from bleached rice straw pulp with bleached wood pulp. These pulps were delivered from RAKTA company for the manufacture of paper, Alexandria, Egypt. The chemical constituents of these pulps are estimated according to the standard methods (11-13) and shown in Table 1.

Chemical additives

- Chitosan from crab shells (degree of deacetylation 86-88%) purchased from Sigma Chemical Co. Inc was used without any further purification as natural polymer additive and powdered (200 mesh) before use. Solution containing 10g of oven-dried chitosan in 500 ml of 1% acetic acid was prepared by stirring vigorously for ~ 20 minutes.
- Cationic starch (0.32 N, % and 1.63 meg/g charge density) and polyacrylamide (BDH Laboratory supplies, with M.W. 5,000,000, and

viscosity of 0.5% aqueous solution at 25°C at out 280 cP), were used as conventional filler retention aids.

- 0 Rosin and alum were supplied by Simo Co. for Paper Manufacture, Bahtem, Egypt.
- 1 Kaolin (Apolda) was used as filler.

Paper making and testing

The rice straw and wood pulps were beaten separately up to the degree of Schopper Reigler (SR^0) 30-33, using a valley beater. The produced beated pulps (never dried) were treated with dilute chitosan in 1% aqueous acetic acid solution. Different variables were examined.

- The percentage of chitosan added (based on pulp weight)
- The pH- value of pulp-chitosan slurry.
- The type of additives used as a retention aid of kaolin, e.g., cationic starch, polyacrylamide and rosin-alum. For the case of using cationic starch the mode of chemical addition is pulp, cationic starch, filler and alum.

The choice of 2% kaolin depends on the fact that there is a reduction in the strength properties accompanies the increase in kaolin beyond 2% percent (6). Unloaded and loaded paper sheets with 2% kaolin were prepared according to the Swedish Standard Method (S.C.A.). The prepared sheets were placed for conditioning at relative humidity 65% and temperature 20°C. The strength and optical properties of paper sheets were determined according to Tappi Standards (14). The amount of kaolin loaded in the paper sheets was determined from the ash content (15). The filler retention percentage, based on added filler, was calculated according to;

$$\text{Retention of filler} = \frac{\text{Ash of paper loaded with filler - Ash of non loaded paper}}{\text{Ash of the added filler}}$$

RESULTS AND DISCUSSION

Effect of chitosan addition on paper properties

***Percentage of chitosan**

Figures 1 and 2 show the variation of strength and optical properties of paper sheets as a function of added chitosan. In absence of filler, it is clear that the addition of chitosan during paper making improves the strength properties of the obtained paper. The maximum improvement was attained at 0.5% chitosan addition. The improvement decreases by increasing the added amount of chitosan up to 1%, but they are still better than control sample (without chitosan); (Fig. 1). As can be seen that (Fig. 2), a slight improvement in the optical properties is noticed compared to strength properties, which increases by increasing the added amount of chitosan. The above improvement in paper properties is probably due to the ionic interaction between chitosan and cellulose (16).

Figures 1 and 2 also obvious that the addition on relatively low percentages of chitosan (0.25&7 0.5% in presence of 2% kaolin filler results in improves the strength and optical properties of paper sheets compared with those obtained in

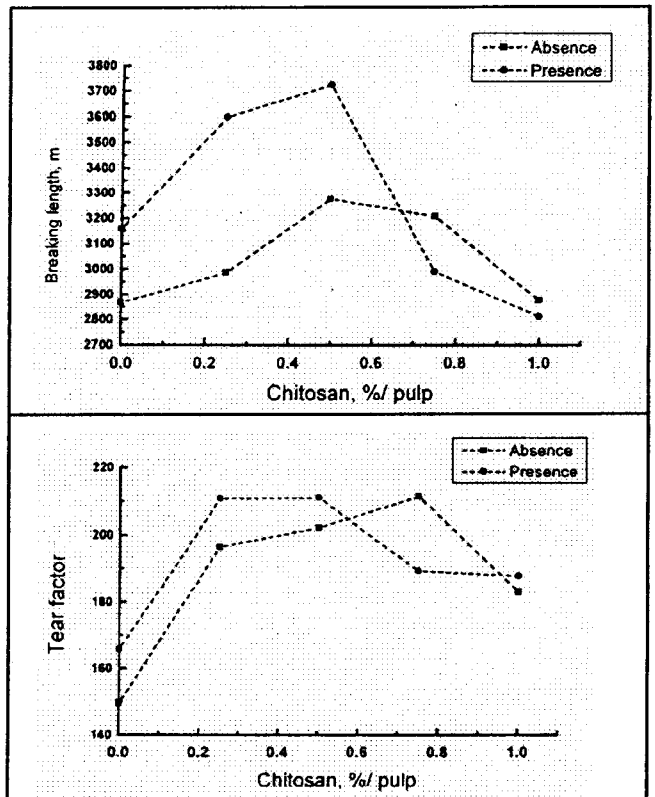


Fig. 1 Strength properties versus chitosan addition in absence and presence of 2% kaolin.

Table 1 Chemical analysis of the raw materials used

Chemical analysis	Bleached rice straw	Bleached wood pulp
α-Cellulose, %	73.45	87.64
Pentosans, %	14.23	8.67
Lignin, %	1.30	0.15
Ash, %	7.31	0.23

Table 2 Strength and optical properties of paper sheets made from using chitosan and rosin-alum additives, in presence of 2% kaolin. (pH~ 4.5).

Additive	Retention, %	Breaking length m	Tear factor	Brightness, %	Opacity, %
-	40.2	3159	165.70	69.2	96.2
0.5% chitosan*	60.26	2745	150.70	70.1	97.1
0.5% chitosan**	10.04	1317	134.00	69.7	95.7
2.7% rosin + alum	8.40	1298	134.90	69.9	97.4

* using dilute AcOH to adjust the pH-value, ** using alum to adjust the pH-value

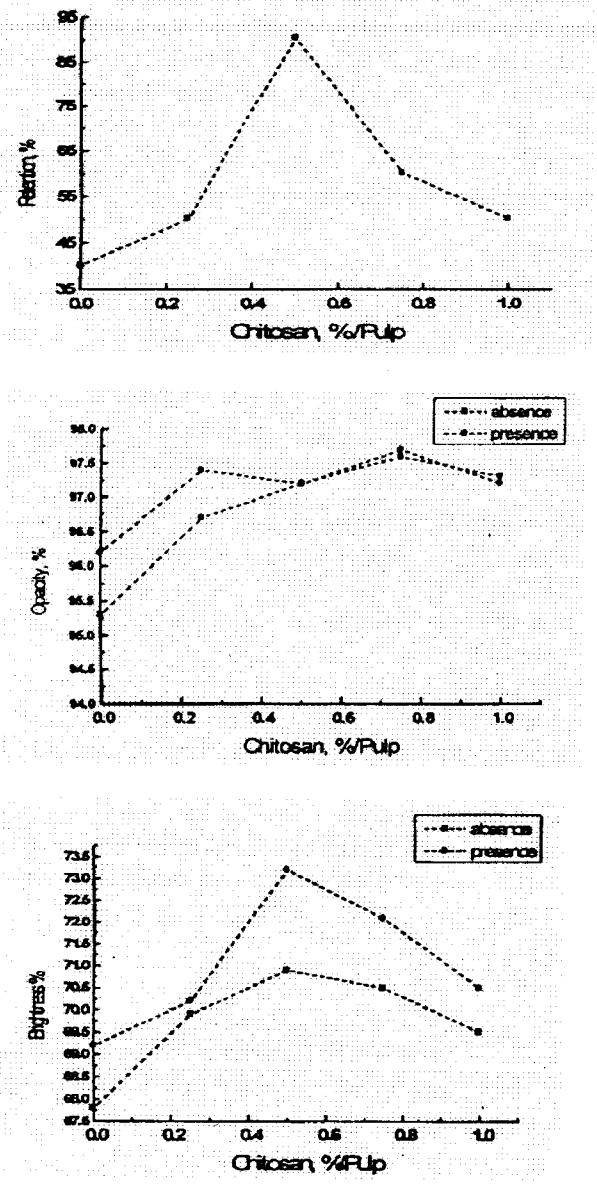


Fig. 2 Retention of filler and optical properties versus chitosan addition in absence and presence of kaolin.

absence of filler. However, the reverse trend is noticed at relatively high chitosan addition (0.75 & 1.0%). At relatively high chitosan addition no significant change in the opacity property of paper sheets is noticed in presence or absence of filler.

The improvement in the strength and optical properties using 2% kaolin, in presence or absence of low percentage of chitosan, may be related to the nature of the filler-fibre interactions, whereas the probability of the low % filler particle (2%) interstices between principal fibres is more than that trapped between it. The latter case has only a detrimental effect on strength property (17). Regarding the retention of filler in the pulp fibres, greatly improvement is observed by increasing the dose of chitosan and the maximum improvement in retention of filler was attained at 0.5% chitosan, where it reached to about 90% as shown in Fig. 2. This is probably related to, the presence of chitosan enhancing the electrostatic attraction between treated fibres and kaolin particles.

***pH-value of the paper slurry**

From the previous effect (Figures 1 and 2) it could be concluded that 0.5% chitosan together with 2% kaolin is the optimum amount to be added as paper additive to attain the maximum improvement in the properties of paper sheet. Further study was carried out on the effect of changing the pH-value during paper making on the paper properties. The results obtained are shown in Fig. 3. The pH-value of the pulp slurry was changed by adding either dilute sodium hydroxide or acetic acid.

From Fig. 3 it is obvious that, changing the pH-value during sheet formation has a pronounced effect on the retention of filler in the pulp fibres, also, the paper properties. Elevating the pH results in the increase of kaolin retention; however, lowering the pH, either by acid or alum, results in the decrease of kaolin retention (Table 2). The

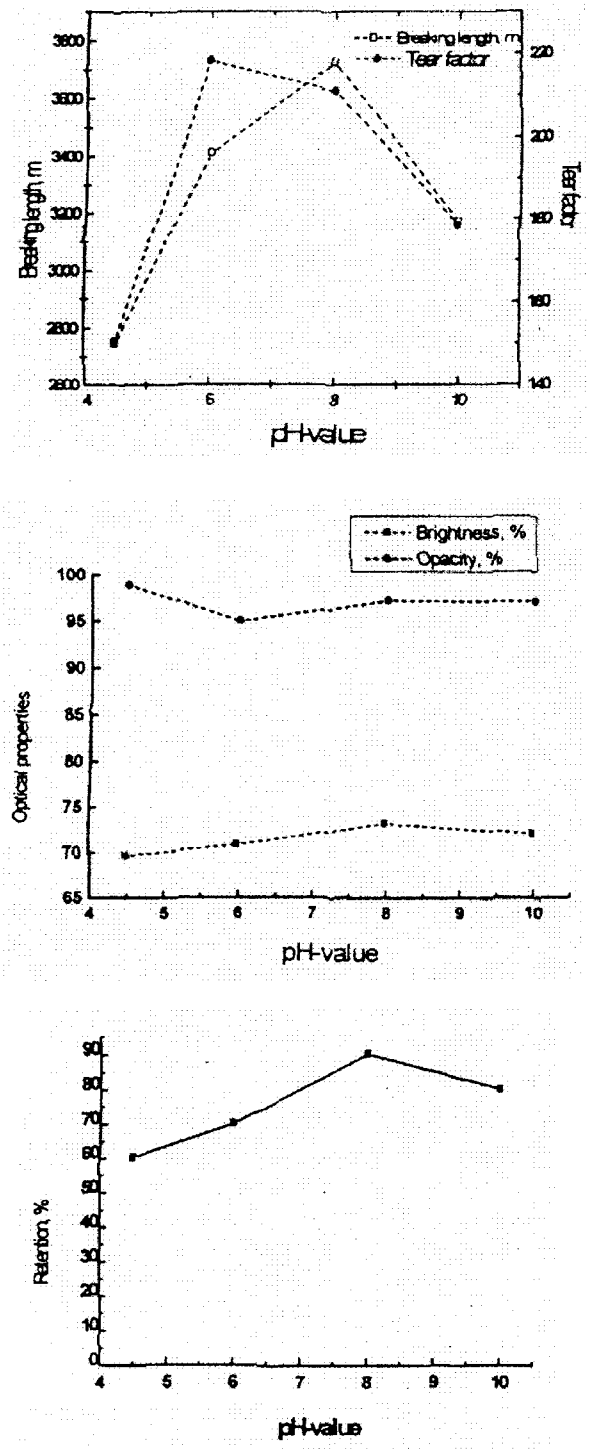


Fig. 3 Retention of kaolin, strength and optical properties versus pH-value of chitosan-pulp slurry.

best improvement in the strength properties is noticed at pH~8.0 and the deterioration in the strength properties of the obtained sheets were observed at low pH-values (below 6). Fig. 3 also shows that, the optical properties (brightness & opacity) are slightly influenced by changing the pH-value of pulp slurry.

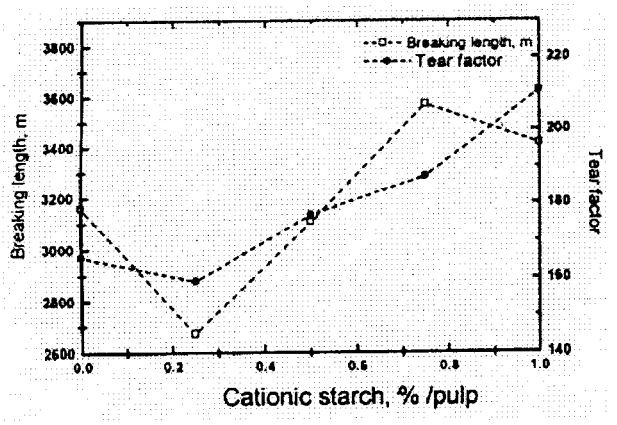
The explanation of the above results may be due to the change in the flocculation action of chitosan to kaolin particle, as a result of changing the pH-value. The relatively high pH-value increases the repulsion between the kaolin particles and increases the electrostatic attraction between chitosan and filler particles. However, at relatively low pH-value the retention of filler results from the flocculation of kaolin particles due to the attraction between the positive edges and anionic basal surface of kaolin. Therefore, at low pH the retention is mainly due to the attraction between chitosan and filler, however, at high pH the retention is mainly the flocculation of filler particles, which leads to reduce the formation of fibre-fibre hydrogen bonds.

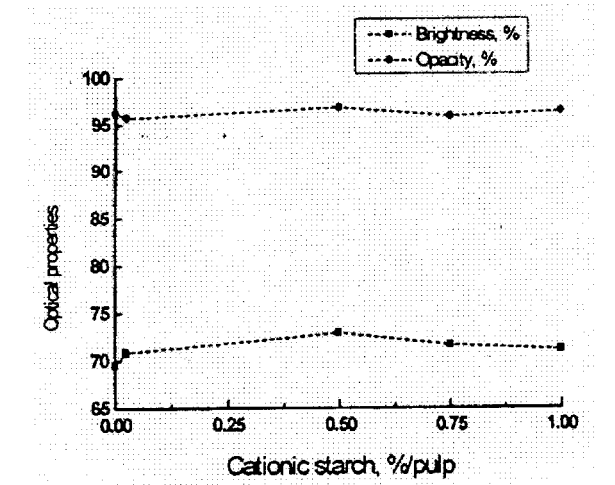
Effect of rosin addition

Table 2 represents the effect of adding 2.7% rosin-alum with 2% kaolin to the pulp furnish on the properties on the produced paper sheets, in comparison with the using of chitosan. Alum-rosin-kaolin is the most widely conventional additive used by local companies for producing most grades of paper products used for writing, printing, wrapping and packaging. From Table 2 it is clear that the addition of 2.7% rosin to pulp slurry deteriorates the mechanical properties of the produced paper sheets compared to those obtained of untreated pulp or 0.5% chitosan addition. In other words, for the case of using rosin-alum system, the strength properties suffer more loss than the case of using chitosan with alum to adjust the pH-value to ~ 4.5. With regard to the optical properties (brightness and opacity) it is clear that a slight improvement in the opacity accompanies the addition of rosin-alum system. The relatively high strength properties obtained when using chitosan compared with rosin-alum system may be attributed to the possibility of the formation of more polymer bridges between the fibres and the filler particles.

Effect of cationic starch addition on paper properties

Fig. 4 shows the variation in paper properties as a function of adding cationic starch %, in presence of 2% kaolin filler. The added alum was used to adjust the pH-value to ~ 4.5. It is clear that, the addition of cationic during sheet making improves the strength properties and retention of filler in the obtained paper sheets. The maximum improvement in strength properties was attained at 0.75% cationic starch. While, the best improvement in retention





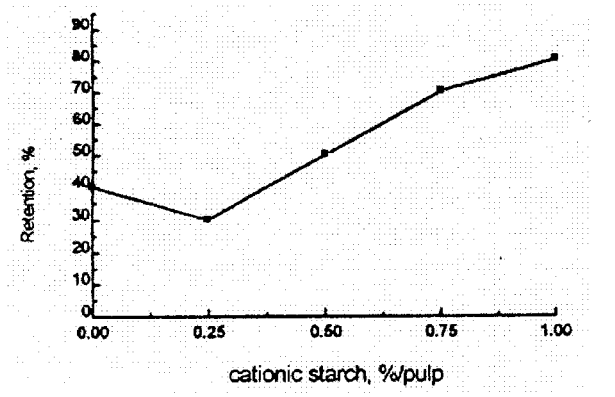


Fig. 4 Retention of kaolin, strength and optical properties versus cationic starch, %

of filler was attained at 1% cationic starch. Regarding to the optical properties, it is clear that a slight change in optical properties was observed compared to the paper without cationic starch. The improvement in paper properties is attributed to the presence of cationic charge on the polymer, which leads to increase the inter-fibre bonding, and to increase of the ability of cationic starch to flocculate the fine (18).

Effect of polyacrylamide addition on paper properties

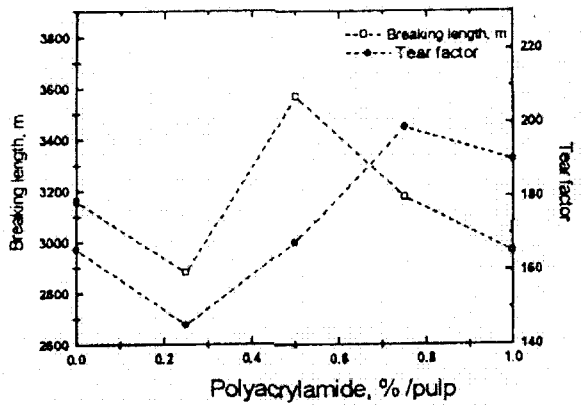
Fig. 5 shows the effect of adding different percentages (0.25, 0.5, 0.75 and 1.0%, based on pulp furnish) of polyacrylamide, with 2% kaolin, on the strength and optical properties of the produced sheets. It can be seen that the addition of polyacrylamide, as the case of previous polymer additives, leads to improve the mechanical and optical properties. The maximum improvement in breaking length and tear factor attained at 0.5% and 0.75% polyacrylamide, respectively. The improvement in the strength properties is related to the improved fibre to fibre bonding. It is also clear from this figure that, the addition of polyacrylamide increases the retention of kaolin filler in the fibre pulp, and the maximum improvement in retention value is noticed at 0.75% polyacrylamide addition.

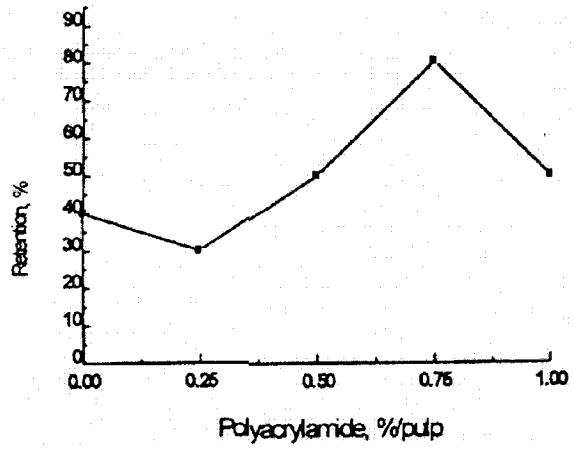
Regarding the optical properties, Fig. 5 shows that a slight change (improve) in opacity properties is observed with increasing the percentages of added polyacrylamide; while the addition of 0.25% polyacrylamide improves the brightness property and no significant improvement in this property is noticed with further increase in the percentage of the added polyacrylamide. The improvement in optical properties is probably due to the higher fines in the produced paper sheets as a result of the coagulation of fines by polyacrylamide.

Comparison between different additives

For comparison, the paper sheets produced from optimum concentrations of prementional paper additives are presented in the Bar graphs (Figures 6 and 7). The paper samples made from untreated furnish pulp, furnish pulp with 2% kaolin, furnish pulp with 0.5% chitosan and 2% kaolin (at pH ~ 4.5), furnish pulp with 0.75% cationic starch and 2% kaolin, and furnish pulp with 0.5% polyacrylamide with 2% kaolin are denoted by samples numbers 1,2,3,4,5 and 6 respectively.

From Figures 6 and 7 it can be noticed that the addition of natural chitosan polymer (sample 3) offers higher improvement in the strength properties (breaking length and tear factor) than other additives. The breaking length values of paper sheets from different additives are in the order chitosan > cationic starch = Polyacrylamide > untreated > untreated loaded with kaolin > rosin-





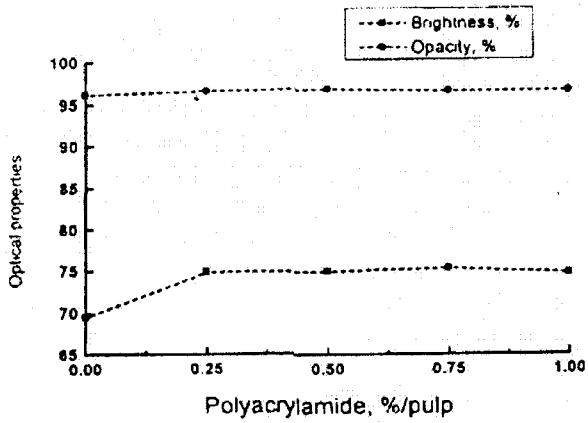
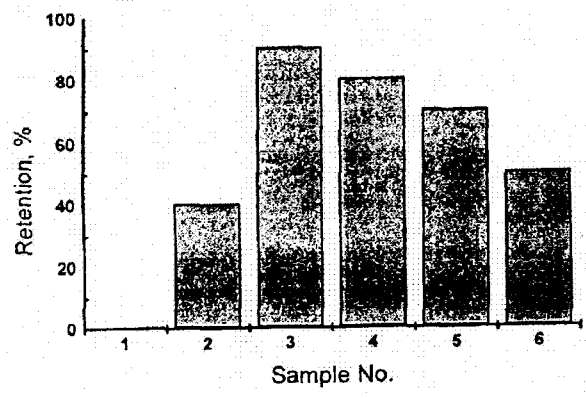


Fig. 5 Retention of kaolin, strength and optical properties versus polyacrylamide, %



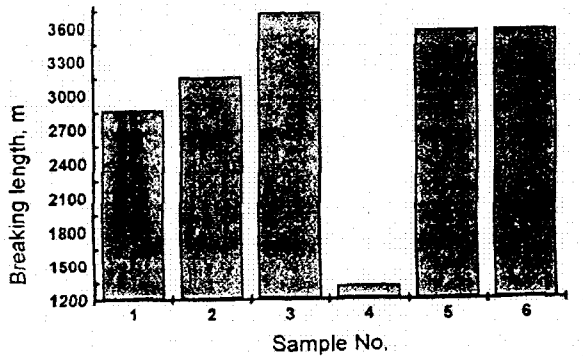


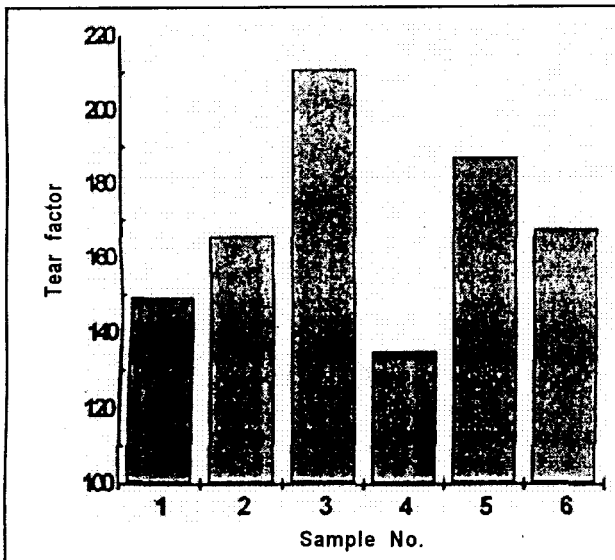
Fig. 6 Bar graph for comparing the effect of various additives filler retention and breaking length of paper sheets.

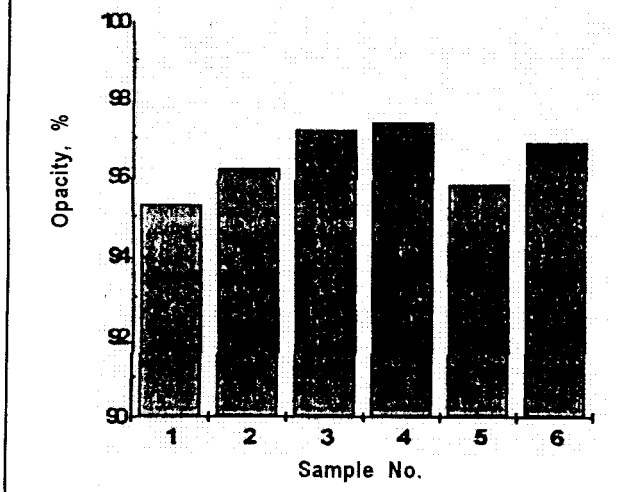
alum. While, for the tear factor it is follow the following order: chitosan > cationic starch > plyacrylamide = furnish pulp loaded with kaolin > untreated > rosin-alum. Moreover, the retention of filler of different paper sheets is in the order: chitosan > rosin> cationic starch > polyacrylamide> furnish pulp loaded with kaolin. Regarding the optical properties, it is clear that the maximum value of each opacity and brightness is obtained from using rosin-alum and polyacrylamide, respectively; while the minimum values of these properties are obtained on using cationic starch and rosin-alum, respectively.

CONCLUSION

The following conclusions were obtained :

Chitosan obtained from carb shels can be used to improve the strength and optical properties of paper sheets made from mixture of bleached rice straw and wood pulp. The paper properties were affected by changing the percemtages of the chitosan addition and pH of pulp slurry during sheet formation. The maximum improvement in the paper property was noticed at 0.5% chitosan addition at pH ~ 8. Using chitosan as paper additive is also effective in increasing the amount of the retained filler (kaolin) in loaded sheets. The retained amount





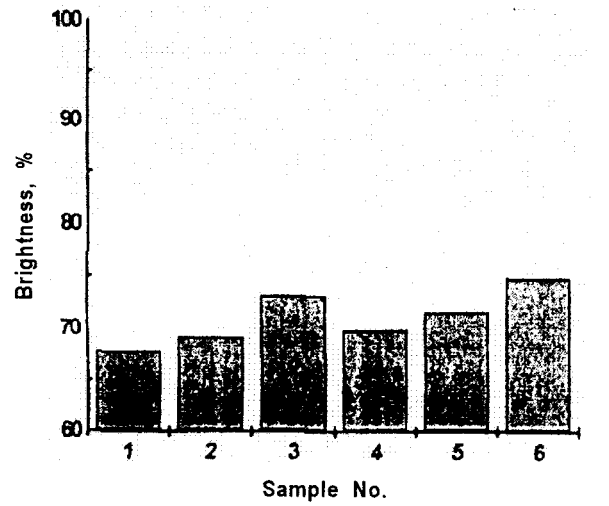


Fig. 7 Bar graph for comparing the tear factor and optical properties of paper sheets produced from adding different additives

of kaolin increases from 40.2 to 90% a result of adding 0.5% chitosan at pH 8. Chitosan addition was more successful for improving the strength and kaolin retention percentage of paper sheets compared with conventional additives, e.g., rosin-alum, cationic starch and polyacrylamide. However, the improvement in optical properties is more pronounced when using rosin-alum and polyacrylamide.

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