Characterization and Influence of Metal-Cellulose Interaction on the Properties of Modified Bleached Bagasse Pulp

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The main purpose of this study is the investigation of the influence of metal incorporation with the cellulose fibres such as bleached bagasse; carboymethylated and hydrolyzed cyanoethylated bagasse pulps. The metal effect on the paper sheets properties of different types of pulps has been illustrated. The study has shown the effect of metal treatment on the blended bleached bagasse pulp with carboymethylated and hydrolyzed cyanoethylated pulps.

INTRODUCTION

The chemical modification of a chemical pulp have important role to increase the interfibre bonds of the paper sheets and as a result, the strength properties of the paper sheets are increased (1). It is known that carboxyl groups are present as minor functional groups in chemical fibre and play significant roles in papermaking. Some of these groups originate from hemicellulose present in native lignocellulosic material, and others are introduced into bleached pulps by oxidative reaction during chemical pulping and bleaching processes. On the other hand, carboxyl groups in pulps affect their flexibility and swelling ability in water, the degree of formation of inter-fibre bonding during pressing and drying processes, and consequently the mechanical properties of dried paper sheets (2-5). However, introducing other carboxylic groups as well as cyanoethyl group into pulps (6-7) could enhance the affinity of cellulose chains toward transition metals. Electrophilicity of the main cellulose chain is considered as a measure of the strength of the interaction of transition metals with cellulose fibres. Concerning the interfibre bonding, starch additive and cellulose acetate are used. Also, grafting and impregnation of paper sheets in resins (8), polymer solution (9) are used to improve the electrical and mechanical properties of paper sheets. Some types of aqueous dispersed polymers have been started to be used for restoration and preservation of books and documents e.g. vinyl-acetate-acrylate copolymers and styrene-acrylate copolymers (10) and polyvinyl acetate-polyvinyl chlorides copolymers (11).

The aim of this study is the investigation of the effect of polymer complexes with $FeCl_2$, $CuCl_2$ and $NiCl_2$ on the mechanical properties of the produced paper sheets. Infrared measurement of the cellulose and its modifications have also been carried out.

EXPERIMENTAL

Materials

The study has been carried out on oxygen bleached bagasse pulp (delivered from Rakta paper Mill, Alex. Egypt) The chemical analysis of the pulp is α-Cellulose 74%, Lignin 2.45%, Pentosan 23.45% and Ash 1.02%.

Method

Interaction of metal salts with pulp

The sample was immersed in the metal salt solutions (1 gpl) with stirring for one minute and keeping at 25°C for 24 hours. The sample was filtered and washed with distilled water. The metal ion concentration in the sample was determined by 220 spectra Varian flame/flamless PC controlled Atomic Absorption Spectrophotometer.

Carboxymethylation

Bleached bagasse pulp was agitated in sodium hydroxide solution(8-20%) for one hour at room temperature. Monochlorlacetic acid was added (20-40%) with stirring for three hours. After the reaction was complete, filtration and washing with distilled water till neutralizing was carried out. Acidification was carried out by using 13% HCl at 60°C for 20 minutes.

The degree of substitution (DS) of CMC was calculated from the carboxyl content as follows:

$$DS = \frac{\text{Carboxyl content (0.16}}{100-(0.059 \times \text{carboxyl content})}$$

The carboxyl content was determined according to an earlier reported method (7).

$$COOH\% = \frac{N X V X 45 \times 100}{\text{Dry weight pulp}}$$

Where

N= normality of iodine solution.

V= volume of iodine solution (consumed blank).

Cyanoethylation

50g of bleached bagasse pulp was agitated in NaOH solution (0.5M) at 25°C for 30 minutes. The sample was filtered until its weight equaled to 120 g (alkali cellulose). Acrylonitrile was added (500 ml) to the reaction mixture and the reaction was carried out at 40°C for 3 hours. Then, the sample was filtered and washed with distilled water till neutralization.

Hydrolysis of Cyanoethylated pulp

Cyanoethylated pulp was hydrolyzed by 2.5% NaOH (wt/wt based on CEC) at liquor ratio 1:50 under reflux for one hour. After hydrolysis, the sample was filtered and washed with distilled water till neutralizing.

RESULTS AND DISCUSSION

Effect of metal ions on the paper sheet properties of bagasse pulp

The properties of the bagasse paper sheets prepared from treatment pulp with metal chlorides are illustrated in Table 1. From this Table, the mechanical properties were improved by the treated of bagasse pulp with metal chlorides. The improvement may be due to the attraction of multivalent metal ions by negative charges existing on cellulosic fibres. It is clear that the sheets treated with $CuCl_2$ have lower strength properties than treated with $FeCl_3$ and $NiCl_2$. This can be attributed to the higher oxidation effect of Cu^{+2} than that in case of other metal ions used. It is noted from Table 1 that the Cu^{+2} has higher metal affinity toward cellulose than the other metal ion used. Although Ni^{+2} has the lowest metal affinity towards cellulose, pulp treated with Ni^{+2} imparts higher mechanical properties than that with of Fe^{+3} and Cu^{+2}. From Table 1, the sizing properties of paper sheets prepared from pulp treated with metal ions have agreed with the sheet density of the produced paper sheet i.e. the higher sheet density, the higher sizing properties.

Table-1 Effect of metal chloride on bagasse paper sheet properties.

Sample	Sheet density (Kg/m^3)	Breaking length (m)	Tear factor	Sizing (sec)	Metal conc. (mg/g pulp)
Bagasse	567	2459	66.86	0.5	-
Bagasse +Fe	610	4280	76.91	2.0	0.1144
Bagasse + Cu	681	4019	74.98	2.5	1.1915
Bagasse + Ni	710	5235	78.21	3.0	0.0347

Effect of carboxymethylation on paper sheet properties

In this part of the study, carboxymethylated pulp was prepared to examine the properties of paper sheets resulting from blending with original

Table-2 Effect of sodium hydroxide and monochloroacetic acid on (DS.) for bagasse pulp

Sample	NaOH % (based on pulp)	Monochloroacetic acid % (based on pulp)	DS.
DS_1	8	20	0.023
DS_2	12	25	0.028
DS_3	14	30	0.033
DS_4	16	35	0.039
DS_5	20	40	0045

Table-3 Effect of carboxymethylation on paper sheet properties

Sample	Sheet density (kg/m^3)	Breaking length (m)	Tear factor	Sizing (Sec)
Bagasse	567	2459	66.86	0.5
DS_1	616	3481	115.90	0.5
DS_2	667	3563	117.51	1.5
DS_3	425	2431	85.06	0.5
DS_4	415	2156	74.35	0.45
DS_5	401	2153	68.63	0.25

bleached pulp. Carboxymethylation was carried out resulting in different DS as shown in Table 2.

The optimum DS was determined according to the properties of paper sheets prepared from the carboxymethylated pulps as shown in Table 3.

The carboxymethylated pulps sample (DS_2) which has degree of substitution 0.028 has the highest sheet properties of breaking length, tear factor, sheet density and sizing. Deterioration of mechanical properties for samples having DS higher than 0.028 may be explained by the higher loss of pentosan that hydrolyzed by NaOH which used in carboxymethylation process. On the other hand, the decreasing of sheet densities and sizing properties may be attributed to the decreasing of hemicellulose, which reduces the bonding between the fibre of paper sheets. Table 4 shows the properties of paper sheets made from the blending of bagasse pulp with carboxymethylated pulp of DS (0.028). From this Table, it is clear that the breaking length and tear factor of the paper sheets of the pulps blended increase by increasing the ratio of the carboxymethylated pulp to origin pulp till 70% 30 ratio (bagasse to carboxymethylated pulp). This can be attributed to the increase of the adhesion between carboxymethyl and cellulose fibres, which enhances the crossing of links between the cellulose fibres in the paper sheets. Also, presence of carboxymethyl cellulose in the paper sheets causes an increase in Vander Weal's bonding (physical bonds) which supports the strength property (13). The decrease in the strength properties at higher carboxymethylated pulp may be attributed to the

Table-4 Effect of blending of carboxymethylated pulp (DS_2) on the paper Sheets Properties

Sample Bagasse : CMC	Sheet density (kg/m^3)	Breaking length (m)	Tear factor (Sec)	Sizing (mg/g pulp)
100:00	567	2459	66.86	0.50
90:10	678	3483	77.62	0.75
80:20	687	3977	78.34	0.75
70:30	687	4039	86.70	1.00
60:40	662	3607	65.46	0.50
50:50	609	3215	57.67	1.00

Table-5 Effect of metal ions on the paper sheet properties of carboxymethylated Pulps with different DS

Sample	Sheet density (Kg/m^3)	Breaking length (m)	Tear factor	Sizing (sec)	Metal conc. (mg/g pulp)
DS_2	667	3563	117.51	0.50	-
DS_2 + Fe	689	3587	117.88	1.75	0.4635
DS_2 + Cu	664	3573	117.60	2.50	1.4301
DS_2 + Ni	675	3662	119.20	0.50	0.0621

emerging of some sort of heterogeneity among the cellulosic fibres, which formed the paper sheets.

Effect of metal ions on carboxymethylated pulp properties

In this part, the effect of metal ions was carried out on the carboxymethylated pulp sample, which shows the best mechanical properties of the prepared sheets. From Table 5 it is shown that, the retention of metal on the carboxymethylated pulp has positive effect on the mechanical properties of paper sheets. This effect can be attributed to the nature of the functional group in cellulose ether (ligand) and consequently of bond strength of metal ions with it. Whereas, the carboxyl ion has a higher absorption capacity than the hydroxyl group in cellulose. From Table 5, it is clear that, slight improvement is observed in sheet density and sizing of the carboxymethlated pulp treated with metal ions. Also, the best mechanical properties of paper were found with carboxymethylated pulp treated with Ni^{+2}. Their, the improvement of the mechanical properties of paper sheets depend on the nature of the retained ions and not to the amount of retained ions. This conclusion can no be demonstrated by the results shown in the Table 5. It is clear that there is no significant increase in properties of the paper sheets by the variation of metal ion concentration.

Effect of metal ions on paper sheet properties of blended bagasse with carboxymethylated pulp

Table 6 shows the effect of metal ions on the properties of paper sheets made from blended bagasse pulp and carboxymethylated bagasse pulp in 70:30 ratio respectively.

It is clear that Ni^{+2} retained on the blended pulp have the highest positive effect on paper sheet properties. From the same Table, pulp with copper chloride produced paper sheets of higher mechanical properties than the pulp with ferric chloride. This can be attributed to the oxidation effect of copper chloride to some hydroxyl groups, destruction of the weak hydrogen bonds and subsequently reordering of the chains with the formation of new and relatively stronger hydrogen bonds (15).

Table-6 Effect of metal ions on paper sheets properties of blended bagasse with carboxymethylated pulp (in ratio 70:30 bagasse : CMC)

Sample	Sheet density (Kg/m^3)	Breaking length (m)	Tear factor	Sizing (sec)	Metal conc. (mg/g pulp)
Blend	687	4039	86.70	1.00	-
Blend + Fe	695	4389	85.78	3.00	0.3548
Blend + Cu	685	3944	83.16	2.00	1.0311
Blend + Ni	705	4462	87.56	2.00	0.0537

Effect of Cyanoethylation on paper sheet properties

Paper sheets produced from hydrolyzed cyanoethylated bleached bagasse pulp has mechanical properties lower than that in case of uncyanoethylated pulp, (Table 7). This is attributed to the sever degradation of the pulp during Cyanoethylation process.

Table-7 Effect of metal ions on paper sheets properties of (HCEC) and blended bagasse with HCEC pulp (in ratio 70:30 Bagasse : HCEC)

Sample	Sheet density (Kg/m^3)	Breaking length (m)	Tear factor	Sizing (sec)	Metal conc. (mg/g pulp)
Bagasse	567	2459	66.86	0.50	-
HCEC	457	162	20.27	-	-
HCEC + Fe	372	1160	41.27	0.50	0.3214
HCEC + Cu	429	879	44.38	0.50	0.8132
HCEC + Ni	393	805	42.88	0.50	0.0246
Bagasse + HCEC	579	3125	79.51	0.75	-
Bagasse + HCEC +	602	3316	81.23	2.00	0.4321
Bagasse + HCEC +	653	3719	86.45	1.00	0.8791
Bagasse + HCEC +	620	3500	84.53	0.75	0.0331

On the other hand, bagasse pulp with hydrolyzed cyanoethylated pulp improves the mechanical properties of the paper sheets. This can be attributed to the presence of carboxyl groups in hydrolyzed cyanoethylated pulp which causes an increase in the bonding strength of the fibres of the paper sheets (Table 7). Treatment of the blended pulp with metal chloride exerts a considerable increase in the mechanical properties of the paper sheets.

CONCLUSION

The interaction between transition metal and the cellulosic fibres has been manifested though the enhancement of the paper sheets properties. Incorporation of metal ions can improve the mechanical properties of the bleached bagasse pulp. Also the metal incorporated with carboxymethylated pulp can enhance the strength properties of paper sheets. The degree of substitution affects amount of metal combined with the cellulosic substrate. The blending has a positive effects upon the physical properties of the blended bleached bagasse pulp with carboxymethylated pulp in the range from 90 : 10 to 70 : 30 (bagasse: CMC). Paper produced from cyanoethylated bleached bagasse pulp has mechanical properties lower than that in case of uncyanoethylated bleached pulp. The mechanical properties of cyanoethylated pulp can be improved by blending with bagasse. The treatment of pulp with copper chloride exerts a considerable increase in the mechanical properties of the sheets.

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