Effect of Oxidized Starch and Inorganic Filler on Paper Properties

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Abstract

Preparation of dialdehydic and dicarboxylic starch were studied. The effect of these materials on the mechanical properties of paper sheets and retention of filler e.g. kaolin and ground $CaCO_3$ was investigated. Discarboxylic starch increased the mechanical properties and also increased the retained filler. The percent of the retained filler was decreased by increasing the amount of added filler; the retained amount of $CaCO_3$ was higher than that in case of kaolin. Addition of $CaCO_3$ in contrary to kaolin increased the mechanical properties of the produced paper sheets. Addition of filler increased the optical properties e.g. opacity and brightness of paper sheets. Infrared spectroscopy of the prepared cationic starch derivatives shows a new band at 1715 cm^{-1}.

INTRODUCTION

The use of mineral fillers in papermaking is increased as the price of pulp and the need for improved paper properties increases. The paper properties including opacity, brightness, bulk, gloss and printability. The common filler in papermaking is white clay for acid paper mills, calcium carbonate for alkaline paper mills, and talc. Fillers are important in papermaking as a raw materials, in printing they are indispensable printability aid. They also used to decrease the cost by opacifying and allowing a substantial reduction in basis weight and simultaneously, fibre consumption. Natural and synthetic polymers are used as retention aids for fillers. The starch distribution in fine paper furnish have shown that, a large proportions of starch is adsorbed on the fibre. It has been suggested that the adsorbed starch on the fines and fillers improve retention of these materials, as well as the paper strength (1,2). Cationic starch, which contains aldehydic groups, can react with hydroxyl group of the cellulose, which is required for its absorption on to the cellulosic fibres. The strengthing effect of charged aldehyde starch results from the formation of strong hemiacetal and acetal bond between the starch and cellulose. These covalent bonds might be responsible for the rigidity and great strength of filler-to-fibre bond (3). These bonds are stronger than the hydrogen bonds and hydrolyze slowly in water at low temperature (4).

The aim of this study is to prepare different cationic starches with different aldehydic and carboxylic groups. Infrared spectroscopy of these cationic starches was studied. The effect of these prepared cationic starches on the properties of the paper sheets as well as its effect on retention of fillers on the fibre of produced paper sheets is also investigated.

EXPERIMENTAL

The materials used in this work are, bleached sulphate wood pulp (Betual rerrucosa) which was beaten to 40°SR in a valley beater; Starch was delivered from El-Naser Compony, Egypt; ground $CaCO_3$ and kaolin are pure commercial grade.

Oxidation of starch

Oxidized starch was prepared as follows (5): a-a-Preparation of 2, 3-dialdehydic starch:

Periodate oxidized starch was prepared by oxidizing 10 g of starch suspended in water ($500cm^3$) with sodium metaperiodate at ambient temperature in the dark for 4 days. Oxidized products were separated by centrifugation as a water-insoluble precipitate. The solid mass was recovered in the form of colourless powder by washing with water, 50% ethanol, and ethanol successively and drying under vacuum.

b - Preperation of 2,3-dicarboxlicstarch sodium salt;

An aqueous suspension (100 cm^3) containing 2,3- dialdehydic starch (5g) was further oxidized with sodium chlorite and acetic acid in a reaction vessel kept at 20-25^{0}C with vigorous stirring. Sodium chlorite was dissolved in an aqueous medium, and then acetic acid was added drop wise from a separating funnel for 1h. The reaction mixture was allowed to react for 6 h, and then was immersed in an ice water and adjusted to pH 8.5 with 10 M NaOH. Oxidized products were precipitated by pouring the reaction mixture to 3 volumes of ethanol and were allowed to stand in a refrigerator for 3 days. The supernetant liquid was removed from the settled product by decantation; the gummy sediment adhering to the bottom of the vessel was scraped out with a spatula and suspended in 50% ethanol. The sediment was separated by repeated decantation of the supernetant liquid and suspended in ethanol. The products (Na Salt) were obtained by washing with ethanol and drying under vacuum.

c-Preparation of 2, 3-dicarboxylic starch:

2,3-dicarboxylic starch Na salt (5g) was suspended in water ($55cm^3$) and adjusted and then was mixed with 3 volumes of ethanol. The precipitate was collected and washed with 70% ethanol till neutrality. The powder was washed in ethanol and petroleum ether and dried in vacuum.

Addition of oxidized starch and filler

8g of beaten wood pulp in $50cm^3$ water was mixed carefully with filler (kaoline or $CaCO_3$ from 5 to 20% based on pulp weight) or oxidized starch (0.5-2% based on pulp weight). In case of kaoline, the pH was adjusted to 5.5 by using alum. In case of addition of oxidized starch and filler, the oxidized starch was added followed by addition of fillers.

Paper making\ Handsheet

The paper sheets were prepared according to Swedish Standard Methods (SCA). The mechanical properties (breaking length, tear factor and burst factor) were determined according to standard methods (6). The retained filler was determined from the remained ash content after burning the paper sheets.

Aging of paper

Aging was carried out at different temperatures (130-150^{0}C) for 1 hour.

Infrared spectroscopy

Infrared spectroscopy was carried out by using KBr disc technique using JASCO FT/IR 3006 (Fourier Transform Spectrometer).

RESULTS AND DISCUSSION

Infrared spectra of starch derivatives

Two kinds of starch derivatives, dialdehydic starch and dicarboxylic starch were prepared. These derivatives were characterized by using infrared spectroscopy. Fig 1 shows the infrared spectra of starch and oxidized starch from wave number 200 to 4000 cm^{-1}. In the spectra a new band appeared at 1715 cm^{-1} in the oxidized starch, which was characteristic of C=O of carboxyl groups. On the other hand, the carboxylic starch produced from oxidation of dialdehydic starch contains a carboxyl group with higher relative absorbance (absorbance of the subscript wave number to the absorbance of the wave number at 1328 cm^{-1} which corresponding to CH rocking of the ring (7) than the aldehydic group.

Moreover, the oxidation process decreased the relative absorbance of CH_2 band intensity at $2930cm^{-1}$, which characterizes the CH_2 group. This means that this group undergoes oxidation forming the CHO or COOH groups. This can be confirmed by increasing the relative absorbance of OH group at 3430 cm^{-1}, which was produced by oxidation of CH_2 group to the carboxylic group.

Table 1. Relative absorbance of the bands of different groups in starch, dialdehydic starch and dicarboxylic starch.

Wave number cm^{-1}	Starch	Dialdehydic Starch	Dicarboxylic starch
3400	1.61	2.11	2.7
2920	1.49	1.35	1.16
1715	-	0.7	1.22
1665	0.85	2.4	1.18
1425	1.02	0.88	1.19
1240	0.8	0.88	0.78
1120	1.64	1.54	1.43
10.65	1.56	1.94	2.
1035	1.6	2.11	2.3

The relative absorbance of the band at 1665 cm^{-1} which is characteristic of the CHO group was higher in aldehydic starch than that in case of starch and carboxylic starch. The relative absorbance of the band at 1120 cm^{-1} which is characteristic of the ether linkage between glucose units of starch decreased by oxidation of starch. This is due to that oxidation of starch, accompanied with some degradation of glucosidic linkage between glucose units.

Effect of starch and its derivatives on the mechanical properties of paper sheets.

Table 2 shows the effect of starch and its derivatives on the mechanical properties of paper sheets prepared from bleached wood pulp. From this table, it is clear that, addition of starch increased the mechanical properties of the sheets produced due to increase of bonding and cross-linking between the fibre in the paper sheets. The mechanical properties of paper sheets increased by increasing the added starch amount. So, the breaking length increased by about 15% by adding 2% starch, while the tear factor increased and reached to its maximum at 1% added starch.

Addition of dialdehydic starch caused an increase of tear factor more than the starch itself

Table 2. The effect of addition of starch and its derivatives on the mechanical properties of the paper sheets.

Addition %	Starch		Dialdehydic Starch		Dicarboxylic Starch	
	Breaking length (m)	Tear factor	Breaking length (m)	Tear factor	Breaking length (M)	Tear factor
0.0	4659	133.68	4659	133.68	4659	133.68
0.5	4733	166.92	4401	206.30	4882	152.07
1.0	4750	169.08	4074	192.43	4921	153.43
1.5	5206	166.34	3710	172.61	5279	153.94
2.0	5387	155.15	3450	167.14	5532	150.33

but decreased the breaking length. This can be attributed to the presence of strong covalent bonds (8) as well as an improvement in fine retention of pulp and internal bonds between fibres (9). Addition of the dialdehydic starch to about 0.5% increased the tear factor to about 14%. By increasing the percentage age of dialdehydic starch to 2% (based on pulp) the tear factor decreased but still higher than that in case of blank (untreated paper sheets) and treated paper sheet with starch.Addition of dicarboxylic starch to the pulp increased the breaking length. This is due to the increasing of the cross linking between the fibres in paper sheets. Increasing of dicarboxylic starch addition to 2% increased the breaking length by about 19%. Moreover the absorption of oxidized starch on the cellulose fibre increases the COOH group and correspondingly increases the strength of dry and rewetted paper (10) From the above results, it is clear that, the addition of dicarboxylic starch improves the mechanical properties of the paper sheets more than dialdehydic starch.

Effect of filler addition on the mechanical properties

Fillers are used mainly to improve the brightness, opacity and smoothness properties of the paper sheet as well as to reduce the production cost. Paper strength is often related to the surface of the filler depending on the particle size of the filler. Addition of ground $CaCO_3$ and kaolin during the paper sheet preparation affect the strength of the paper sheets. Increasing the percentage of the filler, (Table 3,) decreased the retained filler percentage. It is seen that the retention of the $CaCO_3$ on the fibre of paper sheets is higher than that in kaolin. It may be due to the difference in the structure as well as to the particle size and also to the blocky particle of $CaCO_3$ while the kaolin has slakey particle. Also the higher retention of $CaCO_3$ than kaolin is due to the electrostatic attraction between the negatively charged pulp fibre and positively charged $CaCO_3$ (11). The breaking length of the paper sheets, which contains $CaCO_3$, was higher compared with the paper sheets of retained kaolin (12). The breaking length of the paper sheets was decreased by increasing the amount of added kaolin. This is attributed to the reduction in bonded area as a result of the trapping of filler, fibril and fibre fine flocks between fibre areas, which would normally have bonded. Tear factor increased to a maximum value with added 15 and 10% $CaCO_3$ and kaolin respectively. Addition of filler increases the brightness of the paper sheets, it increased from 71.5 to 75.7 and 72.6 in case of addition of $CaCO_3$ and kaolin respectively (Table 5) This can be attributed to the presence of filler in the paper sheets which fill the pores of the paper sheet causing a greater disruption of the fibre network (13).

Effect of oxidized starch on the retention of the filler on paper sheets

From Table 3, it is clear that the optimum addition of fillers occurred by adding 15% $CaCO_3$ and

Table 3. The effect of filler addition on the mechanical properties of the paper sheets

Filer	$CaCO_3$			kaolin		
	Breaking length (m)	Tear factor	Filler retained	Breaking length (m)	Tear factor	Filler retained
5	4659	133.68	-	4659	133.68	-
5	4774	142.99	63.2	4489	132.07	53.8
10	4778	150.10	55.5	4462	140.93	52.8
15	4831	154.20	45.6	4086	133.86	42.0
20	4751	140.30	40.6	4075	130.00	39.0

Table 4. The effect of dicarboxylic starch on the retention of filler on the paper sheets.

Treatment	15% $CaCO_3$			10% kaolin		
	Breaking length (m)	Tear factor	Filler retained	Breaking length (m)	Tear factor	Filler retained
Without Starch	4831	154.2	45.6	4462	140.93	52.8
With 1.5% dicarboxylic starch	4998	174.83	57.9	4729	165.25	59.1

10% kaolin. So the effect of oxidized starch on the retention of this two fillers was studied at these addition %.

From table 4, it is clear that by adding 1.5% dicarboxylic starch, the retention of the filler increased. The addition of the dicarboxylic starch increased the retention of $CaCO_3$ from 45.6 to 57.9% i.e. (27%) and kaolin from 52.8 to 59.1%, i.e. (12%). This can be attributed to the fact that the addition of cationic starch promotes fines and fillers retention and dewatering during paper manufacturing. This causes an increase of fillers retention. The addition of cationic starch improves the internal bonds between paper sheet fibres and fillers (14). Also, the addition of dicarboxylic starch with fillers increased the breaking length and tear factor in case of both $CaCO_3$ and kaolin.

Aging of paper sheets

Table 5 shows the effect of aging on the mechanical and physical properties of paper sheets, with and without retained filler. From this table it is clear that the paper sheets without filler is highly affected by aging. Moreover the mechanical properties decreased by increasing the aging temperature from 130 to 150°C. On the other hand, the paper with retained $CaCO_3$ is more resistant to ageing than the paper sheet without filler and that retained with kaolin. This is due to the fact that the presence of $CaCO_3$ in paper sheets neutralize the acids (produced by oxidation of paper sheets during aging), thus preventing the acid hydrolysis which causes the deterioration of cellulose (11).

Thus, the uses of $CaCO_3$ as filler in paper sheets have an effect on the permanence and the durability of these grades on aging (15).

The same trend was seen in case of the tear factor and burst factor. These two properties have the lower values by aging in paper sheets filled with $CaCO_3$ than other sheets. Moreover, the brightness % is more resistant to aging in the paper sheets filled with $CaCO_3$ than other

Table 5. The effect of aging on the mechanical and physical properties of paper sheets.

Test	Unaged			130°C			140 °C			15°C		
	Blank	$CaCo_3$	Kaolin	Blank	$CaCO_3$	Kaolin	Blank	$CaCO_3$	Kaolin	Blank	$CaCO_3$	Kaolin
Breaking length	4659	4769	4462	4462	4760	4600	4363	4647	4500	4200	4380	4243
Tear factor	134	154	141	132	149	139	125	140	131	120	137	129
Burst factor	38	40	38.4	36.2	35.8	33.4	33.8	34.1	31.2	30.8	33.1	30.8
Bright-ness %	71.5	75.7	72.6	70.1	74.2	70.7	68.8	72.2	69.2	65.2	69.4	66.3

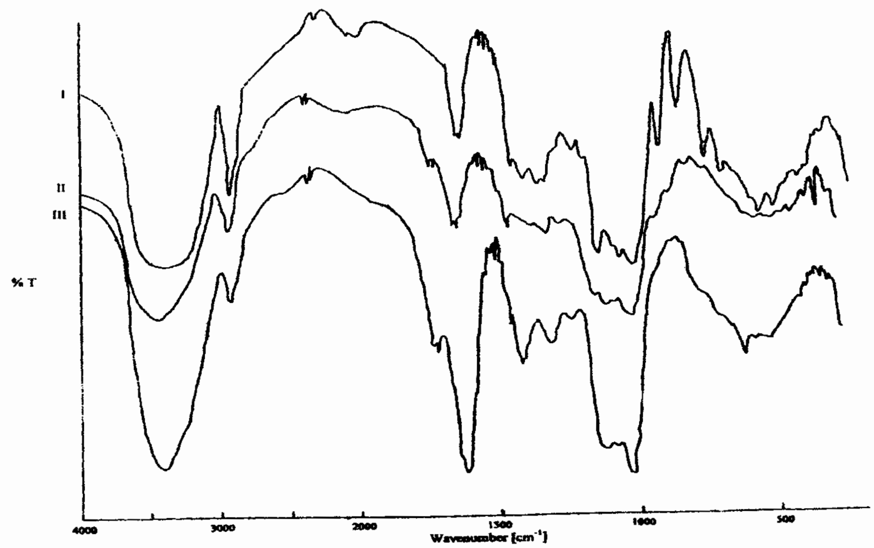

Fig. 1. Infrared spectra of starch and oxidized Starch I Starch, II Dialdehydic starch,

paper sheets, unfilled or filled with kaolin.

CONCLUSION

Addition of starch during the paper sheets manufacture increased their mechanical propeties. Addition of dicarboxylic starch to paper sheets improves their mechanical properties more than addition of dialdihydic starch and untreated starch. Addition of $CaCO_3$ to paper sheets increases the mechanical and physical properties e.g. brightness and opacity of the produced paper sheet more than addation of kaolin. The paper sheets with retained $CaCO_3$ are less affect by aging than the sheets retained with kaolin.

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