Cellulose Hydrazone Derivatives as Additives in Paper Making

Magda G. El-Meligy and Fardous Mobarak

Cellulose and Paper Department, National Research Center, Dokki , Cairo, Egypt

Dialdehyde cellulose hydrazone derivative and cellulose hydrazino complex were prepared through reaction with 2-hydrazino derivative, under suitable selected conditions. These cellulose hydrazone derivatives were evaluated as additives in paper making. The addition of 5% DAC hydrazone derivative or 5% cellulose hydrazino complex under suitable conditions, increased the breaking length of the paper produced from cotton linters by 59% and 30.8 respectively; and 45% and 35% respectively for wood pulp. Also a considerable increase in bursting strength took place. It was found that the addition of DAC hydrazone derivative or cellulose hydrazino complex increased the water absorption of the paper produced from cotton linters whears the water retention inreased from 45% to 78.4% and 77% respectively. SEM pictures were carried out and elucidated the obtained results.

INTRODUCTION

Cellulose which is the basic raw material for paper making and rayon manufacture, occurs in the form of fibres in a wide variety of growing plants .Cellulose is some what unique when compared with many natural or synthetic high polymer in that it contains so many functional hydroxyl groups, both primary and secondary. Therefore a variety of cellulose derivative are produced by etherification, oxidation and alcoholate formation[1,2]. Reacting cellulose fibres under reduced condition for short time result in partial chemical modification while the fibrous structure of cellulose is retained. Thus papers with modified properties can be produced[3]. For instance carboxymethylated cellulose fibre become more hydrophilic and lead to paper with higher strength.

The grafting reaction also alters the physical properties of the paper to suit a particular endues. Paper may be cross linked strengthened made more plastic stiffer, softer and more or less, hydrophbic[4,5]. However, the simplest and oldest way of affecting paper properties is by adding different substance to the pulp. Additives of hydrophilic binders are since long used in paper making. Starch is an example of popular binders. Starch molecule act as cementing agent in interfibre bonding and thus increase paper strength[3].

A cellulose containing fibrous material is prepared by oxidizing hydroxyl group of glucose unit into aldehyde or carboxylic group. It was used to prepare paper or non woven product especially tissue product[6]. Dialdehyde cellulose hydrazone derivatives was used for treatment of sewage wastewater[7]. Polycondensation hydrazine derivatives with fibrous materials, increased the weight of the fabrics by 0.28 - 3.06% and decreased the water sorption and shrinkage. An improvement in fabric strength, crock fastness, light fastness, initial temperature of thermal degradation and self-ignition temperature of the fabrics was noted[8].

In this article, new water insoluble cellulose derivatives are to be evaluated as binder i.e strength promoters for paper. These new paper additives are polycondensation hydrazone derivatives.

EXPERIMENTAL

Materials and methods

Material

Wood pulp (soft wood, sulfite pulp, D.P 870) provided by Rakta company and cotton linters (mill run, D.P 740) provided by factory 18, Abu Zabil were used as raw material for paper making. Viscose wood pulp (soft wood, sulfidity pulp, D.P 705) and 2-hydrazino derivative[9] (2hydrazino- 3, 5, 6, 7 - tetrahydrocy-clopentanothieno [2,3-d] pyrimidin 4 (4 H) one) were used to prepare cellulose hydrazino complex and dialdehyde cellulose hydrazone derivative as additives.

Pulping cotton linters

Pulping was done in an autoclave (two revolution per minutes) at 140°C for 1.5 h, liquor ratio 1:4 (Cotton linters: water) respectively and 3% Na OH based on dry weight.

Preparation of dialdehyde cellulose-hydrazone derivative and cellulose-hydrazino complex:

1- Preparation of dialdehyde cellulose hydrazone derivative[7]

The dialdehyde cellulose (DAC) was added to 2-hydrazino derivative in the ratio 1:2 respectively in dioxane and few drops of piperidine. The reaction was allowed to reflux for about 18 h. Then cooled to room temperature. The product was recovered by filtration and washed properly by absolute ethanol and dried in oven at 60°C.

2- Preparation of cellulose hydrazino complex

The swelling viscose wood pulp was added to 2 hydrazino derivative in the ratio 1:2 respectively in dioxane and few drops of piperidine. The reaction was allowed to reflux for about 30 h.

Then cooled to room temperature. The product was recovered by filtration and washed properly by absolute ethanol and dried in oven at 60°C.

Paper - making

The pulps with 5% of the above additives were beaten in a jokro beater at 6% consistency until they reached 5O°SR.Sheets were prepared by using the sheet former of AB Lorentzen and Wetter (Stockholm, Sweden).

After sheet forming the papers were conditioned for 24 hr at 50 RH and 20°C. The sheets were then subjected to the following analysis and tests.

Analysis

Elemental composition of the prepared additives was determined for C,H,N and S by atomic

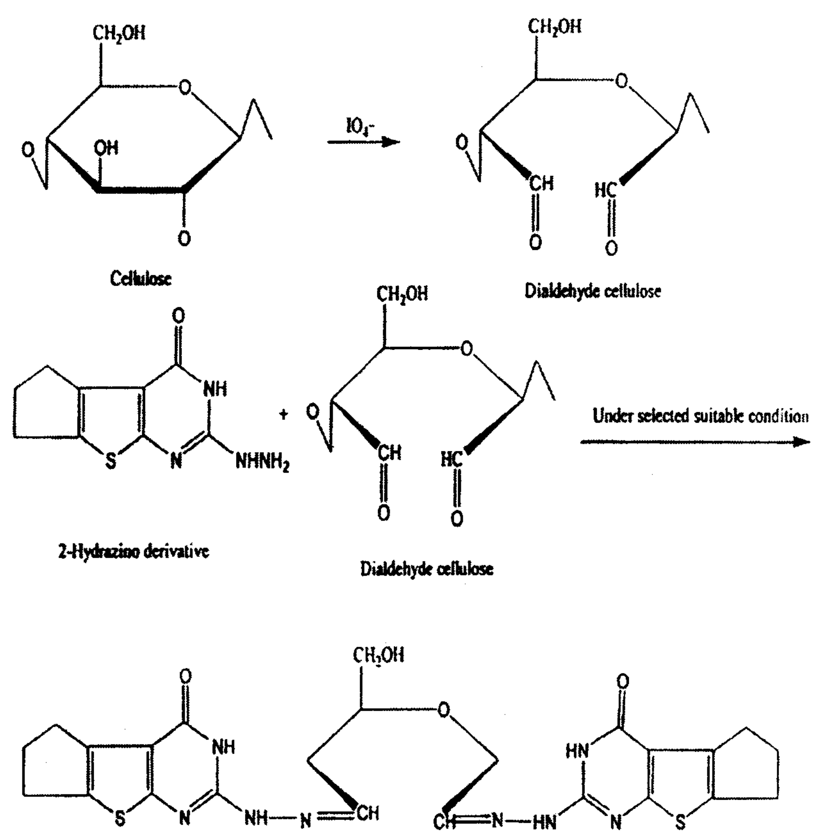

Fig. 1 : Cellulose hydrazone derivative

Table 1 : Elemental composition of C, H, N and S of the additives used

Experiment	Carbon %	Hydrogen %	Nitrogen %	Sulpher %
Viscose wood pulp (Raw material)	42.2	5.86	-	-
Dialdehyde cellulose of viscose wood pulp.	39.57	5.88	-	D
2-hydrazino derivative	47.91	3.02	23.56	13.11
Cellulose hydrazino Complex.	43.38	6.16	3.08	1.37
DAC hydrazone Derivative.	45.27	4.84	16.78	9.9

Table 2: Chemical analysis of pulp

Experiment	α-Cellulose %	Hemicellulose %	Klason Lignin %	Ash Content %
				%
Wood pulp	88.1	8.6	0.33	1
Untreated cotton linters	96.7	1.4	-	0.3
Treated cotton linters	98.5	0.4	-	-

Table 3 : Physical properties of paper made from cotton linters (C.L) filled with additives 5% dialdehyde cellulose hydrazone derivatives and cellulose hydrazino complex.

Experiment	Density g/cm^3	Breaking length m	Increasing percent in breaking length %	Bursting strength kg/cm^2	Increasing percent in bursting strength %
Unfilled C.L	0.33	955	-	0.8	-
C.L filled with cellulose hydrazino complex	0.51	1250	30.8	1.1	30
C.L filled with dialdehyde cellulose hydrazone derivative.	0.53	1520	59.2	1.25	45

absorption spectroscopy (VAIRO EL ELEMENT AR).Both cotton linters and wood pulp were analyzed for alpha cellulose, hemicellulose, Klason lignin and ash content.

Scanning Electron Microscope (SEM)

A piece of paper covered with a gold from one face only and the other face put on the holder, then enter in the scanning electron microscope. (Scanning Electron Microscope, JEOL JXA-840A, Electron micro analyzer).

Physical Tests

Water retention

A piece of paper immersed in water for 24 hour, then put in a special sieve in centrifuge (3000 revaluation/min) for 15 minutes. The piece of paper weighted directly after removing from sieve (x) and put in dry oven for 24 hours at 105°C then weighed (y).

water retention % = (X-Y)/Y.

Density

The density can be obtained by dividing the weight

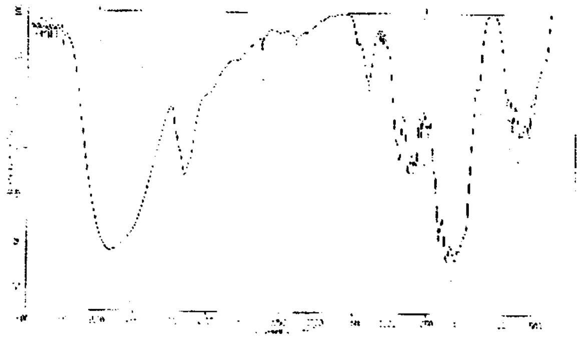

Fig. 2: Infra Red Spectra
Fig. 2a : Infra red spectra of native cellulose

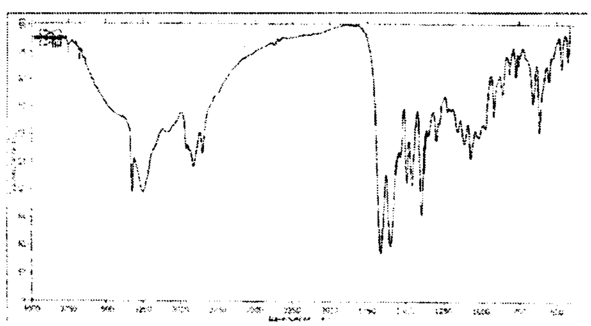

Fig. 2b : Infra Red Spectra of dialdehyde cellulose hydrazone derivative

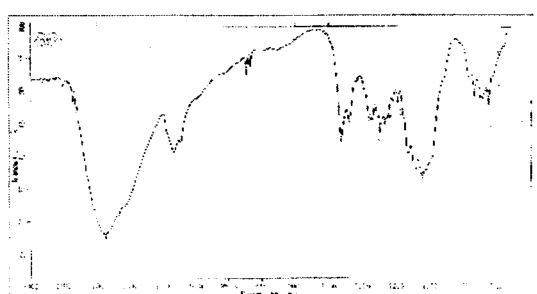

Fig. 2c : Infra red spectra of cellulose hydrazone complex

of sheet on its volume. The volume can be calculated by multiplying the area of the sheet by thickness. The density is disintiguished as g/cm^3.

Breaking length

The tensile strength was estimated according to the German Standard method by means of Karl frank 468 tester (Weinheim Birkenau). Breaking length in m can be obtained from tensile strength according to the following equation: Breaking length (m) =

Tensile strength (kg) X length of strip (m) / weight of strip (kg)

Bursting strength

It was disintiguished as Kg/cm^2 (Mullen tester, B.F. Perkins).

RESULTS AND DISCUSSION

There are two main additives in this work. DAC

Fig. 3: The morphology of cotton linters
Fig. 3a : The morphology of the unfilled cotton linters.

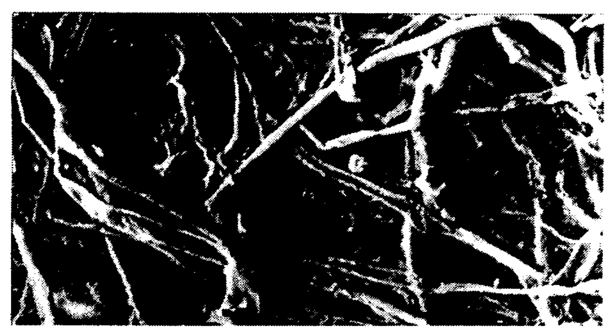

Fig. 3b : The morphology of the cotton linters filled with 5% cellulose hydrazino complex.

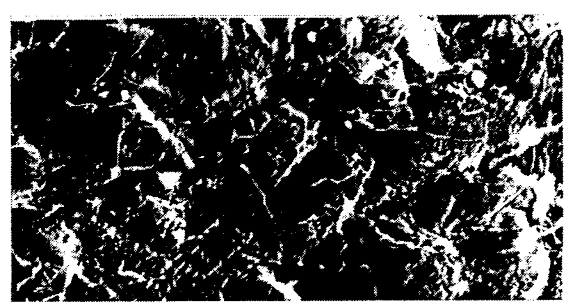

Fig. 3c : The morphology of the cotton linters filled with 5% dialdehyde cellulose hydrazone derivative.

Table 4: Water retention of cotton linters(C.L) paper filled with additives 5% dialdehyde cellulose hydrazone derivative and cellulose

Experiment	Water retention %
Unfilled C.L	45
C.L filled with cellulose hydrazino complex.	77
C.L filled with dialdehyde cellulose hydrazone derivative.	78.4

Table 5 : Physical properties of paper made from wood pulp (W.P.) filled with additives 5% dialdehyde cellulose hydrazone derivatives and cellulose hydrazino complex.

Experiment	Density g/cm³	Breaking length m	Increasing percent in breaking length %	Bursting strength kg/cm²	Increasing percent in bursting strength %
Unfilled W.P	0.38	1360	-	0.75	-
W.P filled with cellulose hydrazino complex	0.51	1840	35.3	1.1	46.7
W.P filled with dialdehyde cellulose hydrazone derivative.	0.53	1978	45.4	1.2	60

Table 6: Water retention of Wood pulp(W.P) paper filled with additives 5% dialdehyde cellulose hydrazone derivative and cellulose hydrazino complex

Experiment	Water retention %
Unfilled W.P	91.3
W.P filled with cellulose hydrazino complex.	67.-5
W.P filled with dialdehyde cellulose hydrazone derivative.	76

hydrazone derivative and cellulose hydrazino complex which were confirmed by elemental analysis (Vario El Elementar) Table 1, and Infra red spectra (FT/IR 300 E Jasco) Figs. 2a,b and c.

Cellulose hydrazino complex can be formed by interaction of the hydrazino molecule inside the cellulose chains[9]. This is due to the formation donor hydrogen bonds between the - OH and - NH group in the cellulose hydrazino complex. DAC hydrazone derivative can be formed by reaction of hydrazine gp ($NHNH_2$) with aldehyde group of dialdehyde cellulose involving - C=NN gp[2,7] as, shown in Fig. 1.

Effect of dialdehyde cellulose hydrazone derivatives and cellulose hydrazino complex on the properties of paper made from cotton linters

The addition of DAC hydrazone derivative and cellulose hydrazino complex in the ratio of 5% based on the dry weight of pulp, increased the breaking length and bursting strength by 59.2%

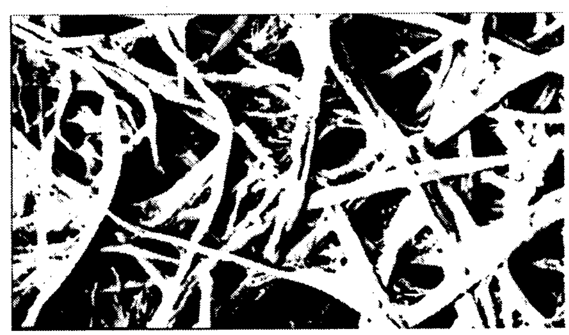

Fig. 4: The morphology of Wood Pulp
Fig. 4a : The morphology of the unfilled Wood Pulp.

and 45% for DAC hydrazone derivative respectively and 30.8% and 30% for cellulose hydrazino complex respectively if compared with unfilled paper as shown in table 3.This means that the DAC hydrazone derivative and cellulose hydrazino complex were spread between the fibres of paper and this lead to the formation of stronger additional hydrogen bond especially in the case DAC

Fig. 4b : The morphology of the Wood Pulp filled with 5% cellulose hydrazone complex.

Fig. 4c : The morphology of the Wood Pulp filled with 5% dialdehyde cellulose hydrazone derivative.

hydrazone derivative.

It was found from table 4 that the addition of 5% DAC hydrazone derivative or cellulose hydrazino complex increased the water retention of the paper made from cotton linters, from 45% to 78.4% and 77% respectively.

Effect of dialdehyde cellulose hydrazone derivatives and cellulose hydrazino complex on the properties of paper made from wood pulp

The addition of DAC hydrazone derivative and cellulose hydrazino complex in the ratio of 5% based on the dry weight of pulp increased the breaking length and bursting strength by 45.4% and 60% for DAC hydrazone derivative respectively and 35.3% and 46.7% for cellulose hydrazino complex respectively if compared with unfilled paper as shown in Table 5. This due to the formation of stronger additional hydrogen bond by these additives between the fibres of paper.

It was found from Table 6 that the dialdehyde cellulose hydrazone derivatives and cellulose hydrazino complex decrease the water retention of the paper made from wood pulp, from 91.3% to 76% and 67.5% respectively.

Scanning Electron Microscope

Figs. 3a,b,c for cotton linters and 4a,b,c for wood pulp shows the morphology of the paper before and after applying additives. It is clear that the spaces between the fibres are filled and some of the fibres were covered by these additives.

CONCLUSIONS

Addition of DAC hydrazone derivative or cellulose hydrazino complex increase the strength properties and density of the produced paper if compared with unfilled paper. Addition of DAC hydrazone derivative or cellulose hydrazino complex increase the water retention of the paper produced from cotton linters. On the other hand, these additives decreased the water retention of the paper produced from wood pulp.

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