Consolidation of Paper by some Binders and Evaluating their Efficiency

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Abstract: The influence of addition of some binders such as starch, polyacrylamide and cationic starch in presence of calcium carbonate (as filler) on the properties of the paper made from cotton linters was studied before and after accelerated artificial aging. Starch addition caused the best results before the accelerated artificial aging with the except ion of the retention property of filler but cationic starch addition resulted in the best properties after the accelerated artificial aging. Thermogravimetric analysis of paper sheets was measured. Activation energy and rate constant for each sample were calculated. [Nature and Science 2010;8(8):207-217]. (ISSN: 1545-0740).

Key words: Cotton linter, starch, polyacrylamide, cationic starch**,** accelerated aging**,** thermal gravimetric analysis**.**

1. Introduction:

Additives of hydrophilic binders has bean used in paper making. Their main function is to promote fiber bonding i.e. to increase the number of interfiber bonding and hence paper strength. These substances are usually hydrophilic compounds such as starch, vegetable gums, synthetic hydrophilic and resin emulsion [1]. If improved binders could be found, they would permit the production of papers with higher porosity, better formation and higher strength. Such paper would also possess, in addition to this other properties, namely higher opacity, better compressibility during printing, increased dimensional stability and reduced curl and cockle during humidity changes [2,3].

Starch is an example of popular binders. Starch molecule act as a cementing agent in interfiber bonding and thus increase paper strength [4]. Today, starch is used in wet end application to dry strength, to improve chemical retention, drainage, formation, printability and reduce surface fuzz[5]. The change of hydrophilicity/ hydrophobicity ratio of the starch polymer and paper surface is possible to reduce significantly penetration and print through of many kinds of printing inks by spreading   less than $0.5 g/m^2$ of starch polymer on uncoated paper surface [6].

Cationic starch is one of the oldest of dry strength additives used in papermaking industry and is still the most important, not only because of its competitive price but also as a result of its dry strength and its capacity to retain fines and filler in paper bulk [7].

Thanks to the cationic groups of starch, the anionic and the fines fiber are retained more efficiency leading to lower organic load in white water (with up to 90% reduction in biological oxygen demand compared to non-cationic starch). This is particularly true for papers with high recycled fiber content (like writing and printing paper). Moreover, cationic starches improve the retention of anionic pigment, which enables higher filler levels [8]. Because of their unique charge properties, cationic starch improves the printability of the paper even in ink-jet printing [9]. Addition of 3% cationic starch provoked the highest value of big flocks in sheet samples [10].

Plolyacrylamides are used as binders, retention aids for fibers and to retain pigments on paper fibers. Plolyacrylamides with small amount of acrylic acid in aqueous two-phase copolymerization can increase the paper strength effectively, when it is used as paper strengthing agent [11].

Addition of plolyacrylamides emulsions in decorative base paper manufacture can significantly increase the ash content of the base paper and improve the paper properties such as formation and two sideness [12]. Addition of 3 or 4% cationic starch alone, acts as a retention aid but when added with cationic polyacrylamide, it acts as dry strength [13].

2. Materials and Methods:

Materials

Cotton linters DP (740) and   - cellulose 96% provided by factory 18, Abu Zabil, is used   as raw material for paper making. Corn starch, polyacrylamide and cationic starch are used for paper binders[14].

IR spectra of native starch and cationic starch

IR absorption of the native starch and cationic starch were recorded using an FT/IR 300 Elasco using KBr discs

Paper making:

The pulps were beaten in a Jokro beater at 6% consistency until they reached 50 °SR. 3% starch, polyacrylamide and cationic starch were added during sheet formation by using the sheet former of AB Lorentzen and Wetter (Stockholm, Sweden). After sheet forming the papers were conditioned for 24 hrs. at 50 RH and 20°C.

Sheets were exposed to accelerated artificial aging for 30 hrs, at 90°C and 50 Relative humidity (RH). The sheets before and after accelerated artificial aging were subjected to the following analysis and tests:

Estimation of - cellulose:

The term - cellulose is defined as the part of cellulose which does not dissolve in 17.5 % sodium hydroxide (w/w). The percentage of - cellulose is investigated according to standard method [15].

Retention of fillers in paper:

Retention % = $\dfrac{\text{Weight of ash}}{\text{Weight of filler added}}$ X 100

Where ash was estimated by burning the material in a muffle furnace in a porcelain crucible first at 400 °C for 30 minutes, then at 850 °C for 45 min [15].

Brightness:

Brightness refers to the light reflected from the surface [15].

Breaking length:

The tensile strength was estimated according to the German standard method by means of Karl Frank 468 tester (Weinheim-Birkenau). Breaking length [15] in meter can be obtained from the tensile strength according to equation

Breaking length = $\dfrac{\text{tensile strength (K gm) X length of strip (m)}}{\text{Weight of strip (K gm)}}$

Tearing resistance

Tearing resistance is the average force in grams required to tear the sheet clamped in the tester [15].

Thermal analysis of paper sheets:

Thermogravimetric analysis (TGA) of paper sheets was measured on a PERKIN ELMER (Thermogravimetric analyzer TGA). A linear heating rate of 10°C / minute was carried out in presence of air.

3. Result and Discussion:

IR Spectra:

Figure (1a & 1b) showed the spectra of native starch and cationic starch respectively. Starch is characterized by two strong and broad absorption peaks occuring at 3000-3900 cm^{-1}(O-H) and at 1000-1250 cm^{-1} (C-O-C). The broad absorption peaks at 3000-3900 cm^{-1} may be contributed by the hydroxyl groups and absorbed moisture through the formation of hydrogen bonding between the group and water.

From figure (1b), it can be seen that the degree of absorbance of cationic starch has changed. The presence of the band at 1742 cm^{-1}indicated the formation of carbonyl group, also the presence of the band at 1647 cm^{-1} is due to presence of C = C, C = N and C-O group in the molecule. The bands at 2856.06 cm^{-1} and 2924.5 cm^{-1} are due to presence of aliphatic – CH$_3$ and – CH$_2$. The presence of the band at 3429 cm^{-1} confirms the formation of –NH and its broadness may indicate the presence of hydrogen bonding through all the molecule.

Measurements of mechanical and optical properties of the produced paper sheets before and after aging.

3% native starch, polyacrylamide and cationic starch (D.S 0.05) were added to the beaten cotton linter (SR º45) during sheet formation. Table (1) shows that all the properties of each sample were affected by accelerated aging.

It is clear from table (1) and figures (2-4) that the native starch has the best strength properties before accelerated aging except retention of filler but has the worth properties after aging. The adhesive qualities of starch for paper making are due to its content of polar hydroxyl group. These groups have a mutual attack for the groups in the pulp and fiber, and set up a fiber-to-fiber bonding and as result, the strength of the sheet is increased before aging[16]. After aging, the starch decomposes and affects on the paper fibers.

It was found from table (1) and figures (2-4) than the cationic starch has the best properties after accelerated aging. Since the cationic starch when added in the wet end, it forms bridges between cellulose fibers. This results in a strong fiber network and so, the paper sheets have the ability to resist the aging [17].

Cationic starch due to presence of positive groups absorbed easily by cellulose fibers (due to presence of hydroxyl groups). So, the higher amount of cationic starch was retained on the cellulose fibers and so on, the additives such as calcium carbonate may be retained on the cellulose fibers when carried by cationic starch solution [18].

Thermal gravimetric analysis (TGA):

TGA is a technique for measuring the weight

loss of material during heating. TGA can give information on the relative thermal stability of cellulose modification and on reactions that occur during heating [19].

Thermogravimetric curves of the studied samples are shown in Figures (5a-5e). In Figures (5a-5e), the curve of each sample can be classified into three distinct zones. An initial slight loss in weight at about 100ºC due to the evaporation of the moisture content in the sample; then a sharp break, occurred in each thermogram, indicating the onset of a decomposition process involving a rapid loss in weight. This break ends by a slight curvature that may be due to the formation and evaporation of some volatile products [20]. Finally, the decomposition rate decreased gradually reaching a constant weight representing carbonization and evaporation of the remainder. T_1 represents the temperature, at which the main decomposition reaction starts, T_2 represents the decomposition temperature.

Table (2) summarizes the initial and main temperatures of the active decomposition reaction of the examined paper samples, represented by T_1 and T_2. From these Figures and table (2) we can note that all samples start to decompose at a temperature ranging from 324-340 ºC. Also, the decomposition temperature T_2 of these samples lies between 362 ºC and 410 ºC.

Calculation of the activation energy:

Assuming the first order reaction,

Where: $-dc/dt = kc$

c is the concentration of the reactant, (t) is the time and (k) is the rate constant. If the concentration is replaced by the observed weight W_t, then

$d (W_o-W_t) / dt = k (W_o- (W_o-W_t)) = k W_t$

Where:

W_o is the original weight of the sample and W_t is the weight at time (t). By integration the above equation.

$-Ln (W_o- (W_o-W_t)) = -Ln W_t = kt + constant$

But at $t = 0$, $W_o-W_t = 0$, hence constant $= -Ln W_o$.

Therefore $Ln W_o/W_t = kt$. If the amount of ash at the end of the reaction is taking into consideration, then

$\log W_o-W / W_t-W = kt$

Where:

W is the weight at the end of the reaction.

A plot $Ln (W_o-W) / (W_t-W)$ against (t) produced a straight line indicating that the degradation follows a first order reaction Figures (6a-6e).

Arrhenius (21) pointed out that since the Van´t Hoff equation for the temperature coefficient of the equilibrium constant (Kc) of a reaction is

$d \log Kc / dT = E / RT^2$

Whereas the low of mass action related the equilibrium constant to a ratio of rate constant (i.e.

$Kc = (K$ forward reaction $/ K$ backward reaction), a reasonable equation for the variation of the rate constant with the temperature is given by,

$d \log K / dT = E_a / RT^2$

By integration $Ln K = -E_a / RT + LnA$.

Where:

(A) is a constant, thus, a plot of log K against the reciprocal of the temperature is a straight line with slop equal to $(-E_a/2.303R)$, where E_a is the activation energy, R is the gas constant.

Table (3) shows the activation energy values of the examined samples and the rate constant for each sample. It is clear that sample of blank (cotton linter) are less thermally stable than the other samples. The activation energy of samples can be arranged as follows: (cotton linter containing $CaCO_3$ > cotton linter containing $CaCO_3$ and starch > cotton linter containing $CaCO_3$ and polyacrylamide > cotton linter containing $CaCO_3$ and cationic starch).

Although cationic starch has lower activation enegy, it was stable to accelerated aging as shown in Table (1) and Figure(4), compared to native starch and polyacrylamide. The lower activation energy of cationic starch may be attributed to its an ionic molecule and lower molecular weight [22,23].

4. Conclusion:

Before accelerated artificial aging, native starch has the best properties than polyacrylamide, cationic starch except retention of filler. After accelerated artificial aging, cationic starch has the best properties than polyacrylamide, native starch. Activation enegy of samples will be in this order cotton linter containing calcium carbonate > cotton linter containing calcium carbonate and starch > cotton linter containing calcium carbonate and polyacrylamide > cotton linter containing calcium carbonate and cationic starch.

Table (1): Physical and mechanical properties of sample before and after accelerated aging.

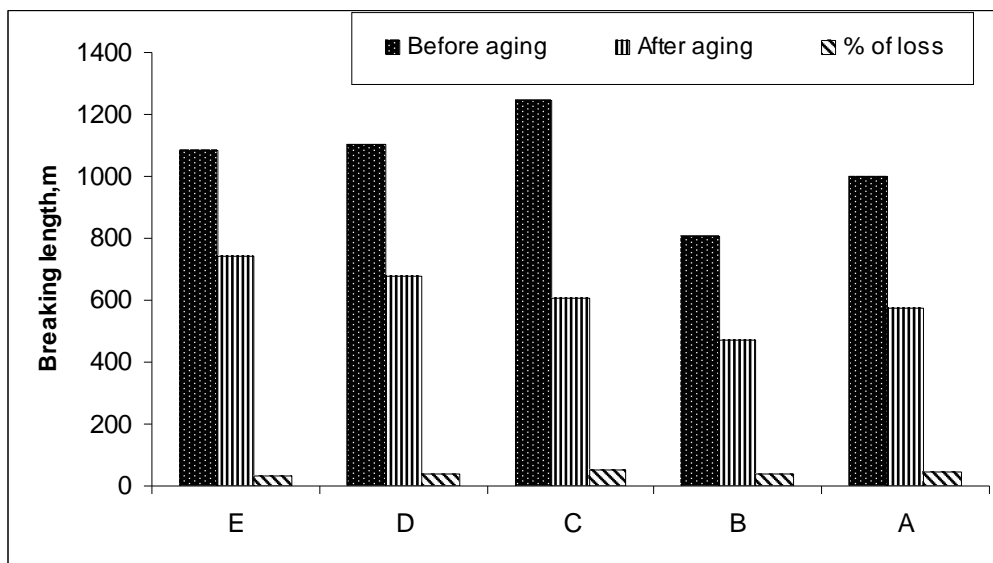| Characterizations		Samples				
		Coton linter (Blank)	Coton linter containing 10% $CaCO_3$	Coton linter containing 10% $CaCO_3$ and 3% Starch	Coton linter containing 10% $CaCO_3$ and 3%Polyacrylamide	Coton linter containing 10% $CaCO_3$ and 3% Cationic starch
pH	B.A.	6.5	6.5	6.5	6.5	6.5
	A.A.	5.5	5.5	5.2	5.5	5.8
	% of loss	15.4	15.4	20	15.4	10.8
- cellulose %	B.A.	96	96	96	96	96
	A.A.	77.4	80.9	44.5	85	90
	% of loss	19.4	15.7	19.3	11.5	6.3
Brightness %	B.A.	77.9	78.8	77.7	76.6	74.1
	A.A.	74.3	75.9	74.3	73	72.6
	% of loss	4.6	3.6	3.9	4.6	2
Retention %	B.A.	-----	13	22.8	28.1	40.9
	A.A.	------	5.1	11.6	24.5	36.1
	% of loss	-----	60.8	49.1	12.8	11.7
Breaking length (m)	B.A.	998.3	809.5	1242.3	1105.6	1080.8
	A.A.	574.2	473.8	603.9	680.3	740
	% of loss	42.5	41.5	51.4	38.5	31.5
Tearing resistance	B.A.	165	135	200	182	177
	A.A.	100	86	110	120	123
	% of loss	39.4	36.6	45	34	30.5

Where B.A. is Before Aging, A.A. is After Aging

Table (2): Thermal gravimetric analysis of the paper obtained from differently treated pulps.

Samples	Temperature of active pyrolysis ºC	
	T_1	T_2
Coton linter (Blank)	329	396
Coton linter containing 10% $CaCO_3$	330	364
Coton linter containing 10% $CaCO_3$ and 3% Starch	332	385
Coton linter containing 10% $CaCO_3$ and 3%Polyacrylamide	336	386
Coton linter containing 10% $CaCO_3$ and 3% Cationic starch	335	395

Table (3): Activation energy of the paper obtained from differently treated pulps.

Samples	$K(min^{-1})$	$E_a(Cal)$
Coton linter (Blank)	0.7451	128.7
Coton linter containing 10% $CaCO_3$	0.470	396.0
Coton linter containing 10% $CaCO_3$ and 3% Starch	0.480	378.7
Coton linter containing 10% $CaCO_3$ and 3%Polyacrylamide	0.634	227.0
Coton linter containing 10% $CaCO_3$ and 3% Cationic starch	0.710	182.6
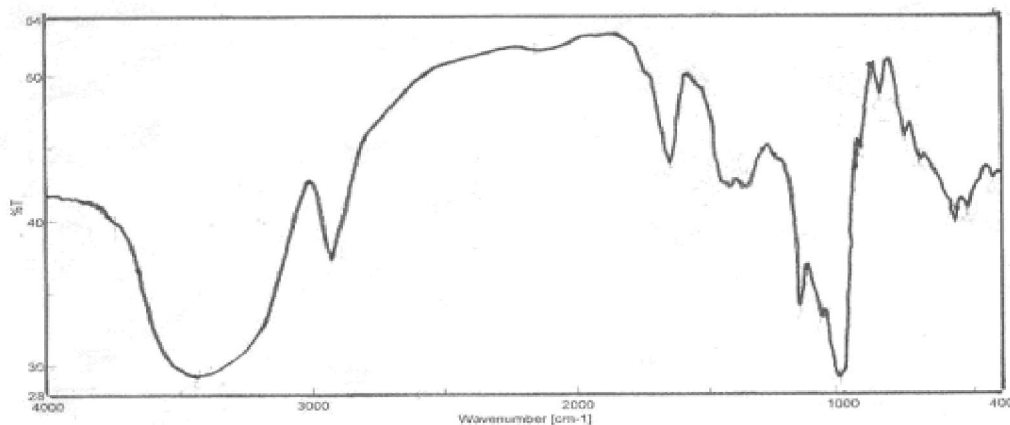
Fig. (1a)IR spectra of native starch
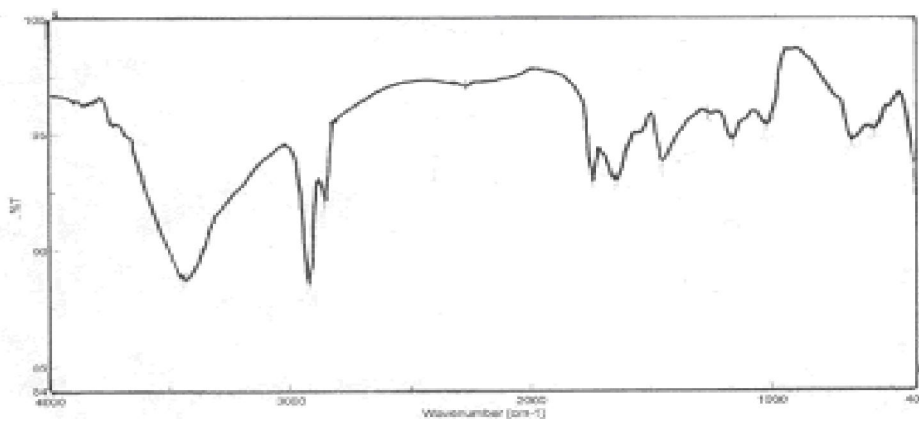
Fig. (1b) IR spectra of cationic starch
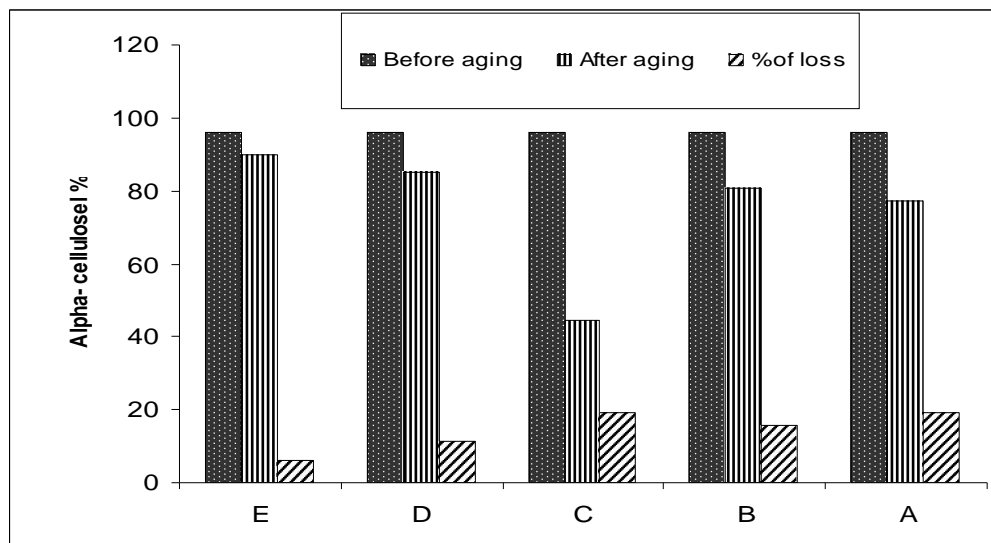
Fig .(2): Alpha cellulose before and after aging .

A. Cotton linter (blank)
B. Cotton linter containing 10% CaCO3
C. Cotton linter containing 10% $CaCO_3$ and 3% starch
D. Cotton linter containing10% $CaCO_3$ and 3% polyacrylamide
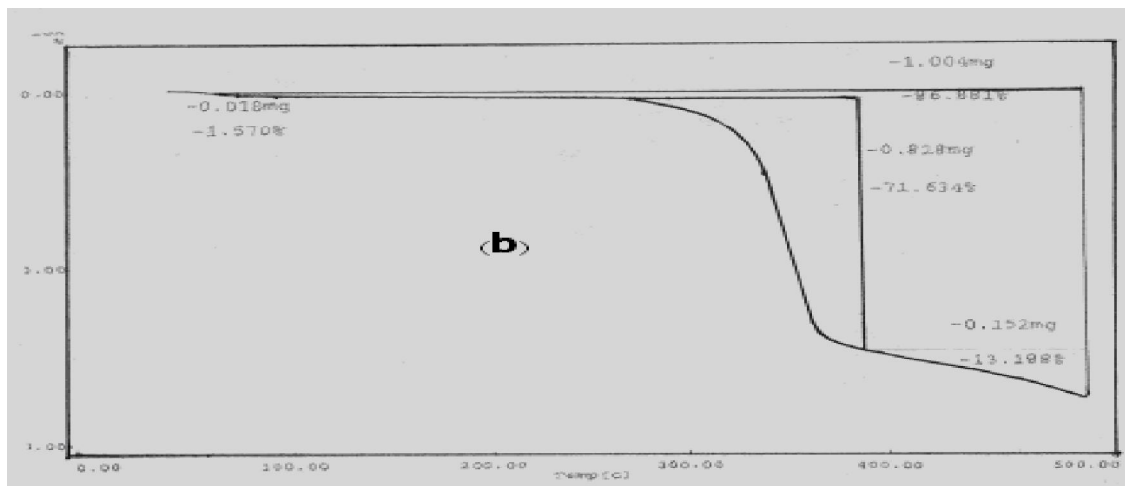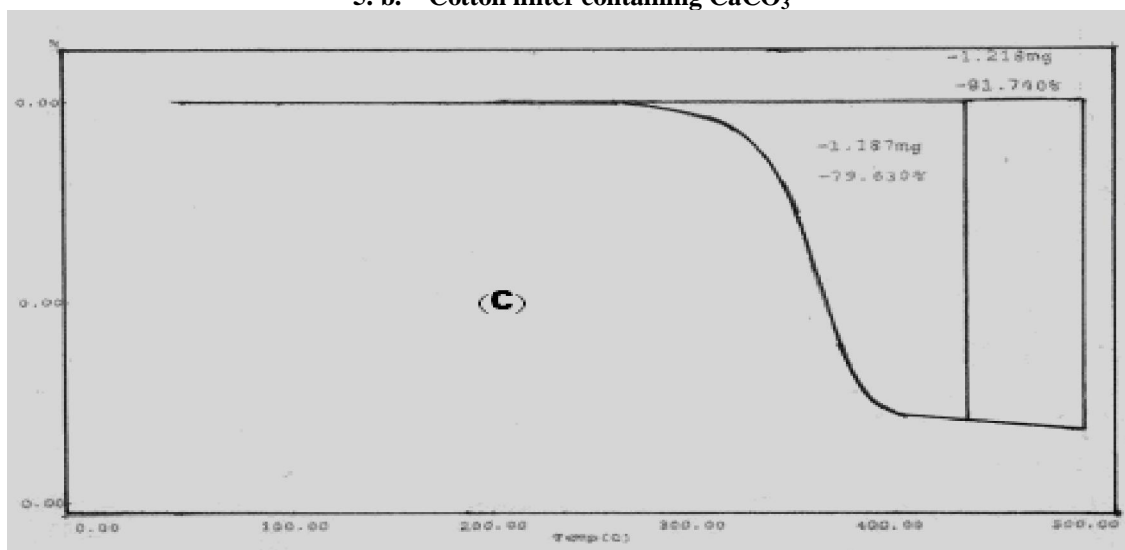E. Cotton linter containing 10% $CaCO_3$ and 3% cationic starch

Fig. (3): Brightness before and after aging.

A. Cotton linter (blank)
B. Cotton linter containing 10% CaCO3
C. Cotton linter containing 10% $CaCO_3$ and 3% starch
D. Cotton linter containing10% $CaCO_3$ and 3% polyacrylamide
E. Cotton linter containing 10% $CaCO_3$ and 3% cationic starch

Fig. (4): Breaking length before and after aging.

A.Cotton linter (blank)

B. Cotton linter containing 10% CaCO3

C. Cotton linter containing 10%CaCO$_3$ and 3%starch

D. Cotton linter containing10% CaCO$_3$ and 3%polyacrylamide

E.Cotton linter containing 10%CaCO$_3$ and3% cationic starch

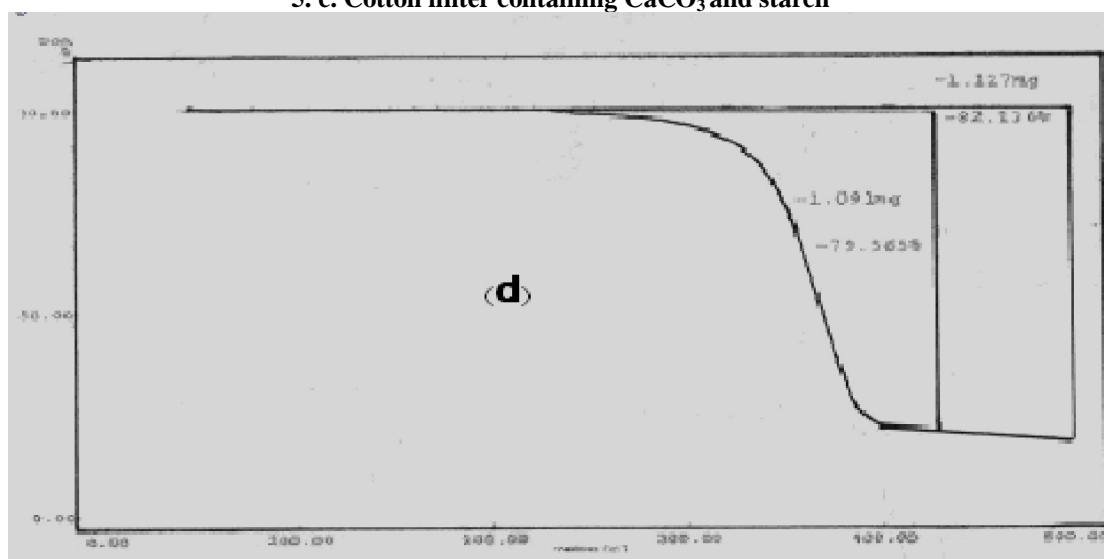**Fig. (5): TGA curve of the paper obtained from Different samples**
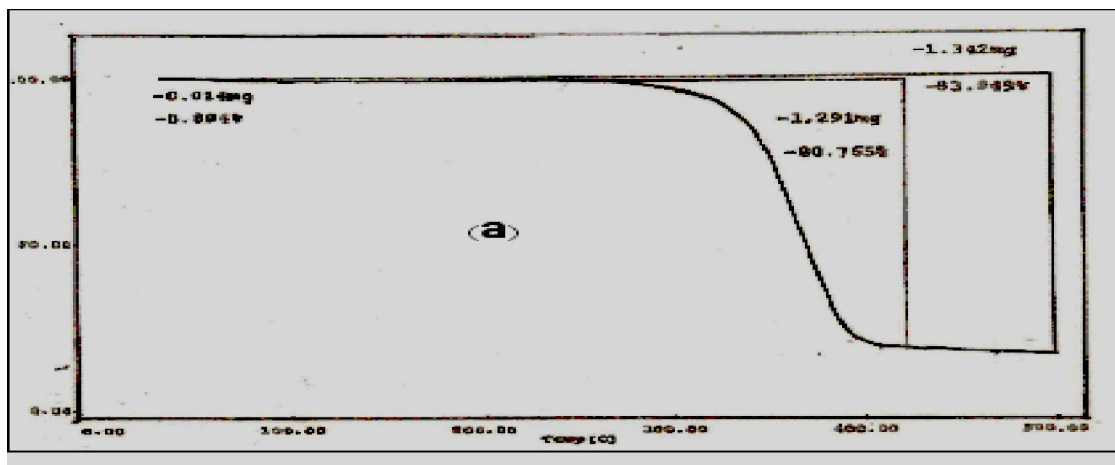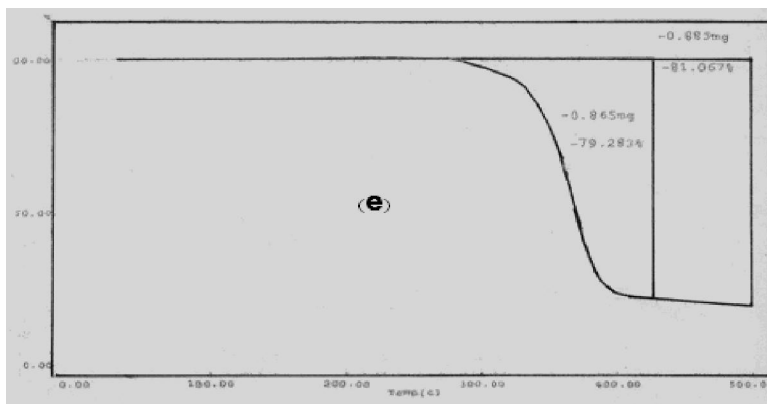

5. a. Cotton linter.

5. b.   Cotton linter containing CaCO$_3$

5. c. Cotton linter containing CaCO$_3$ and starch

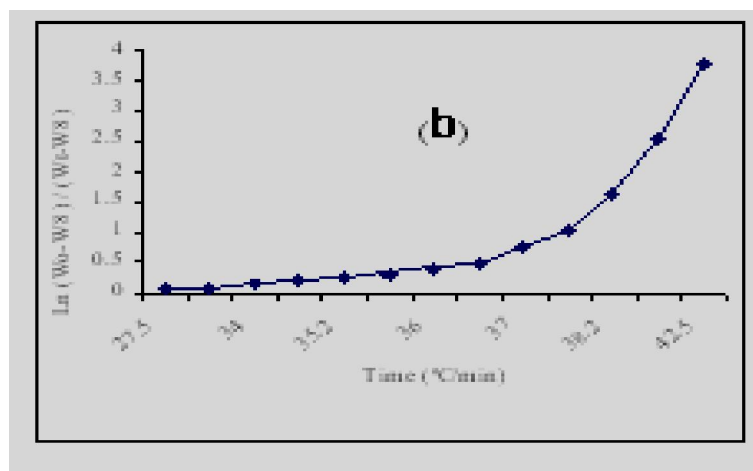**5. d. Cotton linter containing CaCO$_3$ and polyacrylamide**

5. e. Cotton linter containing CaCO$_3$ and cationic starch

Figure (6)   Plot of Ln [(W$_o$-W)] / (W$_t$-W) against time (t) of the paper obtained from differently treated samples.
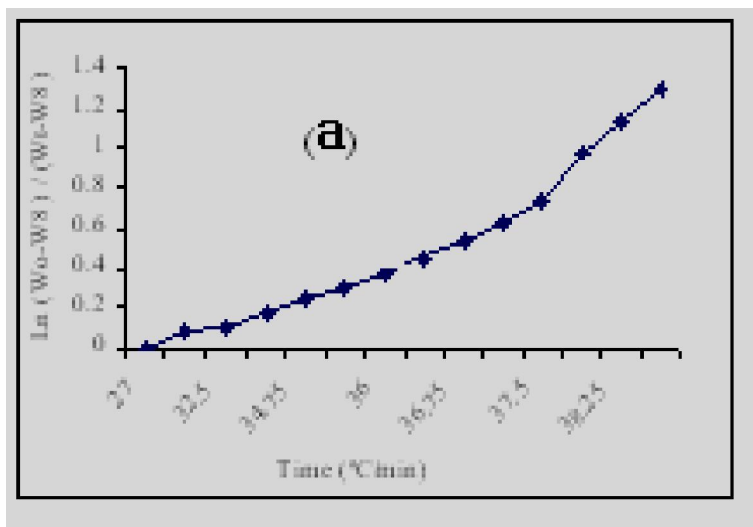
6. a.   Cotton linter,

6. b. Cotton linter containing CaCO$_3$,

6.   c. Cotton linter containing CaCO₃ and starch,

6. d. Cotton linter containing CaCO₃ and polyacrylamide,
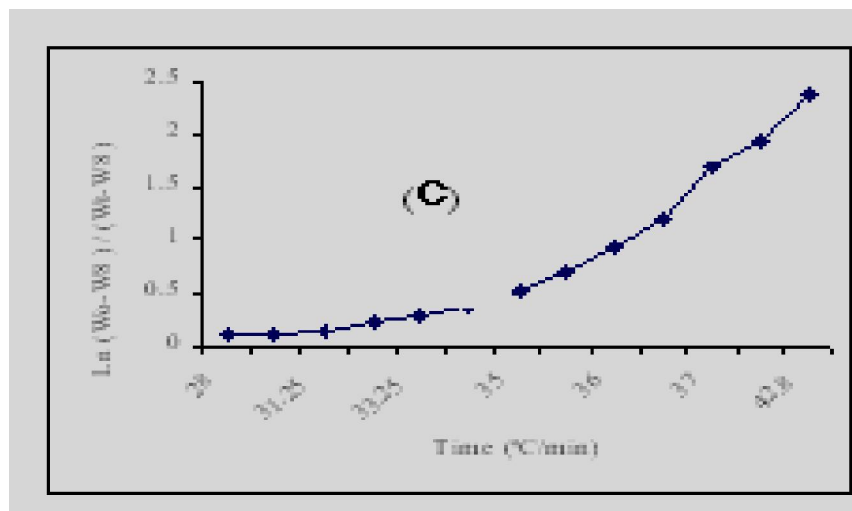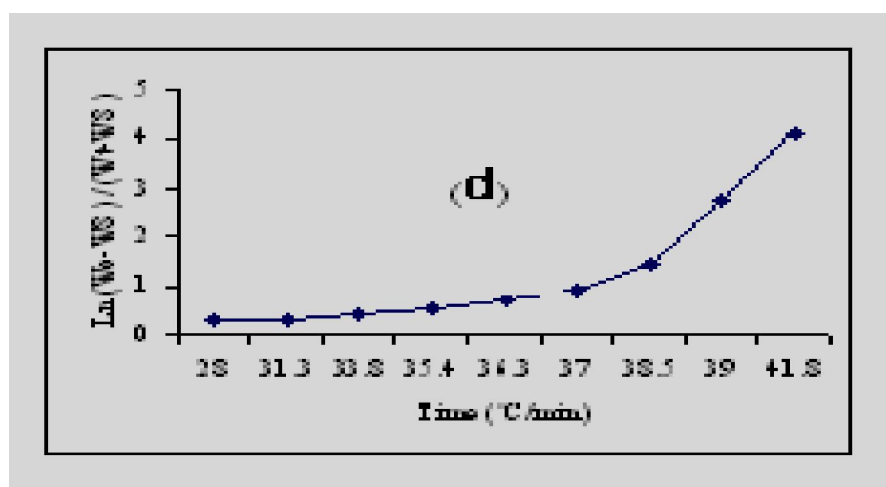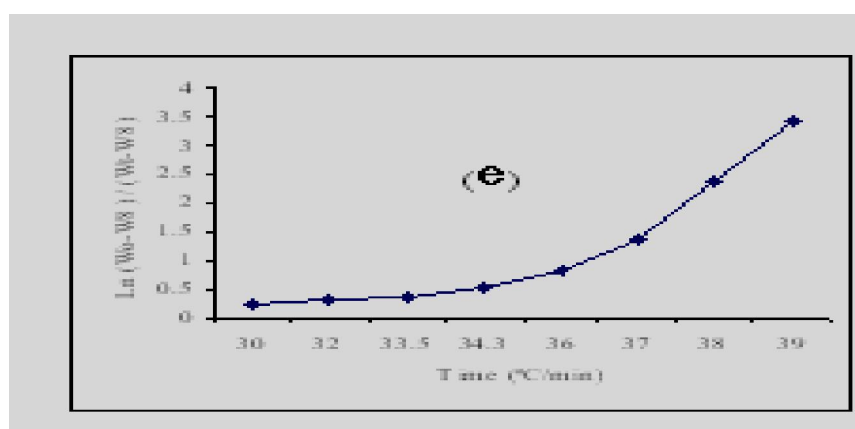

6. e. Cotton linter containing CaCO₃ and cationic starch

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