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Thermal behaviour of starch and oxidized starch

Aisha A.A. Soliman*, Nabila A. El-Shinnawy, Fardous Mobarak

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

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Abstract

Thermal gravimetric analysis, and differential thermal behaviour of unoxidized and oxidized starch were studied. Degradation was found to be first order in sample weight reaction. The activation energy values and the rate constants were calculated from the kinetic of weight loss. Unoxidized starch was found to be less stable than oxidized starch and the stability of the samples was arranged in the order of oxidized starch with 8 g active Cl/l > 4 g active Cl/l > 6 g active Cl/l > unoxidized starch. Volatilization and activation energies of oxidized starch were higher than unoxidized starch. DTA of unoxidized and oxidized starch show that the degradation is exothermic. © 1997 Elsevier Science B.V.

Keywords: Thermal; Gravimetric analysis; Starch

1. Introduction

Thermal gravimetric analysis (TGA) can be employed to determine temperatures and rates of pyrolysis while differential thermal analysis (DTA) curves show the endothermic or exothermic nature of the reactions that accompany pyrolysis and combustion. Such information is very valuable in assessing the chemistry of the thermal decomposition of different products. Activation energies (derived from the Arrhenius equation) and volatilization rates for cellulose and cellulosic materials were determined in 1956 by Madorsky et al. [1]. Many workers [2,3] noted first-order kinetic relationships for the pyrolysis. The thermogravimetric analysis of hemicellulose obtained from different agricultural residues [4] was investigated. Holo- and hemicellulose obtained from agricultural sources are different, mainly in their chemical composition, which certainly affect their thermal behaviour [4]. The principles of major thermoanalytical techniques are reviewed along with factors affecting the results [5].

The aim of the present work is to study the thermal behaviour of starch and oxidized starch by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques and also to calculate the kinetic energy for the degradation reaction and the type of the reaction.

2. Experimental

Maize starch was oxidized with sodium hypochlorite solution (NaOCl) of known concentrations by adjusting the pH at 7 and using a liquor ratio of 10 : 1. The reaction was allowed to proceed for 2 h at 25°C with stirring. The sample was then filtered,

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*Corresponding author.

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washed thoroughly with distilled water and dried at 60°C in an oven [6].

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA), were carried out on starch and oxidized starches using a Perkin–Elmer Thermogravimetric analyzer TGA 7. The heating rate was adjusted to 10 K min^{-1}. Heating was continued to a constant weight in a stream of nitrogen.

3. Results and discussion

3.1. *Thermal gravimetric analysis*

Figs. 1–4 show the TGA of unoxidized maize starch and starch oxidized by 4, 6 and 8 active Cl/l respectively. The figures show the percentage loss in weight as a function of temperature. Three distinct zones can be seen:

a – Represents the evaporation of water and other easily volatile materials below 150°C.
b – The main degradation zone.
c – The propagation reaction.

Table 1 gives the temperature of pyrolysis which are represented in the figures as T_1, T_2 and T_3. T_1 is the temperature of initial pyrolysis, T_2 is the maximum temperature of pyrolysis and T_3 is the temperature of final pyrolysis.

Table 1 shows that non oxidized starch has a higher initial and maximum temperature than starch oxidized by 4, 6, and 8 g active Cl/l.

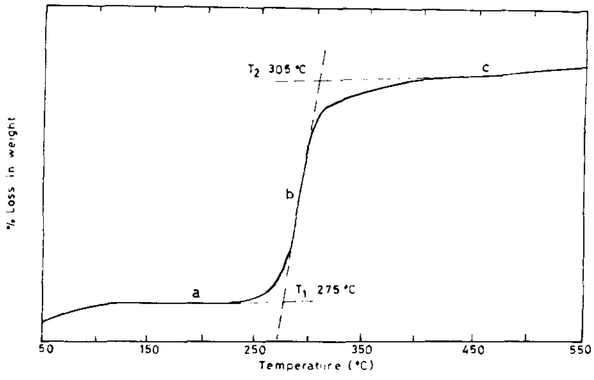

Fig. 1. T.G.A. of unoxidized maize starch.

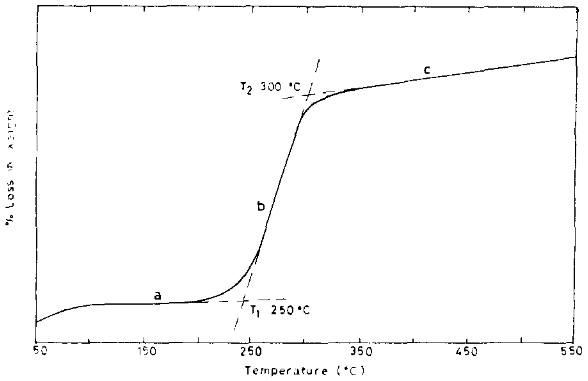

Fig. 2. T.G.A. of oxidized starch by 4 g active Cl/l.

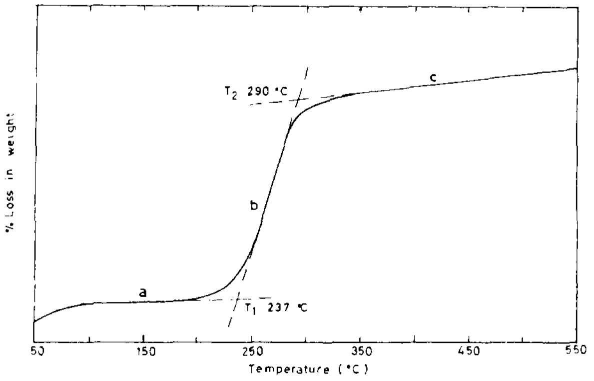

Fig. 3. T.G.A. of oxidized starch by 6 g active Cl/l.

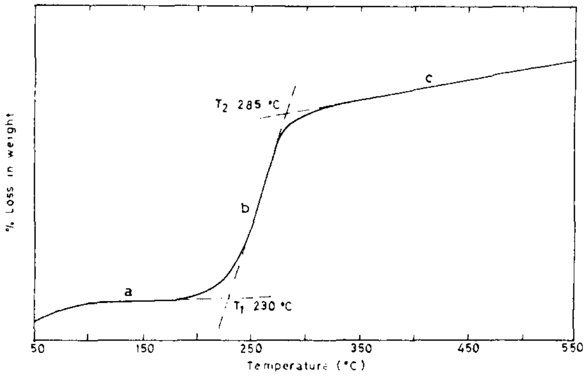

Fig. 4. T.G.A. of oxidized starch by 8 g active Cl/l.

Percent volatilization at 250, 350, 550°C is used to indicate the degradation rate and defined as a percent ratio of weight loss at specific temperature divided by the initial weight.

Table 1
Thermogravimetric analysis of starch and oxidized starch

Sample	Temperature of active pyrolysis (°C)			Volatilization (%)		
	Initial temperature T_1	Maximum temperature T_2	Final temperature T_3	250°C	350°C	450°C
Insoluble unoxidized starch	275	305	—	9	78	84
Starch oxidized with 4 g active Cl/l	250	300	—	16	80	84
Starch oxidized with 6 g active Cl/l	237	290	—	19	76	80
Starch oxidized with 8 g active Cl/l	230	285	—	27	75	82

% volatilization = (weight loss at a specific temperature/initial weight) × 100

Percent volatilization of oxidized starch with 8 g active Cl/l is higher than that of the oxidized starch with 6, 4 g active Cl/l and the unoxidized starch at temperature 250°C.

4. Calculation of activation energy

The data obtained by TGA were analyzed by differential method used by Tang [7]. Assuming a first-order reaction for thermal degradation, the reaction rate constant, k, and the activation energy, E, in the main decomposition temperature region (200–430°C) were calculated from the relation:

$$-\mathrm{d}c/\mathrm{d}t = kc$$

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

$$\mathrm{d}(W_0 - W_t)/\mathrm{d}t = k(W_0 - W_t) = kW_t$$

where W_0 is the original weight before heating, W_t, the weight after heating for a time t, then,

$$-\ln(W_0 - (W_0 - W_t)) = -\ln W_t = kt + \text{constant}$$

but, at t=0, $(W_0 - W_t)$=0, the constant is equal to $-\ln W_0$, and therefore,

$$\ln(W_0/W_t) = kt.$$

If the amount of ash at the end of heating is considered, then,

$$\ln(W_0 - W_\infty) = kt,$$

where W_∞ is the weight at the end of heating (ash). Plots of $\ln(W_0 - W_\infty)/(W_t - W_\infty)$ against t gave straight lines.

Figs. 5–8 indicate that the degradation follows a first-order reaction [8]. The activation energy was calculated by applying the Arrhenius equation [9] where,

$$\ln k = -E/RT$$

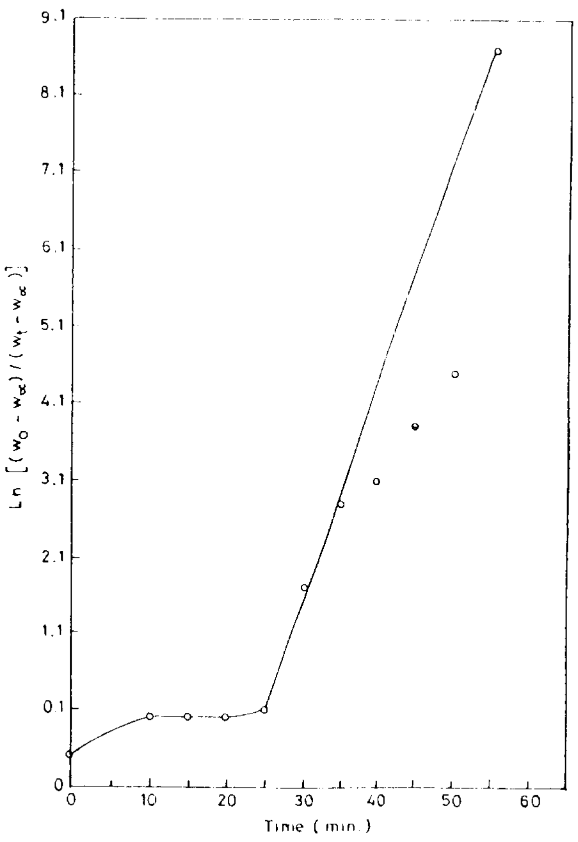

Fig. 5. Plots of $\ln[(W_0-W_\infty)/(W_t-W_\infty)]$ against time of starch raw material (non-modified).

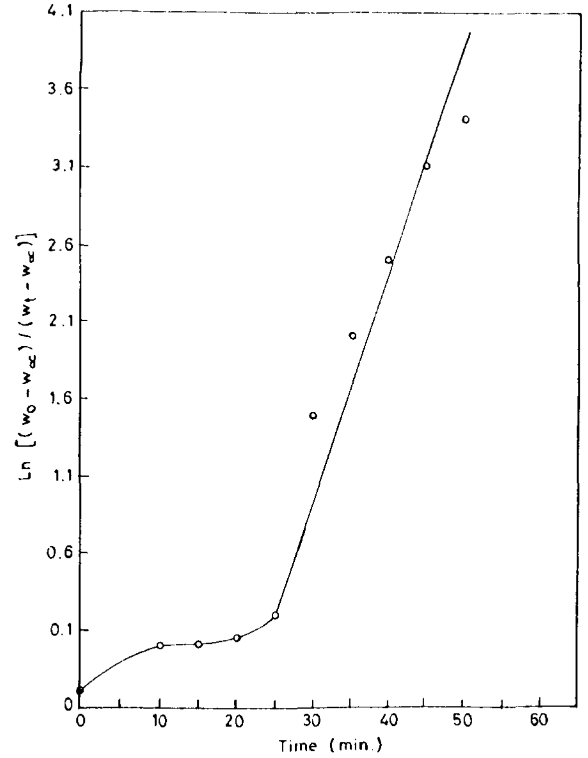

Fig. 6. Plots of $\ln[(W_o - W_\infty)/(W_t - W_\infty)]$ against time of oxidized starch by 4 g active Cl/l.

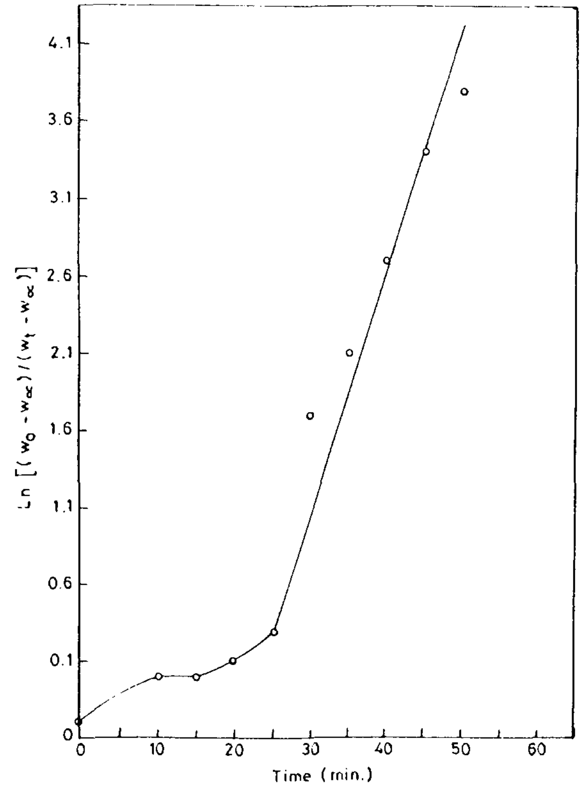

Fig. 7. Plots of $\ln[(W_o - W_\infty)/(W_t - W_\infty)]$ against time of oxidized starch by 6 g active Cl/l.

that is,

$$-E = \ln kRT$$

where, E is the activation energy, R the gas constant and T the absolute temperature.

Table 2 shows the values of the reaction rate constant, k, and the activation energy, E, of the unoxidized maize starch, starch oxidized by 4 g active Cl/l, 6 g active Cl/l and 8 g active Cl/l.

From Table 2 it is clear that activation energy of oxidized starch by 8 g active Cl/l is greater than 6 and 4 g active Cl/l, than the unoxidized starch, which shows that the unoxidized starch is less stable than oxidized starch and the stability of the samples was arranged in the order of oxidized starch by 8 g active Cl/l > 4 g active Cl/l > 6 g active Cl/l > unoxidized starch.

Table 2
Reaction rate constant (k) and activation energy (E) and the carboxyl content for unoxidized starch, oxidized starch with 4 g active Cl/l, by 6 g active Cl/l and 8 g active Cl/l

Sample	k (min^{-1})	E (Kj mol^{-1})	Carboxyl content m.eq. CO_2H/100 g starch
Insoluble unoxidized starch	0.283	1.1445	2.8
Starch oxidized with 4 g active Cl/l	0.145	2.0198	5.8
Starch oxidized with 6 g active Cl/l	0.155	1.7636	6.4
Starch oxidized with 8 g active Cl/l	0.136	2.0868	6.8

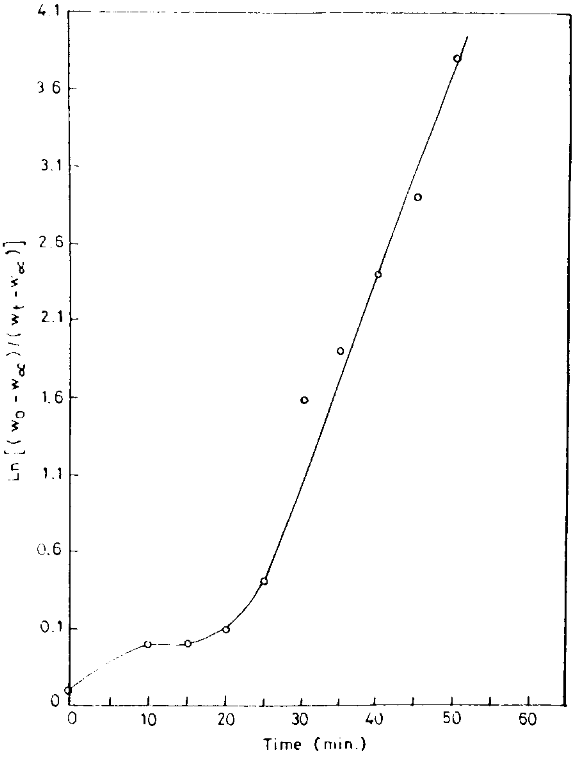

Fig. 8. Plots of $\ln[(W_0 - W_\infty)/(W_t - W_\infty)]$ against time of oxidized starch by 8 g active Cl/l.

The changes in the activation energies for the main degradation step and stability of starch and oxidized starch is due to the change of carboxyl content of oxidized starch.

Fig. 9 illustrates the differential thermal curves (DTA) of unoxidized starch and oxidized starch with 4, 6 and 8 g active Cl/l respectively. It shows that an exothermic reaction is present. In unoxidized starch a peak at 287°C represents the main degradation step. On the other hand, an exothermic peak occurred in oxidized starch by 4, 6 and 8 g active Cl/l at 279, 271 and 267°C, respectively. It should be noted that, the magnitude of this exothermic are much higher and sharper in case of unoxidized starch than oxidized starch. In case of oxidized starch, interference by the oxidation reaction produces a broad peak, which, affects the magnitude of the exothermic [10].

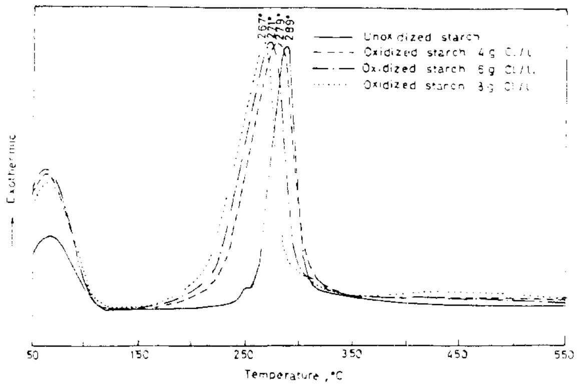

Fig. 9. D.T.A. comparison of unoxidized and oxidized starch.

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