

Thermogravimetric Analysis of Some Chemically Modified Celluloses

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Synopsis

Thermal degradation of carboxymethylcellulose, cellulose acetate, grafted wood pulp, and viscose rayon have been studied using thermogravimetric analysis and differential thermal analysis. The values of rate constant K and the activation energy E were calculated from the kinetic of weight loss using the theory of the first-order reaction. The activation energy of grafted cellulose and viscose rayon was $>$ cellulose acetate $>$ carboxymethylcellulose.

INTRODUCTION

Considerable effort has been expended in the study of thermal decomposition of cellulosic materials, to elucidate the order of reaction and also to estimate the activation energy and the rate of decomposition.¹ Various investigations of cellulose pyrolysis include isothermal studies and dynamic thermogravimetric analysis in different oxidizing and inert atmospheres by many authors.²⁻⁵ Several workers^{2,4,6} noted first-order kinetic relations that may signify that rate control in the systems studied could be associated with transport processes.

The thermogravimetric analysis of celluloses obtained from different sources was investigated by Sefain and El-Kalyoubi⁷ and the same authors⁸ reported thermal behavior of helo- and hemicelluloses obtained from agricultural sources. El-Shinnawy⁹ studied thermogravimetric and differential thermal analysis of carbamoylethylated and cyanoethylated wood pulp.

The aim of the present work is to study the thermal behavior of some chemically modified cellulose samples using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques.

EXPERIMENTAL

Materials

Four chemically modified cellulose samples were used in this study:

1. Carboxymethylcellulose (CMC; the sodium salt), BDH grade, high viscosity of 1500 ± 400 cp for the 1% aqueous solution at 20°C with a DS of 0.7–0.8.
2. Pure cellulose triacetate, provided by AG, Bucks SG (Switzerland), with combined acetic acid of 62.3%.
3. Grafted cellulose 16.8% grafting. The polymerization reaction was carried out by adding 1 g freshly distilled acrylonitrile to 30 ml of 0.01 mol

ceric ammonium nitrate solution containing 1% concentrated nitric acid; then 1 g wood pulp was immediately introduced to the reaction flask, the reaction temperature was 40°C, and the reaction time was 2 h. The grafting percentage was determined from the nitrogen content¹⁰ of the grafted sample.

4. Viscose rayon (as a regenerated cellulose), provided from Esco Co. for Rayon Manufacture (Bahteem, Cairo); samples were cleaned with warm water, then with a mixture of sodium hydroxide and sodium sulfide solutions (desulfurization), washed with water, and then air dried.

Thermogravimetric Measurement

Thermal gravimetric analysis and differential thermal analysis were performed using automatic thermobalance of type NETZSCH Gerätebau GmbH Selb (Bestell-Nr. 348 472C). The furnace was programmed to increase the temperature by 5°C/min, and the heat was continued until a constant weight was attained in a constant stream of air.

RESULTS AND DISCUSSION

Thermal Gravimetric Analysis

Thermogravimetric curves of the four studied samples are shown in Figures 1 through 4. The curve of each sample can be classified into three distinct zones. An initial slight loss in weight due to the evaporation of water, then a rather sharp break, occurred in each of thermograms, 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.¹¹ Finally, the decomposition rate decreased, gradually reaching a constant weight representing carbonization of the remainder. The T_1 represents the temperature at which the main decomposition reaction starts. To measure the thermal stability and decomposition temperature of each sample, straight lines were drawn before and after the initial sharp break in the curves; the intersect of these two lines (T_2) represents the decomposition temperature.

From the four figures we note that CMC starts to decompose at 265°C, but grafted cellulose, viscose rayon, and cellulose acetate start to decompose at 285, 305, and 325°C, respectively. Also, the decomposition temperature of CMC is much lower than that for the other samples, indicating its lower thermal stability. Table I summarizes the initial and main temperatures of the active decomposition reaction, represented by T_1 and T_2 .

The decomposition reaction of viscose rayon was accomplished by two distinct steps that occurred at 345 and 435°C; this behavior may be attributed to softening and then volatilization of the sample.

Calculation of the Activation Energy

Kinetic parameters for decomposition were determined using the procedure described by Tang,¹² which assumes a first-order reaction where the

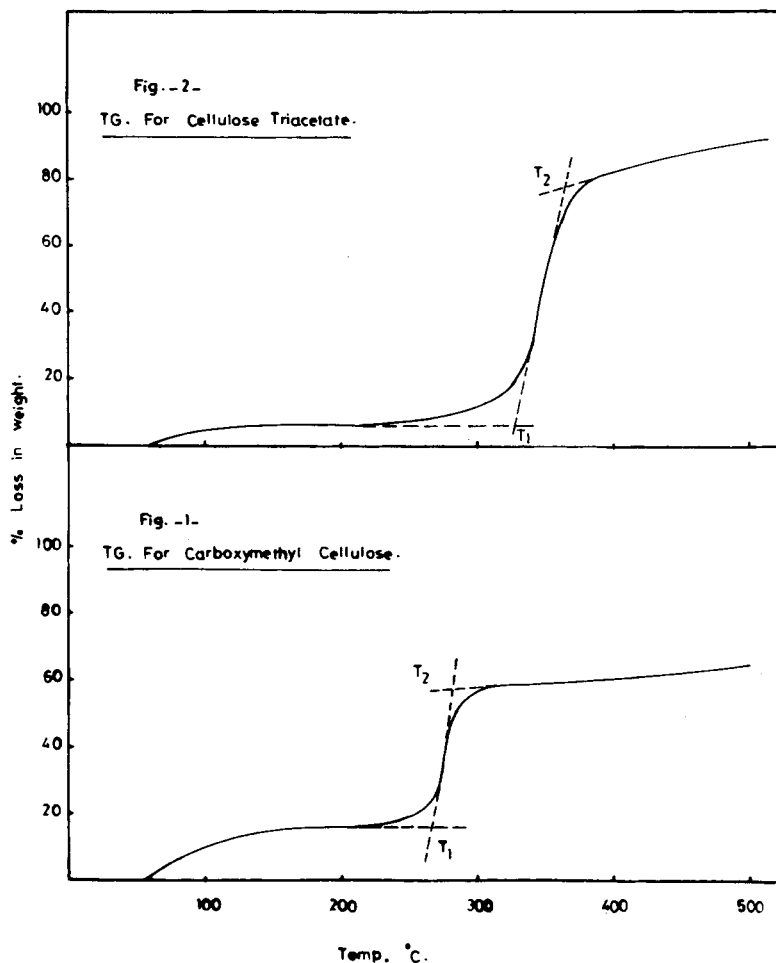


Fig. 1. TG for carboxymethyl cellulose and Fig. 2. TG for cellulose triacetate.

rate of weight percentage loss with time was evaluated as $(dw/dT)(dT/dt)$ and the rate constant K was determined from the expression

$$\frac{dw}{dt} = K(w_f - w_t)$$

where w_f is the final percentage loss, w_t is the weight percentage loss at time t , and K is the rate constant. The activation energy was calculated by applying the Arrhenius equation.¹³ The kinetic parameters are given in Table II.

The high value of E for grafted cellulose and viscose rayon could be due to the complexity of the reaction during the initial weight loss break; the lower value of E for cellulose acetate could be due to the difference in the mechanism of thermal degradation. In the case of CMC, active pyrolysis

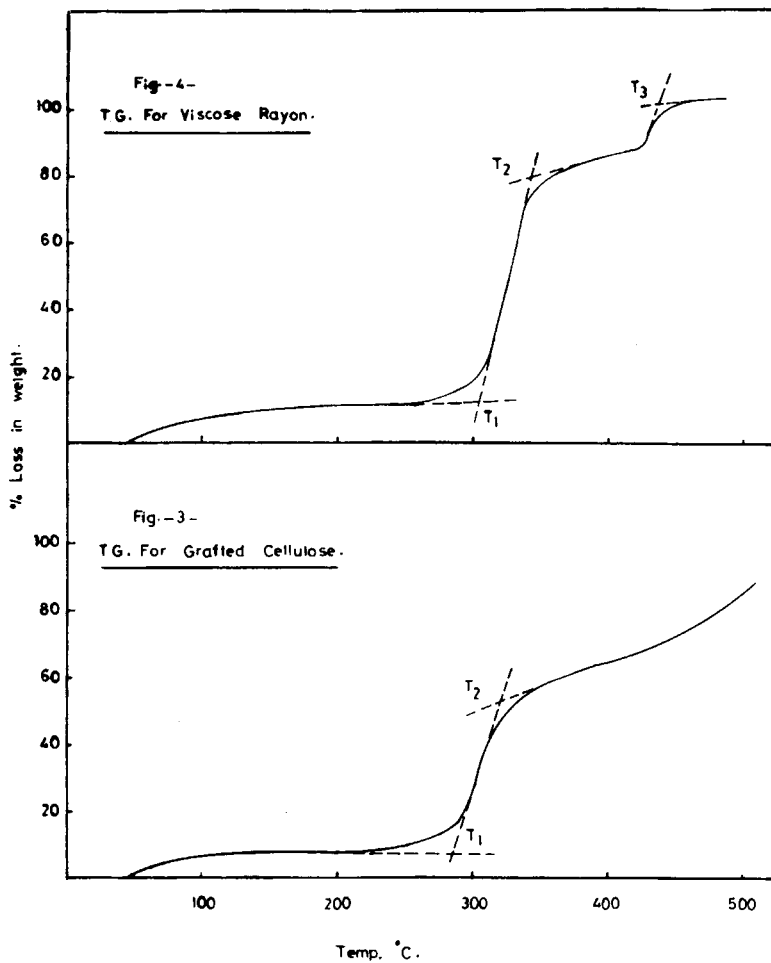


Fig. 3. TG for grafted cellulose and Fig. 4. TG for viscose rayon.

Table I

Sample	T_1 (°C)	T_2 (°C)
Carboxymethylcellulose	265	280
Cellulose acetate	327	358
Grafted cellulose	285	320
Viscose rayon	305	345

Table II

Sample	Rate constant K (min^{-1})	Activation energy E (kJ/mol)
CMC	0.104	26.86
Cellulose acetate	0.174	36.38
Grafted cellulose	0.047	75.22
Viscose rayon	0.045	74.53

takes place at a low temperature due to its lower stability; consequently, it decomposes more easily and rapidly and a low energy will be needed to decompose it. The difference in the activation energy of the samples is due to the difference in their structures, molecular weights, and chemical composition.

Differential Thermal Analysis

Figures 5 through 8 show the DTA curves of the four samples studied. The endothermic nadir around 100°C is due to the evaporation of adsorbed water present in the samples.

DTA curves of CMC and grafted cellulose (Figures 5 and 7) show a high exothermic peak at 280 and 325°C, respectively, which corresponds to the active pyrolysis range in TGA studied for both samples (Table I). A second short and broadly shaped exothermic peak occurs in both DTA curves at 360 and 500°C, respectively, which may be due to a slower oxidation and evaporation or carbonization of the degraded fragments of the pyrolytic products.

It already has been shown that degradation of viscose rayon occurs via two distinct steps at 345 and 435°C, as indicated in Figure 4. The DTA curve of viscose rayon (Fig. 8) also shows that thermal degradation occurs via two

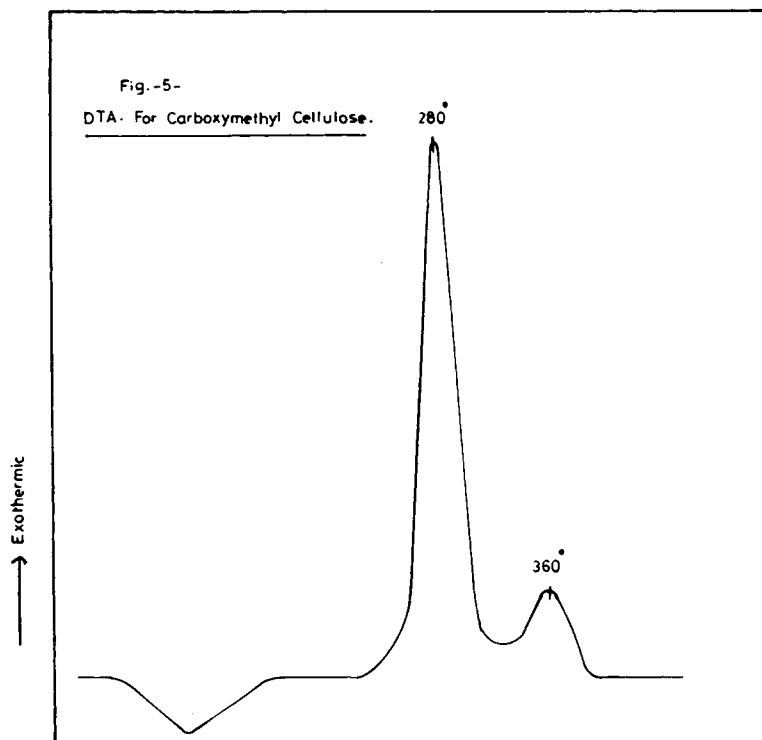


Fig. 5. DTA for carboxymethyl cellulose.

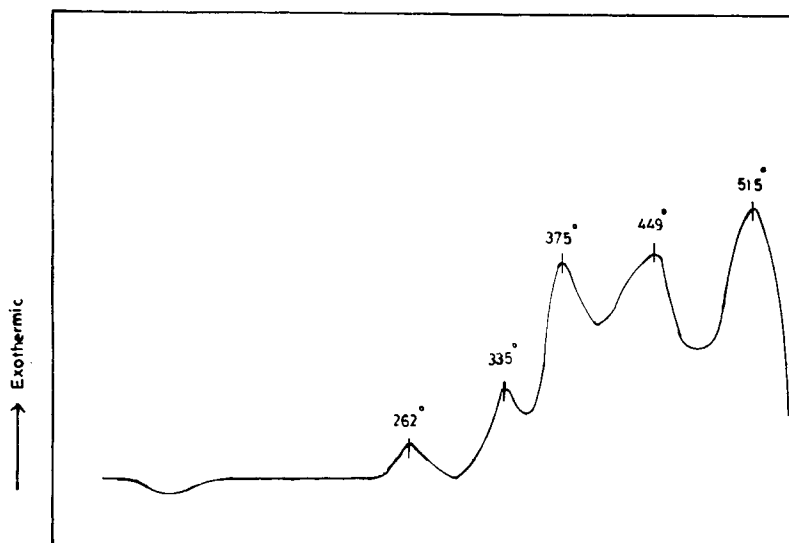


Fig. 6. DTA for cellulose acetate.

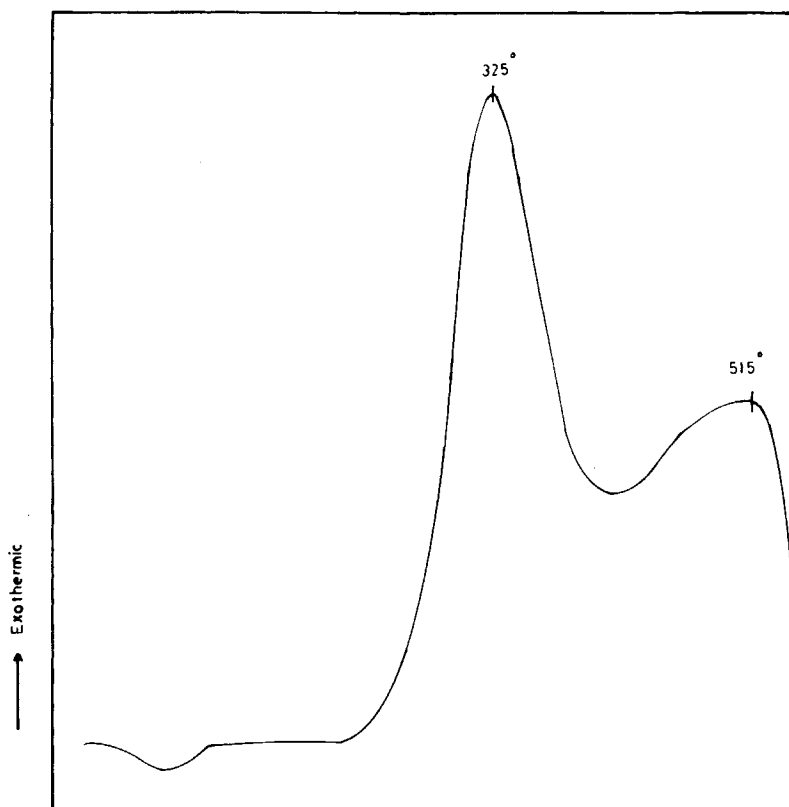


Fig. 7. DTA for grafted cellulose.

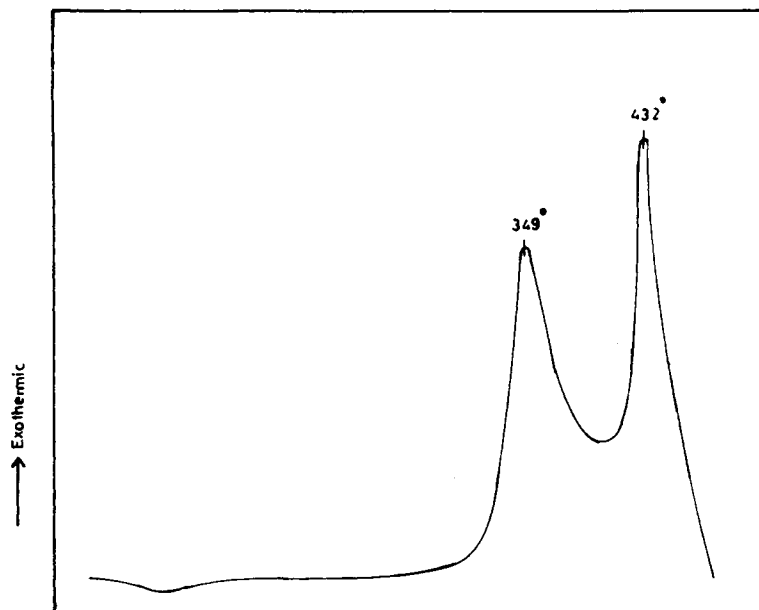


Fig. 8. DTA for viscose rayon.

high and sharp exothermic processes, at the same temperatures; these temperatures, however, could correspond to the softening, then volatilization, of the sample.

The DTA curve for cellulose acetate (Fig. 6) shows five successive peaks. The appearance of these five peaks may be due to different degradation mechanisms or to successive degradation of the acetyl groups of the acetate.

REFERENCES

1. H. Nishizaki, K. Yoshida, and J. H. Wang, *J. Appl. Polym. Sci.*, **25**, 2869 (1980).
2. P. K. Chatterjee and C. M. Conrad, *Text. Res. J.*, **36**, 487 (1966).
3. M. V. Ramiah, *J. Appl. Polym. Sci.*, **14**, 1323 (1970).
4. D. F. Arseneau, *Canad. J. Chem.*, **49**, 632 (1971).
5. Y. Kumagai and T. Ohuchi, *Jpn. Wood Res. Soc. J.*, **20**, 381 (1974).
6. A. Basch and M. Lewin, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 3095 (1973).
7. M. Z. Sefain and S. F. El-Kalyoubi, *Thermochim. Acta*, **75**, 107-113 (1984).
8. M. Z. Sefain, S. F. El-Kalyoubi, and N. Shukry, *J. Polym. Sci.* (1984). **23**, 1569-1577 (1985).
9. N. A. El-Shinnawy and S. F. El-Kalyoubi, *Kolorisztikai Ertesito* (1984), 1985.
10. A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961, p. 256.
11. P. K. Chatterjee, *J. Polym. Sci.*, **6**, 3217 (1968).
12. W. K. Tang, U. S. Forestry Serv., Research Paper FPL 71, 1967, Forest Prod Lab., Madison, Wisconsin.
13. S. Glasstone, *Textbook of Physical Chemistry*, Macmillan, London, 1962, p. 828.

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