Thermochimica Acta, 150 (1989) 33–38
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF CELLULOSE ACETATE

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(Received 2 January 1989)

ABSTRACT

The thermal behaviour of cellulose diacetate (containing different percentages of combined acetic acid) and cellulose triacetate was studied. The differential thermal analysis (DTA) and thermogravimetry (TG) curves of the various diacetates are similar; however, since the triacetate loses its fibrillar structure its DTA curve is completely different. The main degradation step follows first-order kinetics and the activation energies are calculated.

INTRODUCTION

The acetylation of cellulose is considered to be a heterogeneous reaction [1] in which the primary and secondary alcoholic groups in the cellulose molecules possess a similar ability to react in the reaction medium. As the thermal energy is introduced to the fibres, samples start to degrade, and the rate of degradation depends on several factors [2,3]. Many workers have studied and discussed the quantitative and qualitative characteristics of the thermal degradation of the polymers [4]. Differential thermal analysis (DTA) and thermogravimetry (TG) can be used to study this behaviour.

The aim of this study is to investigate the thermal behaviour of cellulose acetate (obtained by the acetylation of cotton linters to different degrees of substitution, represented as percentage of combined acetic acid) and cellulose triacetate.

EXPERIMENTAL

Egyptian cotton linters (99.5% α-cellulose and 0.08% ash) were used in this study.

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0040-6031/89/$03.50

Acetylation

Acetylation was carried out in three steps as follows.

(1) The sample was activated by the addition of glacial acetic acid (30 ml) to the cotton linters (1 g) for 5 min at 80 ° C. The sample was then squeezed ready for the acetylation step.

(2) The activated sample was acetylated using a mixture of glacial acetic acid (20 ml) containing perchloric acid (1 ml l^{-1}) and acetic anhydride (10 ml). The acetylation was performed at room temperature for various periods of time. The sample was then washed with distilled water until neutral.

(3) The sample was stabilized by boiling for a few seconds in distilled water and was then air dried.

For sample 6 equal amounts of glacial acetic acid and acetic anhydride were used to attain a high degree of substitution. A commercial triacetate sample was also used. The percentage combined acetic acid estimation was carried out according to ref. 5.

Thermal degradation

Thermogravimetry and differential thermal analysis were carried out using a thermobalance (Netzsch Geratebau Gabh Selb Bestell No. 348472 C). The heating rate was adjusted to 5 K min^{-1} until a constant weight was obtained. Samples were cut into pieces of about 0.25 cm and samples of 35 and 40 mg were used for the experiments.

RESULTS AND DISCUSSION

Cotton linters acetylated under different conditions possess different percentages of combined acetic acid as shown in Table 1.

Differential thermal analysis

The curves of the five acetylated samples (samples 2–6) and the untreated sample (sample 1) are illustrated in Fig. 1. It is clear that two exothermic reactions are observed during degradation. The first occurs at 603 K and is

TABLE 1

Percentage combined acetic acid in the sample

	Sample					
	1	2	3	4	5	6
Combined acetic acid (%)	0	8.7	15.2	23.4	30.4	43.8

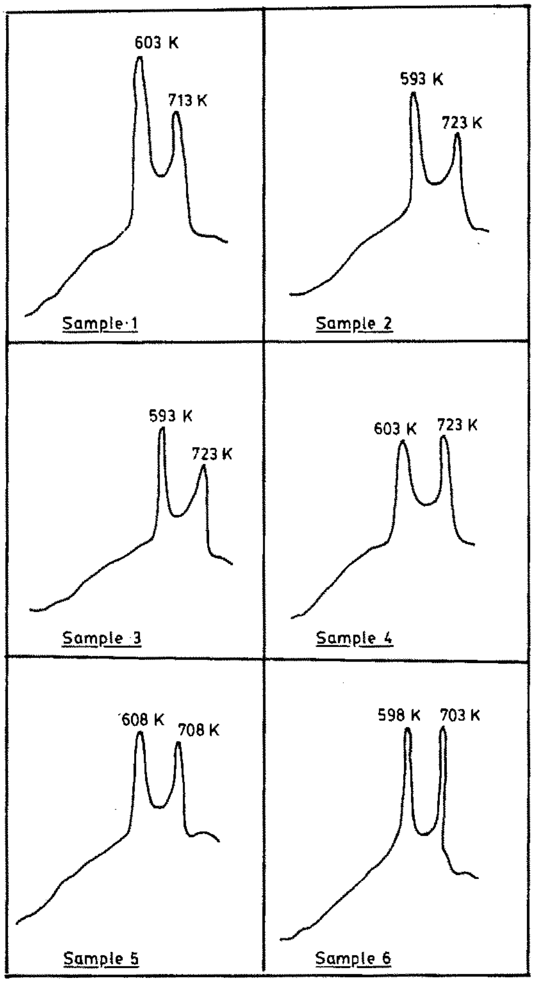

Fig. 1. DTA curves of cellulose diacetate samples.

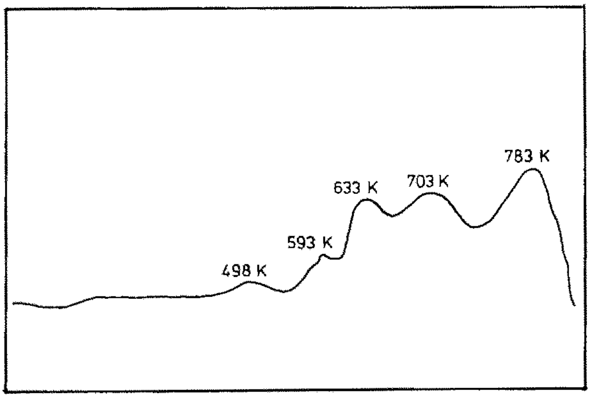

Fig. 2. DTA curve of cellulose triacetate.

related to the random dissociation of the bonds in the cellulosic chains along the fibre axis, i.e. 1,4-β-glucosidic linkages. The second exotherm which occurs at 723 K is related to the degradation of C–C, C–O and C–H bonds in the cycloglucose units. It is also clear from the figure that the amount of combined acetic acid has no effect on the shape of the curves of the exotherms as long as the cellulose retains its fibre structure; it seems that the amount of energy released may be affected. However, if the amount of combined acetic acid is increased this leads to the complete dissolution of the fibres in the reaction; when these are regenerated again by dilution with distilled water, cellulose triacetate is formed but not in fibre form.

The DTA curve of this sample is illustrated in Fig. 2. It is clear that five small exothermic reactions occur at 498, 593, 633, 693 and 783 K which represent the degradation steps of cellulose triacetate.

Therefore from the results obtained it can be seen that the fibre structure has a significant and characteristic DTA curve; removal or loss of this structure leads to a great change in this curve.

Thermogravimetry

Table 2 summarizes the initial, maximum and final temperatures of the active pyrolysis, which are represented in Fig. 3 as T_1, T_2 and T_3 respectively. In general, the initial pyrolytic temperature T_1 is more or less constant for the experimental samples (see Table 2). In addition, the maximum temperature T_2 is constant for the diacetate samples and native cotton linters, but is not well defined for the cellulose triacetate sample (see Fig. 4). The final pyrolytic temperature of cellulose triacetate is lower than that of the native and diacetate samples (628 K compared with 733 K; see Table 2).

It is also clear that the three main steps of degradation (initiation, propagation and carbonization) suggested previously by Chatterjee [6] are

TABLE 2

Thermogravimetry of cellulose (sample 1), cellulose diacetate (samples 2–6) and cellulose triacetate (sample 7)

Sample	Temperature of active pyrolysis (K)		
	T_1 (initial)	T_2 (maximum)	T_3 (final)
1	563	588	733
2	563	593	733
3	573	593	733
4	548	593	733
5	578	593	733
6	578	593	733
7	581	–	628

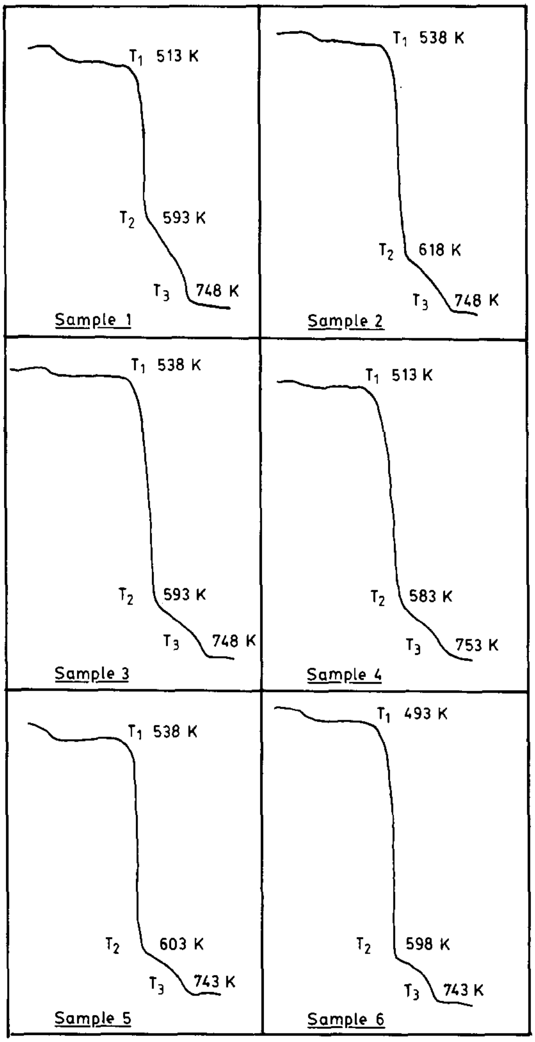

Fig. 3. TG curves of cellulose diacetate samples.

present in the figures; however some curvature is observed for the samples in Fig. 1 between T_2 and T_3 which may be attributed to the fast formation and evaporation of the pyrolytic substances at these temperatures (588–733 K). These substances are not formed during the degradation of cellulose triacetate, so T_2 is not clear in this case.

Elucidation of the order of reaction and the calculation of the activation energies of the experimental samples were carried out according to the method described previously [2,3]. The main degradation step of cellulose diacetate follows a first-order reaction.

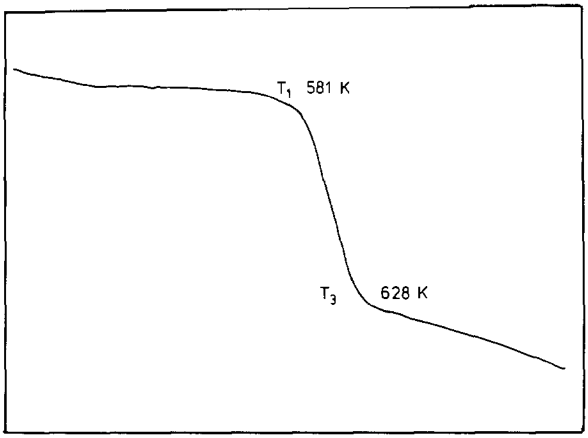

Fig. 4. TG curves of cellulose triacetate.

The activation energy of the triacetate sample is 36.4 kJ mol^{-1}; this can be compared with the activation energies of the diacetate samples which lie in the range 21.1–29.0 kJ mol^{-1}.

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