

## THERMAL DEGRADATION OF $\gamma$ -IRRADIATED COTTON

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### ABSTRACT

The thermal degradation of both pre- and  $\gamma$ -irradiated cotton samples between 25 and 550°C is studied. The weight loss thermogravimetry, the differential thermogravimetry and the differential thermal analysis are discussed.

The results indicate that as  $\gamma$ -dose increases the decomposition temperature is lowered. Also, it is found that the percentages of the residue and the char increase as  $\gamma$ -dose increases. This is attributed to the decrease in the degree of crystallinity and the degree of polymerization caused by  $\gamma$ -dose action.

### INTRODUCTION

This work is a continuation of investigations into the effect of  $\gamma$ -radiation on some properties of cellulose [1]. Previously the author studied the thermal degradation of some cellulosic materials [2]. That study indicates that the cellulose chain degrades in a first order reaction with a rate constant equal to 1.1–3.1  $\text{min}^{-1}$  and activation energy ranging from 72.98–131.20  $\text{kJ mol}^{-1}$  depending on the nature of the cellulosic materials. Also, it is found that the values of the activation energy,  $\Delta E$  and the entropy changes,  $\Delta S$ , increase with an increase in the degree of crystallinity and of polymerization [3].

Charlesby [4] points out that when cellulose fibers are exposed to the effect of ionizing radiation, such as atomic pile radiation or  $\gamma$ -radiation, they are rapidly degraded into a powdery state. Blouin et al. [5] indicate that oxidizing reactions occur as a result of high energy radiation.

The object of the present work is to investigate the effect of  $\gamma$ -doses on the thermal degradation of cellulose.

### EXPERIMENTAL

The starting material was Egyptian cotton fibers containing 91.7  $\alpha$ -cellulose and having  $DP = 620$ . The cotton fibers were sharded and sieved

through 200 standard mesh. The powder sample was washed, purified and dried at 70°C under vacuum until constant weight was reached [6]. To study the effect of  $\gamma$ -dose on the thermal degradation of cellulose, the samples were exposed to 60, 112, 132 and 230 Mrad of radiation by  $^{60}\text{Co}$ .

The degree of crystallinity of the cellulose samples was determined by using the IR spectrum method [7]. The apparatus was the UR-10 full automatic Carl Zeiss Jena double beam IR spectrophotometer. The two absorption bands at 1435 and 900  $\text{cm}^{-1}$  were chosen as crystalline and amorphous band respectively and the base line method of Heigl and White [8] was adopted in determining the absorbance ratio of these two bands, which was taken as the degree of crystallinity of the test samples.

The average degree of polymerization,  $DP$ , was calculated from viscosity measurements [9,10].

The weight loss thermogram, the differential thermogram, and the differential thermal analysis were carried out by using MOM Derivatograph No. 3427 from 25–550°C. The rate of heating was 5°C  $\text{min}^{-1}$  [2].

## RESULTS AND DISCUSSION

Table 1 indicates that both the degree of crystallinity and the degree of polymerization decrease with increase in  $\gamma$ -dose. This decrease may be due to the cleavage of cellulose chains by the  $\gamma$ -dose action. The cleavage leads to oxidation of some of the hydroxyl groups of the cellulose chain to carboxylic groups, the crystalline part of cellulose is distorted and both the degrees of crystallinity and polymerization decrease. The IR spectrum of the irradiated samples exhibits an absorption band at about 1730  $\text{cm}^{-1}$  corresponding to the carbonyl groups [1]. The appearance of such a band indicates that the cleavage of the cellulose chain is accompanied by the formation of carboxylic groups. The IR spectrum of the pre-irradiated sample indicates the absence of the carbonyl groups (at 1730  $\text{cm}^{-1}$ ).

Fig. 1 represents the TG curves for the pre- and  $\gamma$ -irradiated samples of cellulose. The TG curve of the pre-irradiated sample shows a slight weight

TABLE 1

The variation of the degree of crystallinity, the degree of polymerization, the percentage of residue and the percentage of char with  $\gamma$ -dose for cotton

No. of sample	$\gamma$ -dose (Mrad)	Degree of crystallinity	Degree of polymerization	% of residue	% of char
1	0	86.2	620	10.1	8.0
2	60	70.1	576	14.4	10.8
3	112	60.0	503	16.7	15.2
4	130	56.2	422	20.3	18.3
5	230	44.7	298	25.6	22.0

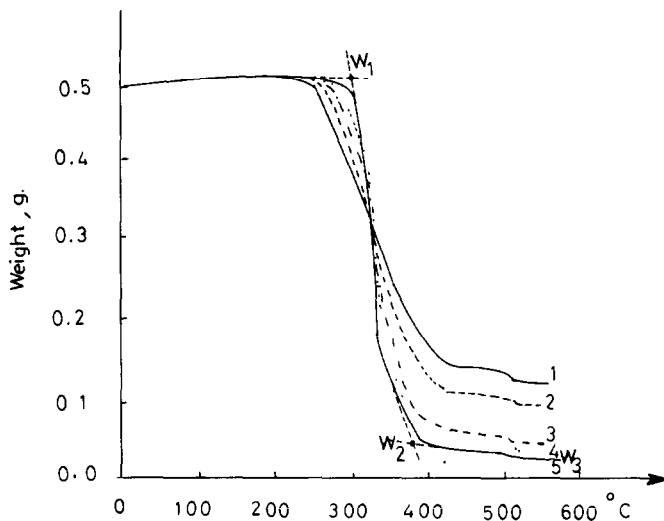


Fig. 1. TG curves of pre- and  $\gamma$ -irradiated cotton.

loss below  $\sim 290^\circ\text{C}$  due to the elimination of the physically absorbed water and some of the volatile materials. Between  $\sim 290$  and  $\sim 390^\circ\text{C}$  there is a drastic weight loss which is due to the main thermal decomposition of the cellulose chains. Between  $\sim 390$  and  $\sim 450^\circ\text{C}$ , the weight loss becomes slight, indicating that there is a further reaction involving the char formation. Above  $\sim 450^\circ\text{C}$ , the weight loss is nearly negligible. The TG curves (Fig. 1, Nos. 2, 3, 4, 5) of the irradiated cellulose exhibit the same general features, with a slight lowering in the temperature at which the drastic weight loss starts. When the  $\gamma$ -dose increases from 60 to 230 Mrad the temperature shifts to lower values (Fig. 1).

For the pre-irradiated cellulose, the percentages of residue and char were calculated from the TG curves and applying the following equations [3]

$$\% \text{ of residue} = - \frac{W_2}{W_1} \times 100 \text{ and}$$

$$\% \text{ of char} = - \frac{W_3}{W_1} \times 100$$

where  $W_1$  is the weight of cellulose, at the start of the thermal degradation,  $W_2$  is the weight of the end of degradation and  $W_3$  is the weight at the end of the experiment, i.e., at  $550^\circ\text{C}$  (Fig. 1). For the pre-irradiated cellulose it is found that the percentage of the residue = 10.1% and the percentage of char = 8%. These values are in good agreement with the values which were obtained by the author in the previous investigation [3]. When  $\gamma$ -doses increase, both the percentage of residue and the percentage of char increase and the degrees of crystallinity and polymerization decrease (Table 1).

Shafizadeh [11] and Chatterjee and Schwenker [12] suggested that the

pyrolysis of cellulose involves two primary decomposition pathways; (a) levoglucosan formation, which occurs above 300°C and (b) dehydration, which occurs below 300°C followed by char formation. Cabradilla [13] concluded that the levoglucosan formation was favored in crystalline or ordered cellulose, while the dehydration and char formation were favored in amorphous or disordered cellulose. Accordingly, the percentage of dehydration and char formation predominates over the levoglucosan formation when the degree of crystallinity decreases, hence the percentage of char increases with  $\gamma$ -dose increase from 60 to 230 Mrad (Table 1).

The DTG curves, Fig. 2, show a maximum peak at  $\sim 360^\circ\text{C}$  for the pre-irradiated cellulose. For the irradiated samples, the intensity of this peak decreases and the peak starts at a lower temperature when  $\gamma$ -doses increases; this may be due to the decrease in the degrees of crystallinity and of polymerization.

Figure 3 shows the DTA curves of the pre- and irradiated samples. The curves exhibit an endothermic decomposition starting at  $\sim 290^\circ\text{C}$  for the pre-irradiated sample and peaking at  $\sim 345^\circ\text{C}$ . To analyze the DTA curves, two measurements of temperature were calculated,  $T_{\text{onset}}$  and  $T_{\text{peak}}$  (Fig. 3).  $T_{\text{onset}}$  is the temperature at the intersection of the extrapolated base line and the extrapolated line of the endotherm.  $T_{\text{peak}}$  is the temperature at the

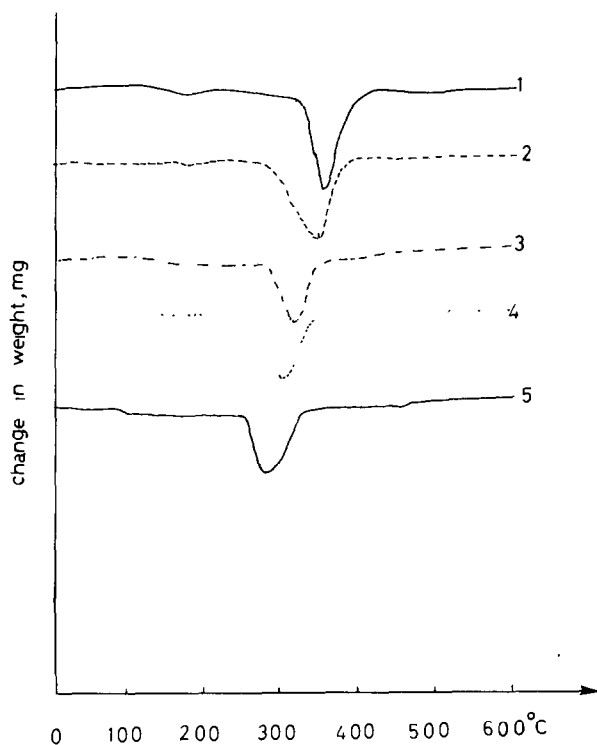


Fig. 2. DTG curves of pre- and  $\gamma$ -irradiated cotton.

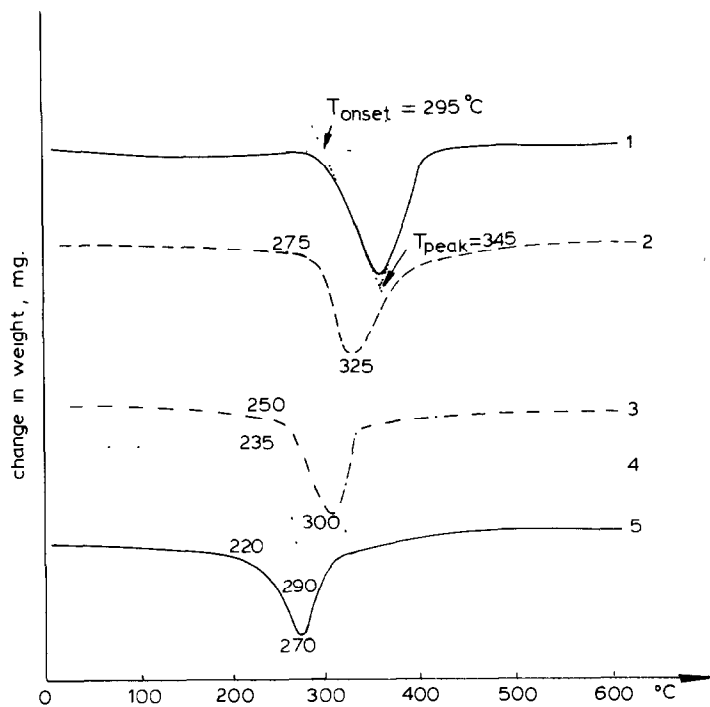


Fig. 3. DTG curves of pre- and  $\gamma$ -irradiated cotton.

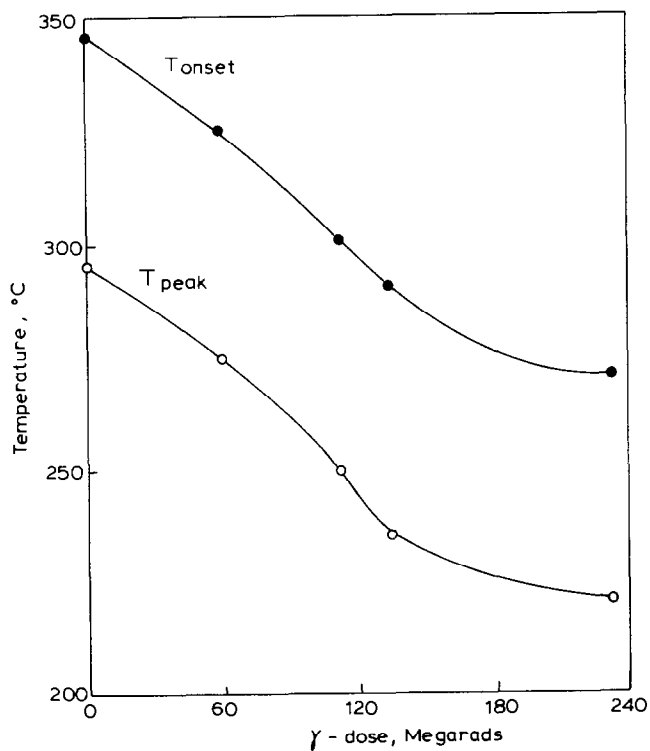


Fig. 4. The variation of  $T_{\text{onset}}$  and  $T_{\text{peak}}$  with  $\gamma$ -dose for cotton samples.

intersection of the extrapolated lines of the endotherm. The variation of the values of  $T_{\text{onset}}$  and  $T_{\text{peak}}$  with  $\gamma$ -dose are represented in Fig. 4. The results indicate that as  $\gamma$ -doses increase or the degree of crystallinity decreases both the  $T_{\text{onset}}$  and  $T_{\text{peak}}$  decrease. This decrease may be due to the increase of activation energy,  $E_a$ , of the crystalline cellulose over that for the amorphous cellulose by an amount equal to the energy required to break the lattice units. Hence the values of  $T_{\text{onset}}$  and  $T_{\text{peak}}$  are lowered by decreasing the degrees of crystallinity and of polymerization.

However, the rate of decrease in  $T_{\text{onset}}$  and  $T_{\text{peak}}$  is fast during the first stages of radiation and becomes slow as the  $\gamma$ -doses increase (Fig. 4). The difference in the rate of decrease may be due to the presence of some oxygen at the start of radiation and the formation of products of reaction having a higher absorption of  $\gamma$ -dose than the original sample [14]. The presence of the oxygen leads to an increase in the rate of degradation, hence the rate of decrease in  $T_{\text{onset}}$  and  $T_{\text{peak}}$  will increase. When the oxygen is consumed, the rate of degradation becomes slow, and the rate of decrease in  $T_{\text{onset}}$  and  $T_{\text{peak}}$  will decrease.

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