

INFLUENCE OF CHANGES IN FINE STRUCTURE ON THERMAL PROPERTIES OF COTTON FIBRES

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(Received January 2, 1987)

Examinations of the structural changes of mercerized cottons in sodium hydroxide or liquid ammonia were followed by determination of the degree of polymerization, sorption ratio and X-ray percentage crystallinity. Comparisons were made of the thermal stability, as indicated by differential thermal analysis and thermogravimetric analysis of the mercerized cottons. A decrease in the percentage crystallinity was found to lower then onset and peak temperatures of the major decomposition reaction. It was also found that the temperature where the major weight loss began increased in the sequence: cellulose III, cellulose II, and cellulose I. Samples in cellulose III crystals form were less thermally stable than samples of cellulose I and cellulose II. It will be noted however that the difference between cellulose II and cellulose III was small. Cotton cellulose II gave a lower yield of levoglucosan than either cotton cellulose I or II.

Several papers have previously been published on studies of the pyrolysis of cellulosic fibres to obtain the necessary knowledge for the development of flame retardants for cotton fibres [1]. Another reason is the importance of pyrolytic processes in providing the volatile molecules that are the immediate fuel in the flaming combustion of cellulosic materials.

The thermal degradation of cellulosic materials proceeds through a series of complex chemical reactions, depending essentially on the nature and duration of heating. It is generally accepted that, when cellulose is heated to high temperatures, it undergoes two principal types of reactions. One involves fragmentation and the formation of volatile molecules, and another involves dehydration and char formation. It has been established that levoglucosan (I) is the major product among the numerous volatile products obtained from celluloses on pyrolysis. Levoglucosan can further react and decompose to provide a series of secondary compounds on prolonged heating, as shown in Fig. 1.

Alterations in the supramolecular structure and the percentage crystallinity of cellulose can influence its thermal stability and consequently the levoglucosan yield on pyrolysis [2]. Golova et al. [3] showed that the packing density of cellulose altered the amount of levoglucosan formed during vacuum pyrolysis. Untreated cotton

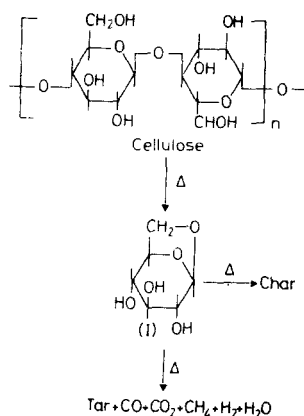


Fig. 1 Formation of levoglucosan and char during the thermal decomposition of cellulose

gave a higher yield of levoglucosan than cotton treated with 10% sodium hydroxide. Basch and Lewin [4] reported a levoglucosan content of 22–35% for cotton on air pyrolysis, and a value of 13–17% for rayon.

In this study, it was of interest to examine the effects of changes in crystallinity and crystal forms induced by chemical treatment of cotton fabrics with sodium hydroxide (25%) or liquid ammonia (at -35°) on its thermal properties.

Experimental

Materials

Bleached cotton fabric print cloth (130 g/m^2) was used.

Preparation of cellulose II

Cotton cellulose I was immersed in 25% sodium hydroxide containing the wetting agent Mercerol (10 g/l) at 20° for 30 min. This process was repeated. The sample was washed with distilled water, and then immersed in 2% acetic acid for 5 min. Fabrics were rewashed in distilled water and air-dried.

Preparation of cellulose III

Cotton cellulose I was immersed in liquid ammonia at -35° for 5 minutes. The ammonia was slowly evaporated off the sample during a 24 hr period. The sample was kept over P_2O_5 to prevent conversion back to cellulose I.

Test methods

Determination of the degree of polymerization

The degree of polymerization, DP, was determined viscometrically by using the nitrate method described by Agster [5, 6].

Moisture regain was determined at 65% relative humidity and 20° under conditions of adsorption. To calculate the sorption ratios of the samples, their moisture regain was divided by that of the untreated control measured under the same conditions of temperature and humidity.

X-ray diffraction patterns of the various cellulose crystal forms were produced with CuK_α radiation with a testure goniometer model PW 1078/25 (Philips). The X-ray crystallinity indices were determined by the method described by Jayme and Knolle [7].

Differential thermal analysis

Differential thermal analysis (DTA) was performed on a portion of the cotton fabric (5 mg) with a differential thermal analyser (DuPont 990) in a dry stream of the selected gas (N_2 atmosphere). The weighed cellulose sample was heated to 500° at a rate of 10 deg/min. Alumina was used as a reference material. The accuracy of reading was ± 0.5 deg.

Thermogravimetry

A weighed portion of cotton fabric (5 mg) was analysed by thermogravimetry to estimate the temperature at which the weight loss reaction began, the percentage residue and percentage char at 500°. Thermogravimetry was run in a nitrogen atmosphere at heating rate of 10 deg/min with a DuPont 990 Thermal Analyser.

Levoglucosan analysis

Gas chromatography (GC) was used to determine the amount of levoglucosan in the tar after vacuum pyrolysis as described by Gabradilla and Zeronian [8].

Results and discussion

One of the methods which has been used to alter the crystalline structure of cotton cellulose is treatment with sodium hydroxide or liquid ammonia, as described previously [9]. The X-ray diffractometer patterns showed that there was essentially complete lattice transformation from cellulose I to cellulose II by repetition of the mercerization process at 20° for $1/2$ hr, and from cellulose I to cellulose III by treating cotton cellulose with liquid ammonia followed by evaporation (Fig. 2).

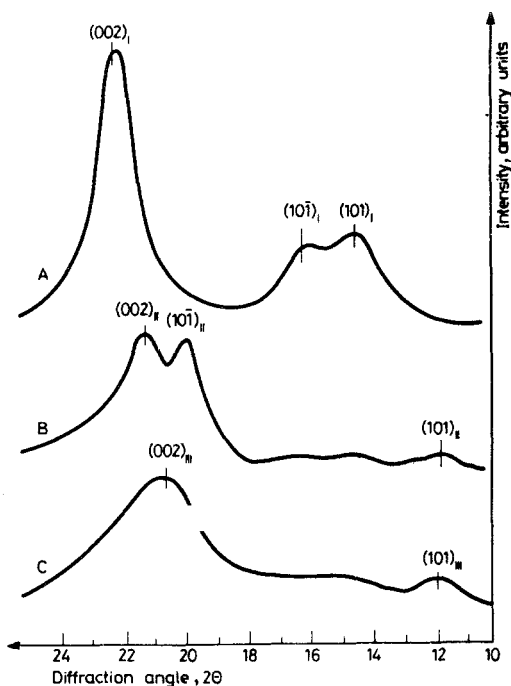


Fig. 2 X-ray diffractograms of cotton. A) cellulose I, B) cellulose II, C) cellulose III

The various cellulose crystal forms were characterized by the degree of polymerization, the sorption ratio and the X-ray crystallinity indices (Table 1). The DP of cellulose I is higher than those of cellulose II and cellulose III, indicating that a reduction in the DP accompanied crystal transformation (Table 1). This lowering of the DP is due to the random chain scission of the glycosidic linkages. The

Table 1 Characterization of the modified cotton fibres

Cell form	DP ^{a)}	S.R. ^{b)}	Disordered fraction, %	Cr. I ^{c)} %	Cell I %	Cell II %	Cell III %
Cellulose I	2300	1.0	21	79	79	—	—
Cellulose II	2060	1.5	40	60	—	60	—
Cellulose III	2100	1.7	62	38	2	—	36

a) DP = degree of polymerization

b) S.R. = sorption ratio = $\frac{\text{moisture regain of sample}}{\text{moisture regain of control}}$

c) Cr. I = X-ray crystallinity, %.

lowering of the DP should be considered in an examination of the thermal analysis data.

Sorption ratios, that give an index of the accessibility of cellulose' hydroxy groups, may also be used to estimate changes in crystallinity [10]. A sample with a sorption ratio greater than unity has a lower crystallinity.

The sorption ratios of cellulose II and cellulose III were higher than that of cellulose I, indicating that a decrease in the percentage crystallinity accompanied crystal transformation. Table I shows that a decrease in the overall crystallinity, with an increase in the disordered fraction of cellulose, resulted on the formation of cellulose II and cellulose III.

The thermal analysis data, as shown by DTA and TG, revealed some differences between the thermal properties of the different crystalline forms of cotton cellulose. Figure 3 shows the DTA curves obtained when samples of cellulose I, II and III were heated under a nitrogen atmosphere. The DTA curves for the various cellulose

Table 2 Differential thermal analysis and thermogravimetry of the modified cotton fibres

Cell form	Differential thermal analysis		Thermogravimetry		
	T^a onset, °C	T^b peak, °C	T^c , °C	residue %	char %
Cellulose I	319	325	325	10	4.4
Cellulose II	310	312	315	22	8.1
Cellulose III	309	313	312	16	7.9

- a) Temperature at onset of major endotherm.
 b) Temperature at peak of endotherm.
 c) Onset temperature of major weight loss.

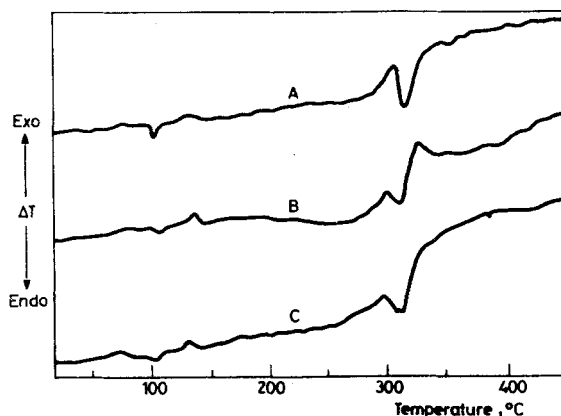


Fig. 3 Differential thermal analysis (DTA) of cotton cellulose. A) cellulose I, B) cellulose II, C) cellulose III

crystal forms show some common features. A pronounced change in the slope and position of the baseline of cellulose III at about 75° is also apparent. This change can be attributed to a glass transition. Following this transition, a relatively sharp exotherm is obtained, with a peak temperature of 135° , indicating a further polymer crystallization. Figure 3 shows a slight endotherm between 110 and 120° , which can be attributed to the volatilization of the absorbed water.

The major endothermic decomposition reactions were affected by transformation of the crystal forms of cotton cellulose. For cellulose I, the endothermic decomposition reaction begins at 319° and extends to 335° , with a peak temperature of 325° . As shown in Table 2, transformation of cellulose I to cellulose II or cellulose III results in a shift of the onset and peak temperatures of the major endothermic reaction to lower temperatures. The lower decomposition temperature merely furnished certain facts, and the mechanisms proposed are in some instances the models devised to explain those facts. The depolymerization of cellulose to levoglucosan, or further to the volatile compounds, was found to occur more easily for cellulose II or cellulose III than for cellulose I. The available evidence indicates that when cellulose is pyrolyzed the non-crystalline regions are the first to be attacked. Rapid cleavage of the chains occurs, with the formation of free radical intermediates (Fig. 4). These facts support the hypothesis that the crystallinity is

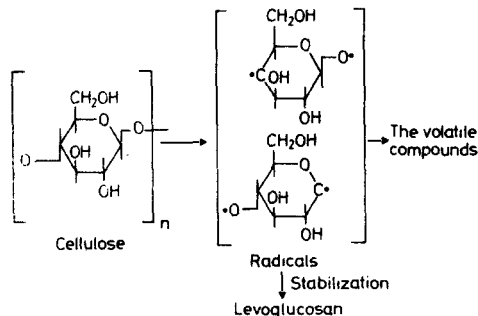


Fig. 4 Intermediate free radical mechanism for cellulose pyrolysis

one of the factors determining the amount of levoglucosan produced during cellulose pyrolysis. The major portion of it was produced from cellulose III (Table 3). From the results described so far, it is self-evident that samples in the cellulose III crystal form are less thermally stable than samples of cellulose I. It is known that levoglucosan polymerizes on heating, so that the char formation depends significantly upon the amount of the polymer present; in turn, this is dependent upon the initial concentration of its monomer, levoglucosan.

Table 3 Amount of levoglucosan produced during cellulose pyrolysis

Cell form	Amount of levoglucosan ^{a)}
Cellulose I	25
Cellulose II	21
Cellulose III	35

a) The levoglucosan content was calculated from:

$$\text{levoglucosan yield} = \frac{\text{weight of levoglucosan in tar}}{\text{dry weight of cellulose}} \times 100$$

A comparison between the TG curves for the various cellulose crystal forms is shown in Fig. 5.

The TG curves were similar for cellulose I, cellulose II and cellulose III. However, there were significant differences in the temperature where the major weight loss begins and in the percentage residue after decomposition.

It is interesting to note that cellulose II decomposes much more rapidly than cellulose I. Cellulose III behaves similarly. In the case of cellulose I, the weight loss

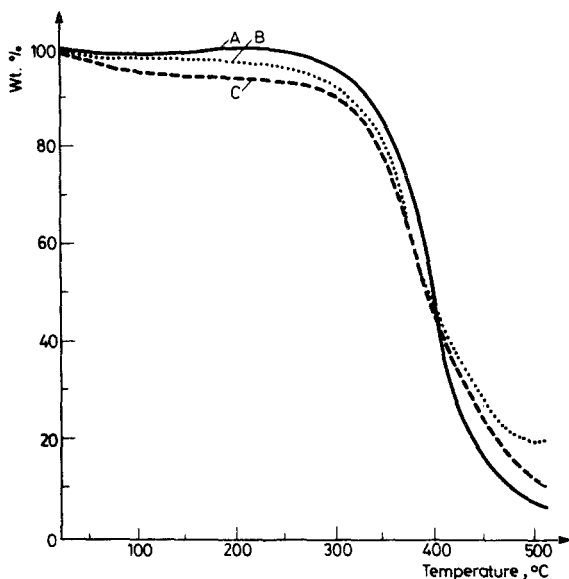


Fig. 5 Thermogravimetric analysis (TG) of cotton cellulose. A) cellulose I, B) cellulose II, C) cellulose III

begins somewhat above 280°, and then accelerates until an inflection point near 325°. The temperature where the major weight loss begins is lower for cellulose II and III. The inflection point for cellulose II is at 315°, and for cellulose III is at 312°. All of these data point to the fact that the thermal stability of the cellulose III crystal form is less than that of cellulose I or cellulose II.

The weight loss after thermal decomposition was 90% for cellulose I (10% residue), 78% for cellulose II (22% residue), and 84% for cellulose III (16% residue).

The percentage char showed differences due to transformation of the cell forms. This transformation resulted in an increase of the percentage char. At 500°, there was 4.4% char for cellulose I. The percentage chars were roughly similar for cellulose II and cellulose III: 8.1% for cellulose II, and 7.9% for cellulose III.

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Zusammenfassung — Strukturelle Veränderungen von merzerisierter Baumwolle in Natriumhydroxid oder flüssigem Ammoniak wurden durch Bestimmung des Polymerisationsgrades, des Sorptionsverhältnisses und der röntgen-Kristallinität verfolgt. Die differentialthermoanalytisch und thermogravimetrisch bestimmte thermische Stabilität der merzerisierten Baumwollen wird verglichen. Eine Verminderung der Kristallinität hat eine Abnahme der Temperaturen zur Folge, bei der die Hauptzersetzungsreaktion einsetzt bzw. mit maximaler Geschwindigkeit verläuft. Es wurde ebenfalls festgestellt, daß die Temperatur, bei der der Hauptgewichtsverlust einsetzt, in der Reihenfolge Cellulose III–Cellulose II–Cellulose I ansteigt. Proben in der Kristallform Cellulose III sind thermisch weniger stabil als die in der Celluloseform I und II. Baumwollcellulose II ergab geringere Ausbeuten an Levoglucosan als Baumwollcellulose I oder III.

Резюме — Исследование структурных изменений хлопка, обработанного раствором едкого натра или жидкого аммиака, было проведено путем определения степени полимеризации, показателя сорбции и процента кристалличности, определенного рентгенофазовым анализом. Методом ДТА и ТГ изучена термоустойчивость различных образцов мерсеризованного хлопка. Установлено, что уменьшение кристалличности вызывает более низкое начало температурного пика основной реакции разложения. Найдено, что температуры начала основной потери веса располагаются в ряд: целлюлоза III, целлюлоза II и целлюлоза I. Установлено, что образцы в кристаллической форме целлюлозы III менее термоустойчивы, чем в целлюлозе I и II. Хлопковая целлюлоза II дает более низкий выход левоглюкозана, чем хлопковая целлюлоза I или III.