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EFFECTS OF STRUCTURAL CHANGES ON THERMAL PROPERTIES AND PYROLYSIS OF MODIFIED COTTON FIBRES

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The changes resulting in the supramolecular structure of cotton fibres after mercerization at different temperatures were investigated by means of X-ray diffraction, sorption measurements and determination of the degree of polymerization. For comparison, corresponding measurements were also carried out after liquid ammonia treatment. Pyrolysis of the mercerized cotton samples showed that the levoglucosan yield of NaOH-treated samples is less than that of untreated or NH_3-treated samples. Comparisons were made of the thermal stability of the modified cotton samples, as indicated by DTA and TG. A decrease in the percentage crystallinity was found to lower the onset and peak temperatures of the major decomposition reactions. An NH_3-treated sample (acetone) was less thermally stable than untreated or mercerized samples.

There are several reasons for studying the pyrolysis of cellulose. For example, such studies are important for the development of flame retardants for cotton fibres [1]. Thermal analysis is a useful technique for assessing the flammability of cellulosic materials. Thermoanalytical techniques can provide an insight into how a cellulosic material might react on exposure to fire, e.g. the nature and temperature of its decomposition, the amount of volatiles versus char residue, etc. The thermal degradation of cellulosic materials proceeds through a series of complex chemical reactions. The reactions are highly influenced by the nature and period of heating, the surrounding atmosphere and impurities. The postulated pyrolysis paths can be depicted as shown in Scheme 1. Heating at lower temperatures favours dehydration and subsequent char formation. Heating at higher temperatures favours the formation of gaseous combustible products. Theories about the pyrolysis mechanisms for cellulose have been based on the origin of two main pyrolysis products: tar and char. Several investigations have established that levoglucosan (1,6-anhydro-β-D-glycopyranose) is the major tar component. A large number of other materials have been identified as cellulose pyrolysis products. However, Glassner and Pierce [2] demonstrated that the chromatograms obtained for

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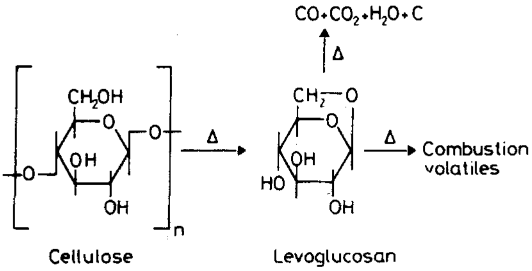
pyrolysed cellulose and pyrolysed levoglucosan were identical, suggesting that the observed peaks from cellulose were actually secondary decomposition products of levoglucosan.



Scheme 1 Formation of levoglucosan and char during thermal decomposition of cotton cellulose

There is evidence that the supramolecular structure of cotton can influence its pyrolysis. Golova et al. [3] reported that the packing density of cellulose altered the amount of levoglucosan formed during vacuum pyrolysis. Basch and Lewin [4] showed that there was a correlation between the crystallinity degree of polymerization and the pyrolysis of cellulose. For a complete understanding of this fact, more analysis needs to be carried out on different cellulose crystal forms. Thus, the major goal of the present manuscript is to evaluate the effects of the changes caused in the X-ray percentage crystallinity and crystal forms by the mercerization of cotton fabrics, depending on the mercerizing temperature or liquid ammonia treatment, when three different methods of removing the ammonia are used, on the thermal properties and pyrolysis of cellulose.

Experimental

Materials

The starting material used was a woven cotton fabric (Printcloth 130 g/m^2).

Chemical treatment

The cotton samples were treated in a tensionless state with 25% (by weight) sodium hydroxide containing the wetting agent Mercerol (10 g/l), for 15 minutes at 20°, for 10 minutes at 60°, and for 5 minutes at 90°. Sodium hydroxide was removed by washing in hot water (70°) for 5 minutes, followed by neutralization with 2% acetic acid for 5 minutes. Fabrics were rewashed in distilled water for 10 minutes and air-dried.

In the case of liquid ammonia, the samples were immersed for 5 minutes at −33°. The ammonia was removed by either dipping the material (for 2 minutes) in hot water (95°) and air-drying, by evaporation and steaming at 100° (for 3 minutes) or by quenching treatment in acetone.

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].

Determination of the iodine sorption value

The iodine sorption values of the cottons were determined by the method described by Nelson et al. [7].

Determination of the moisture regain

Moisture regain was determined at 65% RH and 20° under the 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 analysis

X-ray diffraction patterns of the various cellulose crystal forms were produced with a texture Goniometer model PW 1078/25 (Philips) with CuK_α radiation. The X-ray crystallinity indices were determined by the method described by Jayme and Knolle [8].

Differential thermal analysis

The DTA was performed on a portion of the cotton fabric (5 mg) with a differential thermal analyzer (DuPont 990) in dry 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 the reading was ±0.5 deg.

Thermogravimetry

A weighed portion of cotton fabric (5 mg) was analysed by TG to estimate the temperature at which the weight loss reaction began, the percentage residue and the percentage char at 500°. TG was performed in N_2 atmosphere at a heating rate of 10 deg/min on a DuPont 990 thermal analyser. The percentage residue (i.e., the weight remaining after thermal decomposition), and the percentage char (i.e. the weight remaining at 500°) were calculated from the TG curves and based on the dry weight of cellulose [4].

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 [9].

Results and discussion

When cotton cellulose is treated with sodium hydroxide or liquid ammonia, an unstable complex is formed and extensive swelling occurs. A comparison of the effects of sodium hydroxide on cotton cellulose at different temperatures is shown in the X-ray diffractograms of Fig. 1 and in Table 1. The extent of cellulose lattice conversation varied tremendously with the mercerizing temperature. Caustic mercerization at 20° causes more conversion from cellulose I to cellulose II than is obtained from mercerisation at 90°. Figure 2 illustrates X-ray diffractograms of ammonia-treated cotton cellulose, where the ammonia was removed with hot water (95°), by evaporation and steaming at 100°, or by quenching treatments in acetone. These curves show that the removal of ammonia with hot water (95°) or evaporation and steaming at 100° resulted in the regeneration of cellulose I. When cotton fibres were treated with liquid ammonia and then quenched in acetone, a

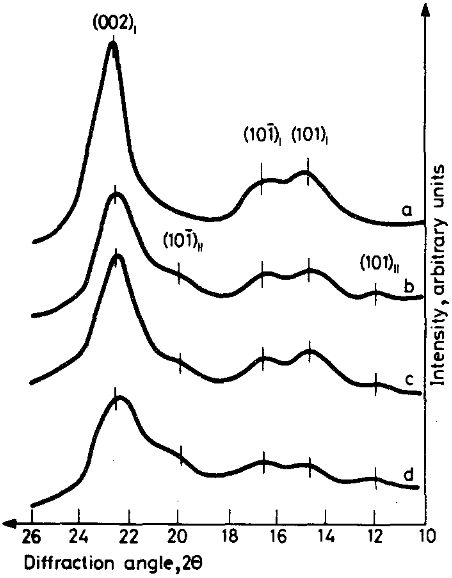


Fig. 1 X-ray diffractogram of mercerized cotton cellulose. A) untreated cotton; B) NAOH (20 °C); C) NaOH (60 °C); D) NAOH (90 °C)

Table 1 Characterization of the modified cotton fibres

Treatment	DP[a]	S.R.[b]	ISV,[c] mg/g	Cr. I[d], %	Cell. I, %	Cell. II, %	Cell. III, %
Untreated	2300	1.0	50	79	79	—	—
25% NaOH (20 °C)	2250	1.3	105	61	37	24	—
25% NaOH (60 °C)	2230	1.26	93	65	43	22	—
25% NaOH (90 °C)	2200	1.25	87	68	48	20	—
NH_3-hot water (95 °C)	2060	1.26	76	69	69	—	—
NH_3-evap.-steam	2280	1.15	57	73	73	—	—
NH_3-acetone	2100	1.35	180	42	—	—	42

[a] DP = degree of polymerization

[b] $\text{S.R.} = \text{sorption ratio} = \dfrac{\text{moisture regain of sample}}{\text{moisture regain of control}}$

[c] ISV = iodine sorption value

[d] Cr. I. = X-ray crystallinity

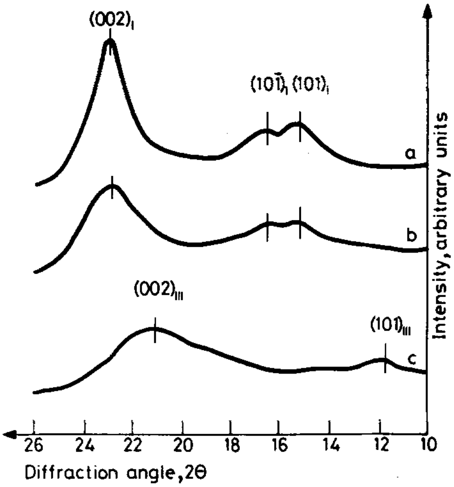


Fig. 2 X-ray diffractogram of NH_3-treated cotton cellulose. A) NH_3-hot water; B) NH_3-evap.-steam.; C) NH_3-acetone

very substantial conversion of the native cellulose III was realised. Generally, all caustic mercerization and liquid ammonia treatments caused a decrease in the overall crystallinity (Table 1).

The differently treated cotton fibres were characterized by the DP, the iodine sorption value and the moisture regain (Table 1). DP of the untreated cotton cellulose is higher than those of the mercerized cotton cellulose and NH_3-treated

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

Treatment	Differential thermal analysis		Thermogravimetry		
	T^a onset, °C	T^b peak, °C	T^c, °C	residue[d], %	char[d], %
Untreated	319	325	325	10	4.4
25% NaOH (20 °C)	305	311	310	25	9.3
25% NaOH (60 °C)	308	317	312	23	8.6
25% NaOH (90 °C)	308	320	313	22	8.0
NH_3-hot water (95 °C)	307	315	312	14	4.6
NH_3-evap.-steam	311	318	320	12	4.5
NH_3-acetone	300	311	305	18	10.0

[a] Temperature of onset of major endotherm.

[b] Temperature of peak of endotherm.

[c] Onset temperature of major weight loss.

[d] Based on dry weight of cellulose [4].

cotton cellulose, indicating that a reduction in the DP accompanied the mercerization and liquid ammonia treatment of the cotton fibres (Table 1). This lowering of the DP should be considered when examining the thermal analysis data.

Methods that give an index of the accessibility of cotton cellulose hydroxy groups, such as iodine sorption and moisture regain, may also be used to estimate changes in crystallinity [10, 11].

The accessibilities to iodine of mercerized and NH_3-treated cottons were higher than that of untreated cotton. To calculate the sorption ratio of a sample, its moisture regain was divided by that of untreated cotton measured at the same temperature and relative humidity. A sorption ratio greater than one indicates that the sample has a lower crystallinity, or a higher accessibility, than untreated cotton. The sorption ratios of mercerized and NH_3-treated cottons were higher than that of untreated cotton, indicating that a decrease in the percentage crystallinity accompanied mercerization and ammonia treatment of the cotton fibres.

Thermal analysis revealed differences between the thermal properties of untreated, mercerized and NH_3-treated cotton fibres. Figures 3 and 4 show the DTA curves obtained for samples of untreated, NaOH-treated and NH_3-treated cotton fibres when heated in N_2 atmosphere. The DTA curves in N_2 had similar patterns, each displaying two sharp endothermic peaks. A pronounced change in the slope and position of the base line occurs at a temperature of about 77°. This can be attributed to a glass transition. Following this transition, a relatively sharp exotherm is obtained, with a peak temperature of 136°, which is due to cellulose polymer crystallization. A slight endotherm at 120° can be attributed to the loss of absorbed water. From the DTA curve for untreated cotton, it can be seen that a

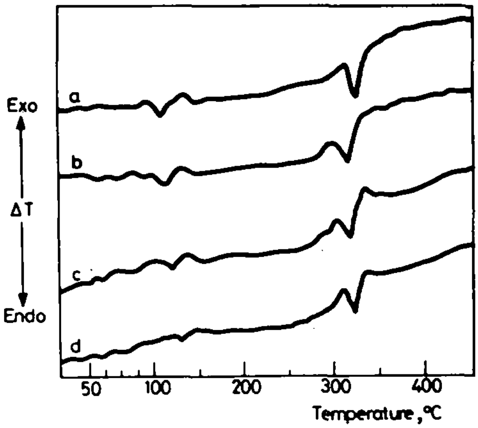


Fig. 3 DTA curves of mercerized cotton cellulose. A) untreated cotton; B) NaOH (20 °C); C) NaOH (60 °C); D) NaOH (90 °C)

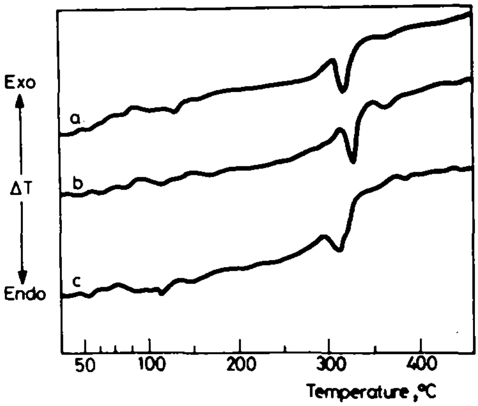


Fig. 4 DTA curves of NH_3-treated cotton celluloses. A) NH_3-hot water; B) NH_3-evap.-steam.; C) NH_3-acetone

major endothermic decomposition reaction begins at 319° and peaks at 325°. The onset and peak temperatures of the major endothermic decomposition reaction were affected by sodium hydroxide and liquid ammonia treatments. Mercerized and NH_3-treated cottons had lower onset and peak temperatures than the untreated cotton. Mercerization at 20° resulted in large decreases in the onset and peak temperatures, as determined from the DTA curves. Liquid ammonia treatment with removal of ammonia by quenching treatment in acetone, also caused drops in both the onset and peak temperatures when compared to either untreated cotton or mercerized cotton. The conversion of cellulose I to cellulose II or III that resulted from the treatment of cotton cellulose I with sodium hydroxide or liquid ammonia may be the cause of the lowered onset and peak temperatures. A slight exotherm above 330° may be due to a small amount of oxygen in the purge gas, which therefore caused exothermic degradation.

The amount of levoglucosan formed during pyrolysis varied for untreated, mercerized and NH_3-treated cotton (Table 3). Mercerized cotton cellulose gave much lower yields of levoglucosan than either untreated or NH_3-treated cotton cellulose. The depolymerization of cotton cellulose to levoglucosan was found to be easier for NH_3-treated cotton cellulose when the ammonia was removed by quenching treatment in acetone. The available evidence indicates that, when cellulose is pyrolysed, the non-crystalline regions are the first to be attached. Mono- and difunctional radicals are formed by the cleavage of glucoside linkages, and these radicals in turn give rise to volatile products including levoglucosan (Scheme 2). The higher levoglucosan content of NH_3-treated cotton cellulose with removal of ammonia by acetone should be due to the lower crystallinity of this sample (Table 1), since a decrease in crystallinity is known to affect the course of pyrolysis.

Table 3 Amount of levoglucosan produced during cellulose pyrolysis

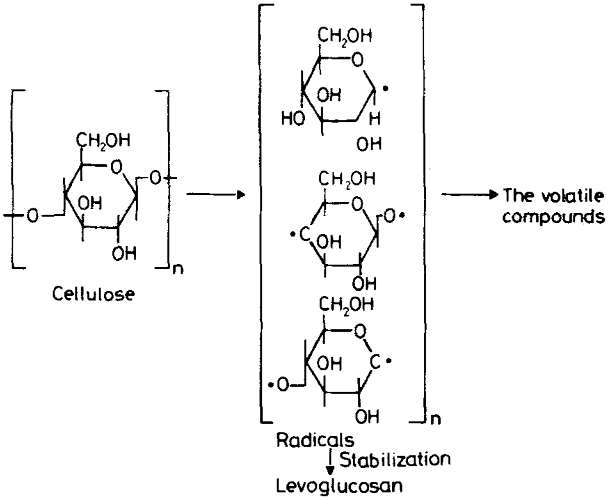
Treatment	Amount of levoglucosan[a]
Untreated	28
25% NaOH (20 °C)	22
25% NaOH (60 °C)	24
25% NaOH (90 °C)	25
NH_3-hot water (95 °C)	27
NH_3-evap.-steam.	27
NH_3-acetone	32

[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 untreated, mercerized and NH_3-treated cotton cellulose is shown in Fig. 5. The TG curves were similar for the untreated, mercerized and NH_3-treated cottons. However, there were differences in the temperatures at which the major weight loss begins, and in the percentage residue after decomposition (Table 2).

It is interesting to note that cotton celluloses mercerized at different temperatures decompose much more rapidly than the untreated cotton cellulose. NH_3-treated cotton cellulose with removal of ammonia by acetone behaves similarly. In the case of untreated cotton, the weight loss begins somewhat above 280°, accaelerates up to



Scheme 2 Intermediate free radical mechanism for cellulose pyrolysis

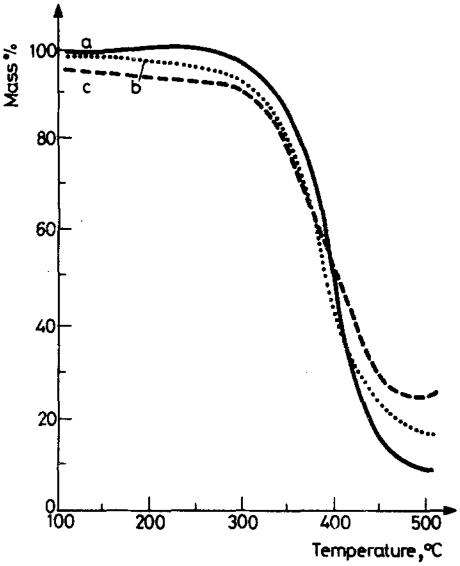


Fig. 5 TG curves of cotton celluloses. A) untreated cotton; B) NH_3-acetone; C) NaOH (20 °C)

an inflection point near 325°. The temperature at which the major weight loss begins was lowered for mercerized cotton and NH_3-treated cotton with removal of ammonia by acetone. The inflection point for cotton mercerized at 20° is 310°, and that for NH_3-treated cotton (acetone) is 305°. All of these data point to the fact that the thermal stability of NH_3-treated cotton (acetone) is less than those of untreated or mercerized cottons.

The weight loss after thermal decomposition was 90% for untreated cotton (10% residue), while it was 75–78% for mercerized cottons (25–22% residue) and 82 for NH_3-treated cotton (acetone) (18% residue).

The percentage char showed differences as a result of mercerization and ammonia treatments.

The amount of char, as shown by TG (Table 2), was higher for the mercerized and NH_3-treated samples. At 500°, there was 4.4% char for the untreated cotton. The percentage char was similar for NH_3-treated cotton with removal of ammonia with either hot water or by evaporation and steaming. The percentage char for mercerized cottons was 8–9.3%. For NH_3-treated cotton (acetone), there was 10% char.

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Zusammenfassung — Mittels Röntgendiffraktionsuntersuchungen, Sorptionsmessungen und Bestimmung deas Polymerisationsgrades wurden die Veränderungen untersucht, die durch die Merzerisierung bei verschiedenen Temperaturen in der supramolekularen Struktur von Baumwollfasern verursacht werden. Zum Vergleich wurden ähnliche Untersuchungen nach Behandlung mit flüssigem Ammoniak durchgeführt. Die Pyrolyse der merzerisierten Baumwollproben zeigt, daß die Levoglukosanausbeute bei NaOH-behandelten Proben geringer ist als bei unbehandelten oder NH_3-behandelten Proben. Aüf Grundlage von DTA und TG wurden vergleichende Betrachtungen zur Wärmebeständigkeit der modifizierten Baumwollproben angestellt. Eine Abnahme de prozentualen Kristallinität senkt die Temperatur für Beginn und Peak der hauptsächlichsten Zersetzungsreaktionen. NH_3-behandelte Proben (Azeton) sind thermisch unbeständiger als unbehandelte oder merzerisierte Proben.

Резюме — С помощью рентгеноструктурного анализа, сорбционных измерений и определения степени полимеризации изучены изменения в надмолекулярной структуре волокон хлопка после их мерсеризации при различных температурах. Для сравнения соответствующие измерения были проведены с волокнами, обработанными жидким аммиаком. Пиролиз мерсеризованных образцов хлопка показал, что выход левоглюкозана при этом меньше, чем в случае пиролиза необработанных образцов или же образцов, обработанных аммиаком. На основе данных ДТА и ТГ проведено сопоставление термоустойчивости модифицированных образцов хлопка. Найдено, что уменьшение процента кристалличности понижает начальные и максимальные температуры основных реакций разложения. Образцы, обработанные аммиаком, менее термоустойчивы по сравнению с необработанными и мерсеризованными образцами.