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Thermal analysis and characterisation of cellulose oxidised with sodium methaperiodate

Silvia Vicini[a], Elisabetta Princi[a], Giorgio Luciano[a], Enrico Franceschi[a,*], Enrico Pedemonte[a], Dagmara Oldak[b], Halina Kaczmarek[b], Alina Sionkowska[b]

[a] *Dipartimento di Chimica e Chimica Industriale, Universitá di Genova, Via Dodecaneso 31, 16164 Genoa, Italy*
[b] *Faculty of Chemistry, N. Copernicus University, Gagarin 7 Street, 87-100 Torun, Poland*

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Abstract

The oxidation reactions of cellulose involve the primary and secondary hydroxyl groups of the pyranose ring and result in carbonyl and carboxyl groups. This reaction can be accompanied by opening the pyranose ring. In any cases the glucosidic bond becomes weaker; the formation of carboxyl groups induces a depolymerisation, thus reducing the polymerisation degree and the physical and mechanical strength of the material. The conversion of 1,2-dihydroxyl groups to dialdehyde by periodate oxidation on cellulose based materials as textiles (flax and cotton) and paper with different composition and characteristics, has been studied. To investigate the cellulose behaviour at different level of oxidation, two different solutions of sodium methaperiodate were used: 0.1 and 0.4 M, for different times of treatment. The oxidised samples become "models" to investigate the different levels of degradation in real materials. Thermal analysis is convenient and reproducible, and is a useful method for characterising heterogeneous organic materials from plants. In this research we have examined the assignment of the exothermic transition in DSC analysis of paper, flax and cotton and its components in order to understand their thermal behaviour in more detail and to evaluate the effect of the oxidation treatment on the thermal behaviour. The aim of our work is to correlate the level of degradation of the oxidised samples with the natural ageing of the real cellulose based materials. The results obtained suggest information in the restoration and conservation field of cellulosic materials.

Keywords: Paper; Textiles; Dialdehyde cellulose; Methaperiodate oxidation; Differential scanning calorimetry

1. Introduction

Cellulose is the most extensively used natural polymer and represents a renewable natural source for organic materials. The main reactions acting on the structure of cellulose and causing its alteration are photo-degradation, acid hydrolysis, oxidation, and biodegradation. A complete analysis of them is quite complex, since these phenomena are all related to each other. In order to a better understanding of the reactions related to the natural oxidative ageing of the textiles, in the present paper we will consider only the oxidation process.

The oxidation reactions of cellulose involve the primary and secondary hydroxyl groups of the pyranose ring and result in carbonyl and carboxyl groups. This reaction can be accompanied by the opening the pyranose ring. In any cases the glucosidic bond becomes weaker; the formation of carboxyl groups induces a depolymerisation, thus reducing the polymerisation degree (DP) and the physical and mechanical strength of the material [1].

The conversion of dihydroxyl groups to dialdehyde by methaperiodate oxidation is a useful method widely used in derivatisation of cellulose to active the polymer at further reactions [2]. The crystalline fraction of cellulose complicates this reaction; thus the periodate oxidation on cellulose based materials as textiles (flax and cotton) and paper with different composition and characteristics, has been studied to understand the influence of crystallinity.

Periodate oxidation is a highly specific reaction to convert 2,3-dihydroxyl groups in two aldehyde groups, without significant side reactions [3]. When applied to glucose in the cellulose chain, this reaction cleaves the C2–C3 bond, according to the mechanism of Malaprade reaction [4,5]. The

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* Corresponding author. Tel.: +39-010-353-6082;
fax: +39-010-362-8252.
E-mail address: franceschi@chimica.unige.it (E. Franceschi).

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application or the quantitative understanding of this reaction has been hampered by complication arising from hemiacetal formation of aldehyde and crystalline nature of cellulose. The resulting compound is the dialdehyde cellulose (DAC) [6,7].

The oxidised samples become "models" to investigate the different levels of degradation and therefore the ageing degree in real materials. To investigate the cellulose behaviour at different level of oxidation, two different solutions of sodium methaperiodate were used: 0.1 and 0.4 M, for different times of treatment. Increasing the reaction time and the methaperiodate concentration, the degradation is more considerable. Since periodate oxidation of cellulose proceeds gradually from the amorphous to the crystalline phase, prolonged reaction time and higher oxidant concentration could be necessary to access into the inner region of the polymer.

The large number of studies published on thermal decomposition of cellulose is explained by important practical interests regarding fire safety [8], production of chemicals [9], high temperature applications as insulation material in electrical transformer [10].

Thermal analysis is a convenient, reproducible, and therefore useful method for characterising heterogeneous organic materials from plants. Cellulose, hemicelluloses and lignin, which are present in cellulose based materials, have been analysed by DSC [11,12]. In this research we have examined the assignment of the exothermic transition in DSC analysis of paper, flax and cotton and its components in order to understand their thermal behaviour in more detail.

The oxidised samples have been investigated by thermal analysis in order to evaluate the effect of the oxidation treatment on the thermal behaviour. The final aim of our work is to correlate the level of degradation of the oxidised samples with the natural ageing of the real cellulose based materials.

The results obtained suggest information in the restoration and conservation field of cellulosic materials.

2. Experimental part

2.1. Materials

The cellulose substrate was a Whatman no. 1 filter paper. This type of paper is obtained from cotton linters and can be considered as pure cellulose; its DP value is 1230. The textiles used in our research were linen "Artemisia" and cotton "Ghinea", supplied by Zecchi, Florence, Italy. Textiles were oxidised without preliminary treatments of scouring because any additives were absent; therefore the oxidative processes have been performed on natural untreated textiles, to prevent interference from extraneous substances.

Sodium methaperiodate ($NaIO_4$, 99.8%), cuproethylendiamine (CED), hydroxylamine hydrochloride and potassium bromide were laboratory grade products from Aldrich, used without further purification; deionised water was used throughout the work.

2.2. Methods

2.2.1. Methaperiodate oxidation

To investigate the cellulose behaviour at different level of oxidation, two different solutions of sodium methaperiodate were used.

The treatments were carried out for different times of reaction:

- linen: 2, 4, 8, 24, 48 h ([$NaIO_4$] 0.1 M); 2, 6, 24 h ([$NaIO_4$] 0.4 M);
- cotton: 4, 24, 120 h ([$NaIO_4$] 0.1 M); 2, 4, 6, 24, 48 h ([$NaIO_4$] 0.4 M);
- paper: 2, 8, 24, 48, 72, 120 h ([$NaIO_4$] 0.1 M); 1, 2, 6, 24, 48 h ([$NaIO_4$] 0.4 M).

The ratio sample/solution was kept for all experiments 1 g of sample for 100 ml of solution. The samples have been mixed in a closed vessel with the methaperiodate solution and the mixture was stirred gently at room temperature in the dark.

At the end of the oxidation processes the samples were filtered, washed with deionised water up to neutral conditions and dried.

For estimating the effects of the oxidation, viscosity measurements were performed in CED at 20 °C; constants $K = 1.5$ and $a = 1$ were used in the empirical equation ($\mathrm{DP} = K[\eta]^a$) [13].

The aldehydic content in the DAC samples has been determined converting DAC to nitrogen-containing derivative (oxime) by Schiff base reaction with hydroxylamine hydrochloride [6,14]. The better conditions for this reaction are the following.

Amine reagent (0.02 mol) was dissolved in 100 ml of pH 4.4 acetate buffer (0.1 M) and therefore 100 mg of DAC sample were added. The mixture was stirred at room temperature for 48 h. At the end of the reaction, the product was washed with deionised water, filtered and dried at 80 °C for 24 h. The elemental composition and the nitrogen content of the oximes obtained were determined by EA 1110 CHNS-O gas chromatographer.

2.2.2. FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra have been recorded with a FT-IR Bruker IFS 66 spectrometer with a Globar source (silicon carbide brought up to incandescence), equipped with a water cooling system and OPUS data processing program. Samples were analysed in transmittance, with accumulation of 50 scans and a resolution of 2 cm^{-1}.

Approximately 1 mg of sample was pressed into discs of variable thickness of potassium bromide. Thermal treatment of the discs was carried out to eliminate the humidity from the fibres, to prevent the overlapping between water peaks and carbonyl peaks of the DAC in the FT-IR spectra [1]. To this purpose, the discs were dried in oven at 80 °C for 2 days. The water content under normal laboratory conditions (25 °C and 65% RH) is about 2.4% for linen, 5% for cotton and Whatman paper, from moisture regain measures [15] performed in our laboratory.

2.2.3. Thermal analysis

Thermal analysis was carried out on 5–10 mg samples in an aluminium holder using two different calorimeters, either under nitrogen (70 $cm^3\ min^{-1}$) or oxygen (120 $cm^3\ min^{-1}$) flow.

A DSC Mettler Toledo 831^e was used with oxygen flow; the analysis was performed between room temperature and 650 °C at heating rate of 5 °C min^{-1}.

A TA Instrument DSC Modulated 2920 was used with nitrogen flow. The samples were cycled for 20 °C min^{-1} from 20 to 150 °C. Then, the samples were quenched and scanned for the second time with the temperature ranging from 20 to 450 °C at the rate of 5 °C min^{-1}.

3. Results and discussion

3.1. Oxidation

Since periodate oxidation of cellulose proceeds gradually from the amorphous to the crystalline phase, prolonged reaction time and higher oxidant concentrations could be necessary to access into the inner region of the polymer [16,17].

In this study several oxidations with different time of treatment and different concentration of methaperiodate solution were carried out. Increasing the reaction time and the methaperiodate concentration, samples degrade more extensively and a weight loss for all the samples has been observed, i.e. for linen oxidised for 24 h with 0.1 M $NaIO_4$ the weight loss is about 20%. Actually higher concentrations of the oxidant solution reduce the time necessary to reach a greater degree of oxidation. The oxidation modifies the aspect of materials, which become more stiff and brittle. When the oxidation conditions are very strong, they show a yellowing-brownish colour.

Finally the oxidation on cotton and linen involves different results; in particular, in the same conditions, linen undergoes ageing phenomena heavier than cotton. This fact could be due to the presence of lignin in linen; following the TAPPI T222 om-88 [18] the 3% of lignin has been evaluated in our fabric.

Table 1 shows the polymerisation degree of the three materials as a function of oxidation time and $NaIO_4$ concentration. By increasing the concentration of the oxidising agent, DP decreases faster; therefore the methaperiodate involves a strong depolymerisation of cellulose. Untreated textiles show a similar DP while the one of paper is lower; the decreasing of DP of paper is less rapid then textiles.

The aldehydic content in the DAC samples has been determined; in Scheme 1 the steps for this determination are reported.

By chromatographic analysis the nitrogen content (wt.%) of each sample was calculated. This value is directly related to the percentage of aldehydic groups, because the oximation reaction is quantitative. By a simple equation, the moles of carbonyl groups per 100 g of cellulosic samples and their number per 100 glucose units were found.

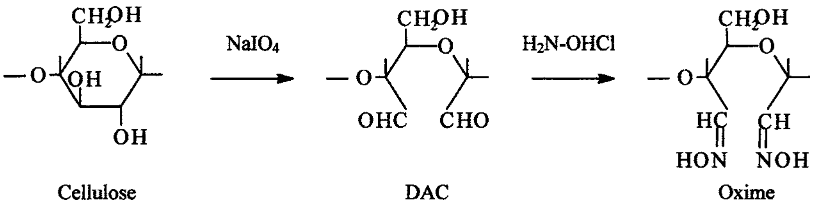
Table 2 shows the different oxidation degrees of paper, linen and cotton aged at different oxidation times and with different concentrations of the oxidising agent.

Table 1
DP of paper and textiles oxidised with different sodium methaperiodate concentration

$t_{oxidation}$ (h)	Paper	Linen		Cotton	
	0.1 M	0.1 M	0.4 M	0.1 M	0.4 M
0	1230	1930	1930	2130	2130
0.25	–	–	–	260	180
0.5	–	–	140	240	130
1	240	220	130	200	–
2	185	190	100	–	110
4	170	150	–	140	–
6	–	–	50	130	70
8	165	145	–	–	–
24	160	90	15	–	–

Table 2
Oxidation degree (CHO number per 100 glucose units) of paper and textiles calculated by hydroxylamine hydrochloride method

$t_{oxidation}$ (h)	Paper		Linen		Cotton	
	0.1 M	0.4 M	0.1 M	0.4 M	0.1 M	0.4 M
2	0.46	–	–	3.0	–	2.2
4	–	2.6	0.76	–	0.96	–
6	–	–	–	4.0	–	3.5
8	–	–	1.4	–	–	–
24	3.9	–	2.6	8.3	2.9	5.2
48	–	–	3.7	12	–	5.9
120	5.6	–	–	–	5.4	–
240	–	–	–	–	6.5	–



Scheme 1. Transformation of cellulose in oxime by hydroxylamine hydrochloride method.

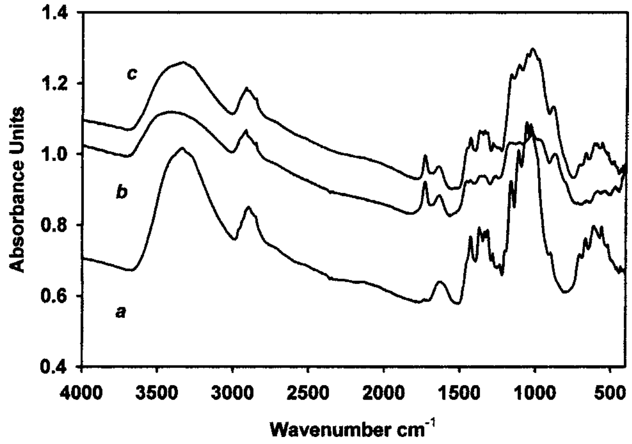


Fig. 1. FT-IR spectra of: (a) untreated cotton; (b) cotton oxidised for 24 h with 0.4 M $NaIO_4$; (c) cotton oxidised for 72 h with 0.1 M $NaIO_4$.

Linen treated with sodium methaperiodate 0.1 M for 48 h contains four aldehydic groups per 100 glucose units; this value doubles oxidising for only 24 h with 0.4 M $NaIO_4$. The oxidation of cotton with methaperiodate solution 0.1 M for 5 days introduces five aldehydic groups per 100 glucose units, as well as the treatment for 24 h with a solution 0.4 M.

Therefore, increasing the oxidation time, the number of aldehydic groups rises at the two methaperiodate concentrations used. Moreover, the values obtained show that the time necessary to reach a greater degree of oxidation is reduced increasing the oxidant concentration.

For oxidation with 0.1 M $NaIO_4$, linen and cotton show a comparable number aldehydic groups for the same time of treatment. Instead, oxidising with methaperiodate 0.4 M, for times longer than 6 h, linen shows a degree of oxidation greater than cotton.

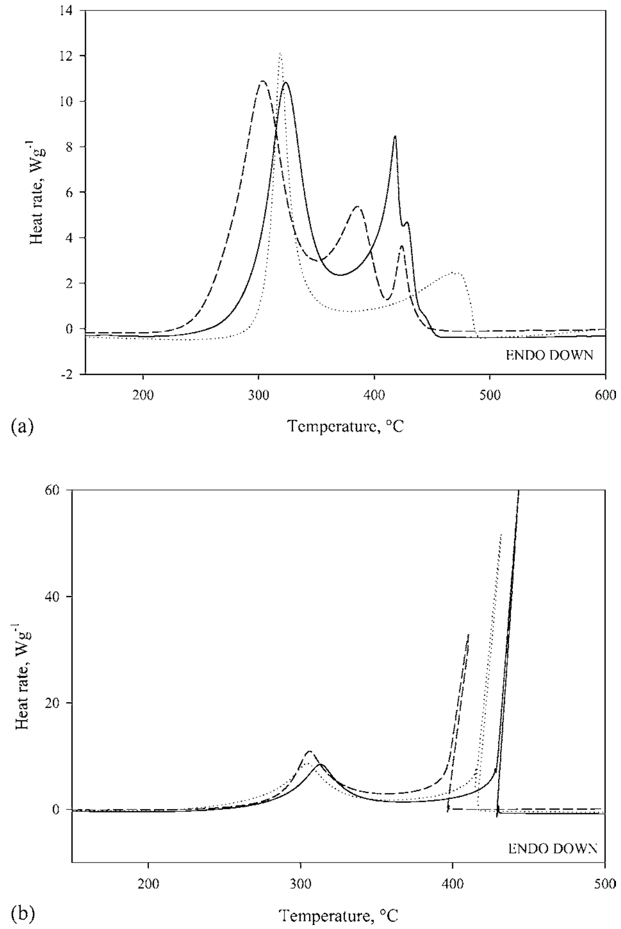


Fig. 3. (a) DSC curves of untreated materials in oxygen: (—) linen; (···) paper; (- - -) cotton. (b) DSC curves of oxidised materials in oxygen ([$NaIO_4$] 0.1 M for 24 h): (—) paper; (···) cotton; (- - -) linen.

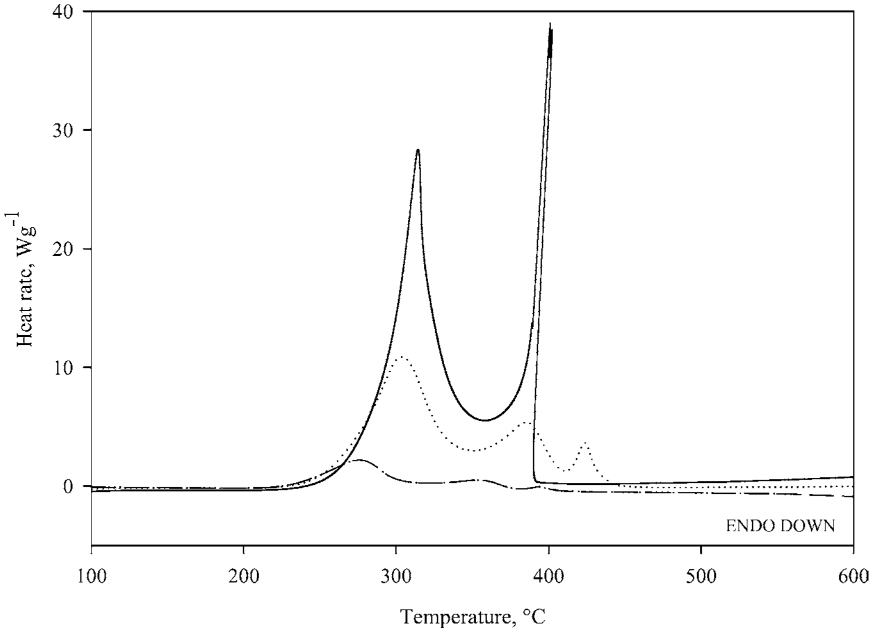


Fig. 2. Influence of scanning rate in oxygen on untreated cotton: (—) 10 °C min^{-1}; (···) 5 °C min^{-1}; (- - -) 1 °C min^{-1}.

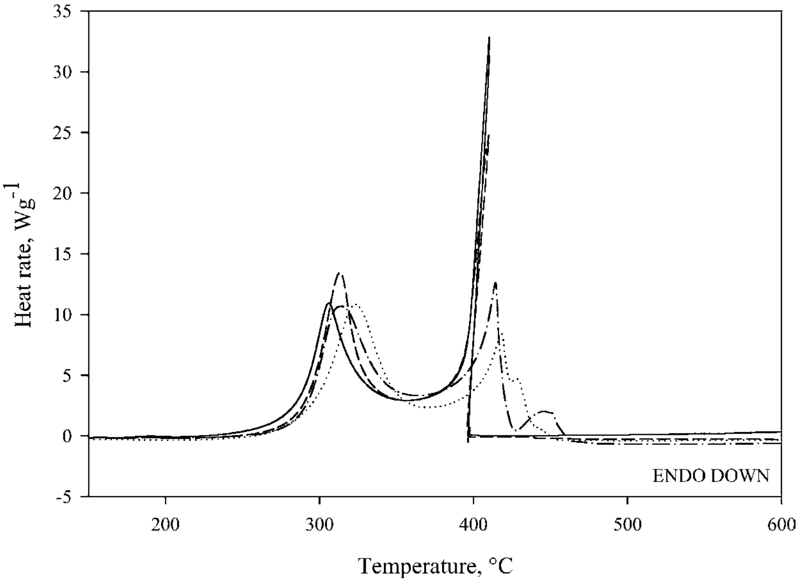


Fig. 4. DSC curves in oxygen of oxidised linen with 0.1 M $NaIO_4$ for: 2h (–·–); 8 h (- - -); 24 h (—); untreated material (· · ·).

The oxidation of linen with 0.4 M $NaIO_4$ for 48 h introduces the highest number of aldehydic groups per 100 glucose units (i.e. 12) and the sample looks very degradated.

3.2. FT-IR spectroscopy

The oxidation leads to the presence of two characteristics bands of DAC in the 1720 and 880 cm^{-1} regions; they increase from a small shoulder to a distinct band increasing the oxidation level. The broad band at 880 cm^{-1} can be assigned to the hemiacetal and hydrated form of the dialdehyde cellulose; the sharp band at 1740 cm^{-1} is characteristic of carbonyl groups stretching [19,20].

FT-IR analysis, both of untreated and of oxidised samples, is complicated owing to the high affinity of the samples with water. In fact the band of the absorbed and bonded water is in the region of carbonyl group (between 1635 and 1670 cm^{-1}) and sometimes it can be very broad and can hide the bands of the carbonyl groups. Moreover, in the oxidised samples the identification of the functional groups is complicated because aldehyde, keto and carboxyl groups of oxycellulose absorb in a very narrow region of the spectrum, between 1720 and 1780 cm^{-1}.

For samples oxidised with methaperiodate the identification of the aldehydic group is more difficult, since dialdehyde cellulose can exist in partially or completely hydrated

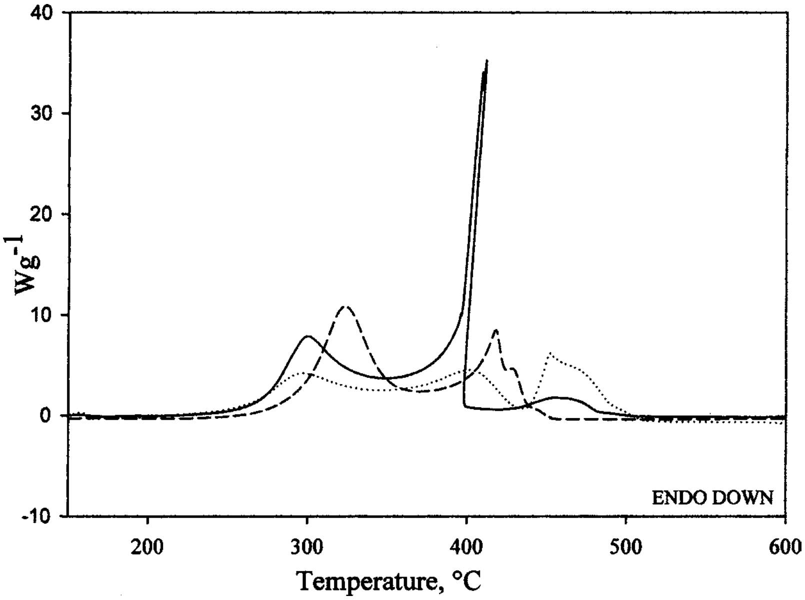


Fig. 5. DSC curves in oxygen of oxidised linen with 0.4 M $NaIO_4$ for: 2 h (—); 6 h (· · ·); untreated material (- - -).

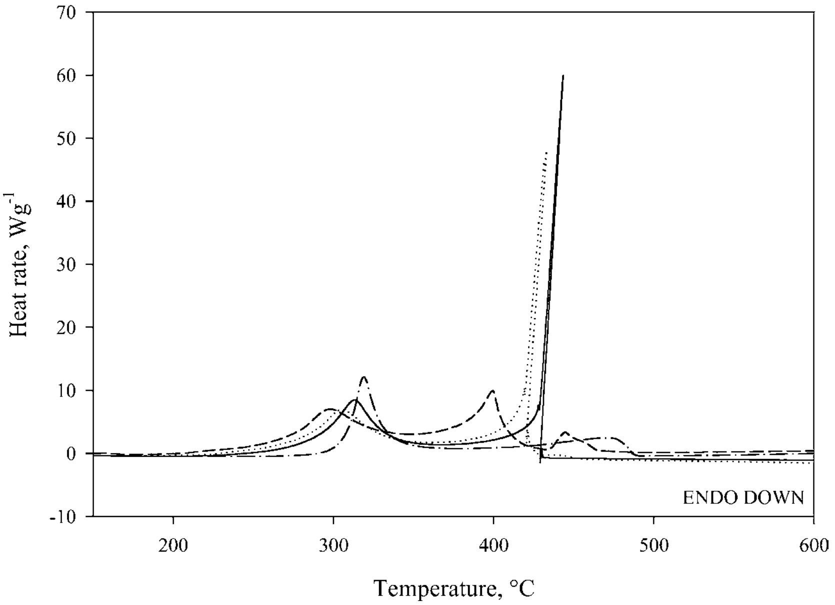


Fig. 6. DSC curves in oxygen of oxidised paper with 0.1 M $NaIO_4$ for: 24 h (—); 48 h (···); 72 h (- - -); untreated material (–·–).

form, as hemiacetal or as hemialdale, i.e. under forms that do not present a classical peak of the aldehydic carbonyl. For this reason, in order to reduce the amount of water, the samples discs were submitted to thermal treatment before FT-IR analysis: comparing the spectra of freshly prepared KBr discs with the same discs after thermal treatment, it was observed that the characteristic absorption at 1720 cm^{-1} for the carbonyl groups stretching becomes more evident, while the band of the water decreases. The finding suggests that the DAC involves structure containing water molecules.

The spectra of cotton, untreated and oxidised, are shown in Fig. 1; we can observe the aldehydic band at 1720 cm^{-1} after oxidation.

FT-IR analysis allows to evaluate qualitatively if the oxidation reaction leads to the formation of dialdehyde groups in the cellulose chain and semi-quantitatively the oxidation degree, by comparison of the absorbency of two bands:

- C=O stretching at 1720 cm^{-1};
- CH_2 stretching at 2900 cm^{-1}.

This evaluation does not allow to exactly calculate the degree of oxidation; therefore only the hydroxylamine hydrochloride method permits the aldehydic content determination.

3.3. *Thermal analysis of the dialdehyde cellulose*

The thermal degradation of cellulose and DAC in nitrogen and in air have been extensively studied [11,21,22]. The degradation of cellulose is composed of a set of concurrent and consecutive reactions.

Firstly the influence of heating rate on thermal decomposition in oxygen has been investigated. From experimental results, the suitable scanning rate is 5 °C min^{-1}; in Fig. 2 we can observe three peaks less broad than that the sample analysed at 1 °C min^{-1}. With faster rates (i.e. 10 °C min^{-1}) the scanning is not meaningful.

The pattern of DSC curves obtained in oxygen (see Figs. 3–7) is different from that observed in nitrogen (Fig. 8).

The experimental results show that the samples scanned in air and oxygen have the same thermal behaviour.

The strong exothermal at about 340 °C is attributed to charring and oxidation of the products of thermal decomposition of cellulose [23]. A second peak observed at just above 400 °C for textiles and at 480 °C for paper is likely to be due to oxidation of the char. In some cases this peak is very intense and sharp and it might indicate self-ignition of the char.

The shape and the peak temperatures in the DSC curves of untreated materials are different (Fig. 3a); these differences become less evident in the oxidised samples (Fig. 3b). The peak at 390 °C in the untreated cotton could be attributed to the starch; it is always used as finishing agent for textiles [24]. During the oxidation the methaperiodate solution removes this additive and consequently the corresponding peak disappears.

For every oxidation performed on textiles (Figs. 4 and 5) and paper (Fig. 6) the peak at 340 °C shifts to lower temperature and this effect is more evident when the oxidation conditions are stronger. The shift can be explained assuming that the oxidised cellulose is already degraded with a large fraction of oligomers and therefore less energy is necessary for their thermal decomposition. Fig. 7 shows the decrease of the first peak temperature of paper in function of oxidation time, where every value is represented with the experimental deviation.

In this way we can evaluate the level of degradation in the materials.

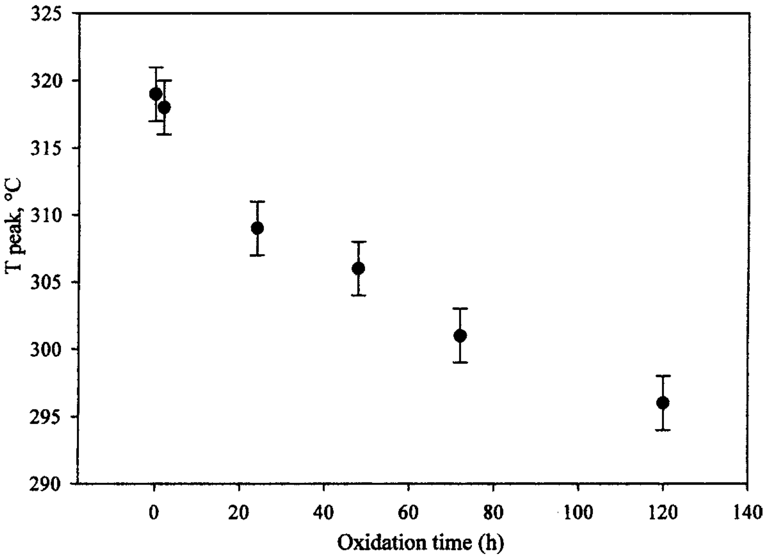


Fig. 7. Temperature of the first peak in function of the oxidation time (paper with 0.1 M $NaIO_4$), where every value is represented with the experimental deviation.

Underivatised cellulose in nitrogen decomposes through the formation of levoglucosan (1,6-anhydro-β-D-glucopyranose) and its further decomposition to breakdown products, as C, CO, CO_2, H_2O, and combustible volatiles. Chemical modification of cellulose is known to significantly change the thermal decomposition behaviour, i.e. the temperature range of decomposition usually shifts to lower temperature side [25]. The dialdehyde cellulose obtained here showed basically the same behaviour. The decomposition of unmodified cellulose in nitrogen started at about 300 °C. The DSC curves also show a characteristic change by oxidation of cellulose. The decomposition temperature of DACs shifted to lower temperature side with increase in the degree of oxidation (see Fig. 8). Beside the large endothermic peak of the original cellulose, a new broad endothermic peak at 200–220 °C appears, for cotton oxidised with methaperiodate 0.1 M for long times (24 and 120 h). These changes are likely to be associated with facilitated thermal scission of covalent bonds leading to the generation of volatile substances.

The solid residues in the pans after DSC scanning in nitrogen of cotton oxidised 0.4 M for 24 h have been analysed with FT-IR measurements. The characteristic absorptions of glucosidic structure at 1200–900 cm^{-1} (see Fig. 1b) decreases in intensity where weight loss occurs (residue at 300 °C). Complete disappearance of this structure is

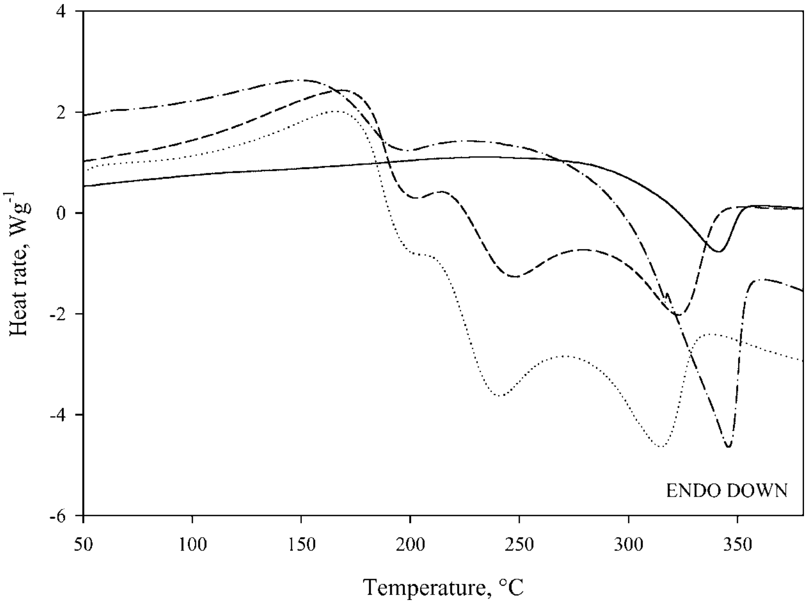


Fig. 8. DSC curves in nitrogen of oxidised cotton with 0.1 M $NaIO_4$ for: 2 h (–··–); 24 h (- - -); 120 h (···); untreated material (—).

observed in the residue at 450 °C. It is likely that at this temperature a cross-linked unsaturated aliphatic–carbonylic structure is formed, which might be the precursor of the char.

4. Conclusions

The studies here reported give an insight in understanding the structural changes occurring when cellulosic materials are oxidised.

The oxidation reaction has been performed by sodium methaperiodate. The quantitative evaluation of oxidation degree, usually underestimated due to the transformation of aldehydic groups in hemiacetal species, has been performed by a hydroxylamine hydrochloride method. By this chemical method the number of aldehydic groups introduced in oxidised materials is rapidly evaluated.

FT-IR spectrum of linen oxidised with a high methaperiodate concentration for long time of oxidation shows an aldehydic band more intense than the corresponding band observed in cotton and paper under the same oxidation condition. This results are also confirmed by the increase of the aldehyde content by hydroxylamine method.

DSC curves of the oxidised samples show changes in respect to the starting materials depending on the oxidation time and on the concentration of the oxidant. For every oxidation performed on textiles and paper the peak at 340 °C shifts to lower temperature and this effect is more evident when the oxidation conditions are stronger. The shift can be explained assuming that the oxidised cellulose is already degraded with a large fraction of oligomers and therefore less energy is necessary for their thermal decomposition.

In this way it is possible to obtain a model to investigate the natural ageing of real materials with the same level of degradation of the artificially oxidised samples.

The results obtained suggest information about the conservation of cellulosic materials in the cultural heritage field. It is well known that, before an accurate restoration work, it is necessary to analyse the historic objects and to know deeply their degradation level. Therefore, the thermal analysis applied on models of the same nature seems to be a suitable analytical technique for this aim.

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