Thermal Degradation of Linen Textiles: The Effects of Ageing and Cleaning

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Thermal degradation of modern and ancient linen fabrics was investigated by DSC and FTIR analysis in order to find a possible correlation between thermal behaviour and the age of linen. A similar pattern to that for cotton degradation was found, and the essential influence of impurities occurring naturally or occasionally was found. Moreover, in the case of old linen fabrics, a cleaning treatment can induce chemical degradation, which is favoured by fibre-weakening, as confirmed by SEM analysis. Although a possible ageing effect seems to be hidden by interference sources, thermal data can provide very helpful information about the status of an ancient linen fabric.

1. INTRODUCTION

The radiocarbon dating of ancient linen fabrics has recently received a critical evaluation in the experimental work of Kouznetsov and Ivanov (1995,1996) and of Kouznetsov *et al* (1994,1995,1996a,b) dealing with the age of the Shroud of Turin. In these studies, old linen samples were thermally treated in an artificial atmosphere containing combustion gases, CO and CO_2, in the presence of water and silver as catalyst, in order to simulate the conditions of the 1532 Chambéry fire, which caused serious damage to the Shroud.
According to these authors, the consequent fire-induced carboxylation of cellulose could give rise to a significant error in radiocarbon-dating results.

Taking into account the fact that many problems concerning the Shroud of Turin are still unsolved, a more general investigation of the thermal degradation of linen fabrics seemed to be very desirable in order to reach a better knowledge of the modifications induced in cellulosic fibres by heating. Moreover, the experiments reported in the work of Kouznetsov and his collaborators were carried out in air only, and a comparison with the results of pyrolysis of linen fabrics in an inert atmosphere was not reported.

Another method of measurement of the age of cellulose fibres by using X-rays was proposed by Kalyanaraman (1981,1984,1985,1987). This work demonstrated that the orientation of cellulose crystallites in an ancient cotton fabric is a function of its age since the polymer decomposes by slow oxidation. In the case of old linen fabrics, however, the correlation is strongly affected by treatments applied in fibre preparation, whereas the results could be utilised to estimate the age of the fibre if it underwent natural degradation only (Kalyanaraman, unpublished results).

On the other hand, thermal analysis was chosen by Calamari *et al*. (1990) to estimate the extent of cotton-weathering, since cotton fibres were found to follow very different and very characteristic patterns of thermal degradation, depending on the amount of naturally occurring impurities at the time of pyrolysis. An analogous investigation on flax fibres has not been previously reported.

In the present work, the thermal degradation of a modern linen fabric after heating in air and in an inert gas was investigated by differential scanning calorimetry (DSC) and Fourier-transform infra-red (FTIR) analysis. The results were compared with those obtained by working with two ancient known-age linen fabrics, which had been morphologically characterised by scanning electron microscopy (SEM). This study was carried out with the aim of finding a possible correlation between thermal behaviour and the age of linen fabrics that could justify the proposal for using thermal analysis for investigating the age of ancient linen fabrics such as the Shroud of Turin.

2. EXPERIMENTAL

2.1 Materials

The modern undyed linen fabric was kindly supplied by Linificio & Canapificio Nazionale. Two ancient linen fabrics were both Egyptian; the older was derived from a burial cloth, of 2500 BC, found in Assiut, whereas the other was of 1200 BC.

2.2 Cleaning of Textiles

Textile samples were treated with a 10% NaOH aqueous solution at the boil for 1 h, then washed thoroughly with deionised water, and finally dried in an electric oven at 100°C for 3 h. Some samples were bleached for 1 h with a 3.5% solution of hydrogen peroxide in a 10% NaOH boiling aqueous solution and then washed and dried as before.

2.3 SEM Analysis

The samples were mounted in aluminium specimen stubs with double-sided adhesive tape and coated with a 20-nm-thick gold layer in a rarefied argon atmosphere at 0.1-0.2 mbar, an Emitech K 550 Sputter Coater being used with a deposition current of 20 mA for 180 s. Microscopical investigation was performed with a Cambridge S 240 SEM, with an acceleration voltage of 15 kV and a 16-mm working distance.

2.4 Thermal Treatment and DSC Analysis

Textile samples were treated at the chosen temperature in a small oven closed and fluxed by air or nitrogen. After the treatment, the samples were rapidly cooled to ambient temperature. DSC analysis was performed in a Mettler TA 3000 apparatus equipped with a DSC 20 cell purged with nitrogen. The temperature program was set in the range from 50 to 450°C at a heating rate of 20°C/min. The experimental data were collected on a computer by using the Mettler Graphware TA72 program.

2.5 FTIR Spectrometry

The linen samples were examined in KBr pellets obtained by pressing the pulverised material at 1% concentration. The FTIR spectrophotometer was an ATI Unicam Genesis model, and the spectra were collected with the aid of WinFirst software.

3. RESULTS AND DISCUSSION

In a typical DSC thermogram of cellulosic fibres, there is generally an endothermal peak in the range 370-395°C, which has been shown to be primarily due to the production of levoglucosan (Shafizadeh, 1985). In the case of cotton fibres, this peak is sometimes partly or completely masked by an exothermal effect around 380°C, attributed to a base-catalysed cellulose-dehydration reaction that takes place in the presence of alkaline ions such as those of potassium (Calamari *et al.*, 1990).

Table I
DSC Data of the Decomposition Peak of the Modern Linen-fabric Samples after Various Thermal and Cleaning Treatments

Sample	Thermal Treatment	Temperature Peak (°C)	Enthalpy (J/g)
Unwashed	None	392.0	–29.3
Unwashed	200°C, 20 min in N_2	391.9	–23.2
Unwashed	300°C, 20 min in N_2	385.4	–5.0
Unwashed	200°C, 20 min in air	388.7	–11.3
Unwashed	250°C, 20 min in air	385.4	–9.1
Unwashed	280°C, 20 min in air	399.1	12.7
Unwashed	300°C, 20 min in air	387.9	98.8
Washed with NaOH	None	392.4	–183.4
Bleached	None	388,4	–145.6
Bleached	280°C, 20 min in N_2	386.2	–153.7
Bleached	280°C, 20 min in air	381.4	–169.0

In Table I, peak temperatures and enthalpy values of the thermal decomposition of the modern linen-fabric samples after various thermal and cleaning treatments are reported. According to ICTA (International Confederation for Thermal Analysis), the minus sign indicates endothermic changes in enthalpy. Moreover, in Fig. 1, DSC thermograms of the modern unwashed linen fabric, before and after thermal treatment in air at 300°C for 20 min, are compared, and a thermogram of a sample washed with NaOH is also reported.

The behaviour of the unwashed linen fabric subjected to various thermal treatments in air clearly shows the masking effect of an exothermal reaction on the endothermal cellulose decomposition. Hence only a global exothermal effect was observed after treating the samples over 250°C. The treatment in nitrogen, however, caused more limited thermal effects.

The marked influence of cleaning on the enthalpy value of the endothermal peak at 392°C is evident and confirms the trend observed for cotton fibres. Moreover, a thermal treatment on the bleached samples shows minor influence on the DSC data.

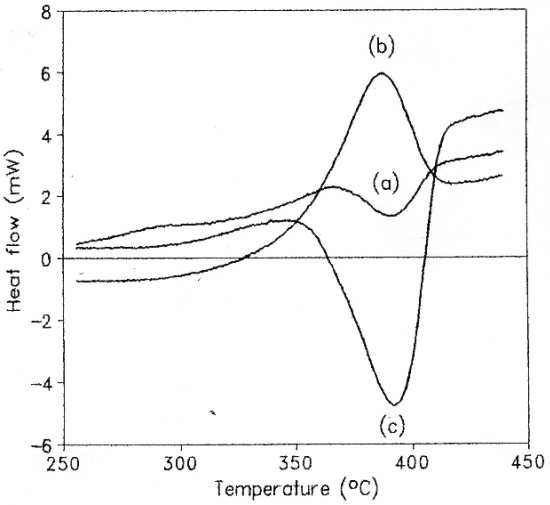

Fig. 1 DSC thermograms of the modern linen fabric: (*a*) unwashed; (*b*) unwashed, after thermal treatment in air at 300°C for 20 min; and (*c*) washed with NaOH

Table II
DSC Data of the Ancient Linen Fabrics after Thermal and Cleaning Treatments

Sample	Treatment	Temperature Peak (°C)	Enthalpy (J/g)
1200 BC	None	389.5	–140.7
1200 BC	280°C, 20 min in air	380.9	–131.9
1200 BC	Washed with NaOH	363.0	78.9
2500 BC	None	354.0	56.1
2500 BC	280°C, 20 min in air	355.2	142.1
2500 BC	Washed with NaOH	356.3	119.3

In Table II, the peak temperatures and enthalpy values that are observed in thermograms of both ancient linen samples are reported. In Fig. 2, thermograms of these linen fabrics are compared.

The linen sample of 1200 BC gives a thermogram very similar to that of the modern cleaned fabrics, even after a thermal treatment in air at 280°C for 20 min. The older sample, however, shows an exothermal peak around 355°C with a strong enthalpy increase after thermal treatment; the exothermal effect is retained, even if somewhat reduced, after washing with NaOH. This exotherrtt is attributable to β-cellulose decomposition as observed in a thermogram of a cotton boll and plant trash (Calamari *et al.*, 1990). Surprisingly, even the fabric of 1200 BC exhibits a similar exothermal peak at 363°C after washing with NaOH.

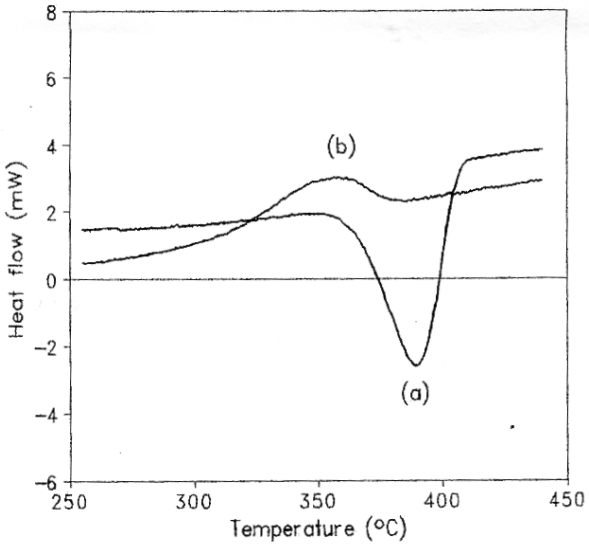

Fig. 2 DSC thermograms of the original ancient linen fabrics: (*a*) sample of 1200 BC; and (*b*) sample of 2500 BC

The substantially different behaviour of the ancient linen textiles was clarified by SEM analysis. In Figures 3-6, the micrographs of both linen samples are reproduced. The sample of 1200 BC (Fig. 3) shows the typical appearance of clean flax, but the fibres seem to be broken at some points, revealing a degree of weakening that can justify the sensitivity of this sample to NaOH-washing. On the other hand, the fabric of 2500 BC shows, besides many breakages either along the warp fibres (Fig. 4) or along the weft fibres (Fig. 5), a considerable amount of vegetable matter and other non-fibrous impurities (Fig. 6), so its anomalous thermal response is clearly understood.

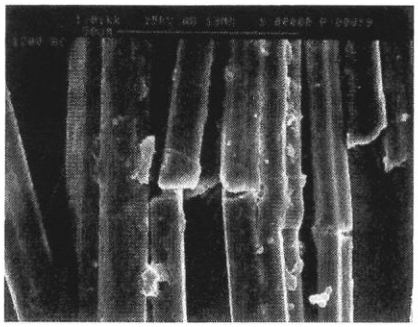

Fig. 3 SEM micrograph of the linen sample of 1200 BC

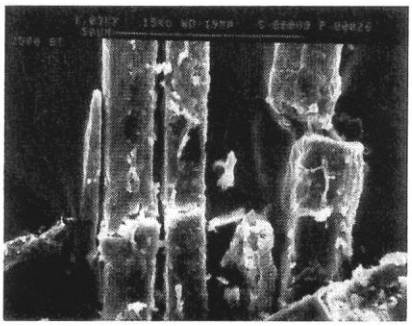

Fig. 4 SEM micrograph of the linen sample of 2500 BC, showing breakages along the warp

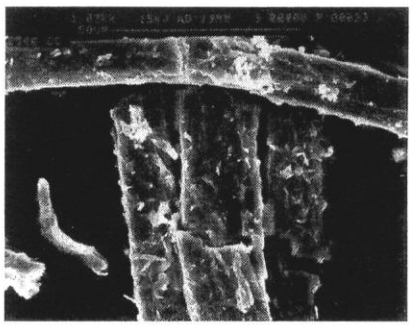

Fig. 5 SEM micrograph of the linen sample of 2500 BC, showing breakages along the weft

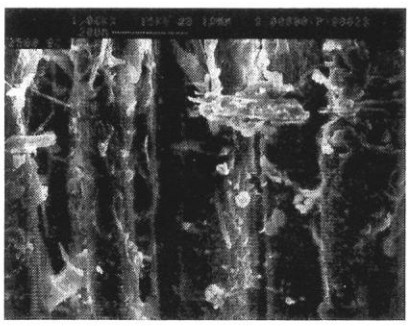

Fig. 6 SEM micrograph of the linen sample of 2500 BC, showing vegetable matter and non-fibrous impurities

The chemical modification induced in linen fibres by a thermal or cleaning treatment was investigated by FTIR spectrometry. In the range of absorption of carboxyl and carbonyl groups, two peaks are found, at 1728 and 1639 cm^{-1}, which appear to be influenced by thermal treatment. An analogous pattern is shown by the older linen fabric, whereas, in the spectrum of the original linen sample of 1200 BC, one peak at 1648 cm^{-1} is observed. The spectra of the original linen samples are compared in Fig. 7, and the spectra of the modern linen fabric before and after thermal treatments in air are reported in Fig. 8. The spectral data are summarised in Table III.

Table III
FTIR Spectral Data of Linen Samples Subjected to Various Treatments*

Sample	Treatment	Absorbency at:			Absorbency
		1728 cm–1 (A1)	1648 cm–1 (A2)	1639 cm–1 (A3)	Ratio (A1 /A3)
Modern	None	0.21	–	0.34	0.62
Modern	200°C, 90 min in air	0.20	–	0.32	0.63
Modern	200°C, 90 min in N_2	0.21	–	0.33	0.64
Modern	250°C, 20 min in air	0.31	–	0.35	0.89
Modern	280°C, 20 min in air	0.37	–	0.35	1.06
Modern	300°C, 20 min in air	0.47	–	0.43	1.09
Modern	300°C, 20 min in N_2	0.35	–	0.33	1.06
1200 BC	None	–	0.26	–	–
1200 BC	280°C, 20 min in air	0.23	–	0.31	0.74
2500 BC	None	0.43	–	0.51	0.84
2500 BC	280°C, 20 min in air	0.66	–	0.67	0.99
Modern	Washed with NaOH	–	0.30	–	–
Modern	Bleached	–	0.27	–	–

*The absorbency values have been normalised by assuming as reference the absorbency of the maximum peak (1075 cm^{-1}).

A thermal treatment of the modern linen fabric in air increases the absorbency of both peaks, but the peak at 1728 cm^{-1} is increased more by a temperature increase (Fig. 8). Hence the absorbency ratio, as reported in Table III, is a better index of the chemical modification induced by heating. This effect is smaller in nitrogen. Both the ancient linen fabrics show a similar pattern.

It is noteworthy, however, that the modern linen fabric subjected to a cleaning treatment gives only the peak at 1648 cm^{-1}, like the original fabric of 1200 BC. This spectral pattern, which is shown by microcrystalline cellulose, can be easily ascribed to the cleanliness of these samples and confirms the DSC data. Moreover, in various cellulose samples, the peak at 1648 cm^{-1}, attributable to a carbonyl group, appears to be shifted to 1639 cm^{-1} in the presence of the peak at 1728 cm^{-1}, which is very likely due to a carboxyl group.

From the literature, it is known that cellulose can undergo a variety of reactions by heating, such as depolymerisation, oxidation, or decomposition (Shafizadeh, 1985). The formation of carbonyl and carboxyl groups in cellulose heated to 190°C in air and in nitrogen was verified. Moreover, the rate of carboxylation in air was found to be about twice that of carbonylation, whereas in nitrogen the extent of the formation of oxidised groups was about a half of that in air. Thus the spectral data of linen fabrics fully agree with these observations and confirm that the cellulose carboxylation occurs in air as well as in nitrogen by pyrolysis, even in the absence of combustion gases. Hence the hypotheses regarding the thermal degradation and chemical modification of old linen textiles reported by Kouznetsov and Ivanov (1995,1996) and Kouznetsov *et al.* (1994,1995,1996*a,b*) appear to be not sufficiently proved, since the thermal degradation of cellulosic fibres shows a more complex pattern than the proposed model.

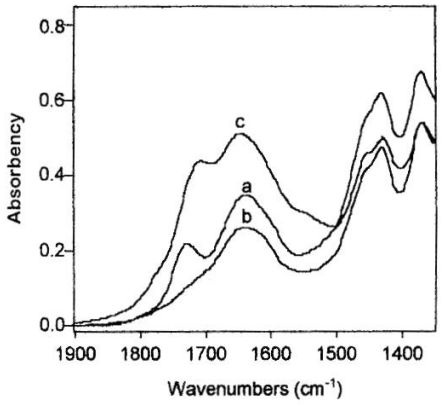

Fig. 7 FTIR spectra of original linen samples: (*a*) modern sample; (*b*) sample of 1200 BC; and (*c*) sample of 2500 BC

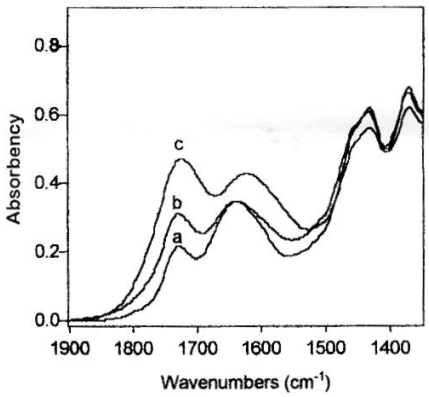

Fig. 8 FTIR spectra of the modern linen fabric: (*a*) untreated; (*b*) after treatment in air at 250°C for 20 min; and (*c*) after treatment in air at 300°C for 30 min

4. CONCLUSIONS

On the basis of DSC- and FTIR-analysis data, the thermal degradation of linen fabrics was thoroughly explained, and a similar pattern to that of cotton degradation was found. The essential influence, however, of textile cleaning on thermal behaviour was clearly demonstrated. Hence the thermal degradation of linen is mainly affected by naturally or occasionally occurring impurities. Moreover, a cleaning treatment of ancient linen can induce chemical degradation, which is favoured by fibre-weakening, verified by SEM analysis. Hence a possible ageing effect could be hidden in any case.

On the other hand, even if the proposal of thermal analysis alone for investigating the age of old linen fabrics seems to be not sufficiently promising, thermal data can provide very helpful information about the status of an ancient linen fabric, such as the Shroud of Turin, allowing a better understanding of the complex thermal-degradation phenomena of these fibres.

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REFERENCES

Calamari, T.A., Donaldson, D.J., and Thibodeaux, D.P., *1990.* Distinguishing Weathered from Unweathered Cotton by Thermal Analysis. *Amer. Dyest. Rep.,* **79**, No. 7, 42-47.

Kalyanaraman, A.R., 1981. X-ray Orientation Measurements of Cotton Fibres Using Yarn Samples. *Text. Res. J,* **51**, 722-724.

Kalyanaraman, A.R., 1984. Ageing and Fall in X-ray Orientation of Cellulosic Fibres. *Text. Res. J.,* **54**, 354-355.

Kalyanaraman, A.R., 1985. An X-ray Method of Dating Archaeological Fibre Artefacts. *MASCA J.,* **3**, 186-188.

Kalyanaraman, A.R., 1987. Cellulose Degradation and its Measurement. *Indian J. Pure Appl. Phys.,* **25**, 497-498.

Kouznetsov, D.A., and Ivanov, A.A., 1995. Near-IR Spectrophotometric Technique for Fast Identification of Carboxycllulose in Linen Fibres - A Preliminary Report. *Text. Res. J.,* **65**, 236-240.

Kouznetsov, D.A., and Ivanov, A.A., 1996. A Laboratory Model for Studying Environmentally Dependent Chemical Modifications in Textile Cellulose. *Text. Res. J.,* **66**, 111-114.

Kouznetsov, D.A., Ivanov, A.A., and Veletsky, P.R., 1994. Detection of Alkylated Cellulose Derivatives in Several Archaeological Linen Textile Samples by Capillary Electrophoresis/Mass Spectrometry. *Anal. Chem.,* **66**, 4359-4365.

Kouznetsov, D.A., Ivanov, A.A., Veletsky, P.R., Charsky, V.L., and Beklemishev, O.S., 1995. A Laboratory Model for Studies on the Environment-dependent Chemical Modifications in Textile Cellulose. *New J. Chem.,* **19**, 1285-1289.

Kouznetsov, D.A., Ivanov, A.A., and Veletsky, P.R., 1996*a*. Analysis of Cellulose Chemical Modification: A Potentially Promising Technique for Characterising Cellulose Archaeological Textiles. *J. Arch. Sci.,* **23**, 23-34.

Kouznetsov, D.A., Ivanov, A.A., and Veletsky, P.R., 1996*b*. Effects of Fires and Biofractionation of Carbon Isotopes on Results of Radiocarbon Dating of Old Textiles: the Shroud of Turin. *J. Arch. Sci.,* **23**, 109-121.

Shafizadeh, F., 1985. Thermal Degradation of Cellulose. In *Cellulose Chemistry and its Applications* (edited by T.P. Nevell and S.H. Zeronian), Ellis Horwood, Chichester, West Sussex, England, pp.266-289.