Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 349–358

THERMOANALYTICAL CONTRIBUTION TO THE STUDY ON PAPER DEGRADATION
Characterisation of oxidised paper

E. Franceschi, D. Palazzi and E. Pedemonte

Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy

Abstract

In this paper we studied the effect of oxidation on paper stability by means of simultaneous differential thermal analysis and thermogravimetry. In our laboratory we oxidised Whatman n. 1 chromatography grade paper and performed thermal analyses both on non-oxidised and on 6, 21 and 96 h oxidised samples. The results showed characteristic thermal effects, particularly performing the experiments under oxygen flow: it was noticed that the temperature of the main cellulose degradation DTA peak gradually decreases with the paper oxidation degree. An application of this method was extended to the study of differently oxidised parts of a 1948's book.

Keywords: cellulose, oxidation, paper stability

Introduction

This work is a part of a project which deals with paper consolidation, in the field of Cultural Heritage conservation; it requires a very accurate characterisation of paper, in particular concerning the oxidation products.

It is well-known that aged paper shows discoloration and brittleness, if compared with non-aged paper. The most common paper degrading chemical agents are: humidity, environmental and/or intrinsic acidity (intrinsic acidity is caused by some sizes, such as rosin or gelatine/alum, which can release acids by hydrolysis), heavy metals, light, oxygen. Besides cellulose, paper is also composed by other substances, such as sizes, fillers, addictives and, depending on the raw materials, lignin, hemicellulose, etc.

Discoloration and embrittlement are caused by two main reactions: hydrolysis and oxidation. The first reaction occurs both in acidic and in alkaline environment and affects the cellulose glucosidic bond [1]; acidic hydrolysis is more common than alkaline and it is the cause for cellulose depolymerisation. Oxidative degradation [2] is the second reaction affecting paper stability: it transforms the cellulose hydroxyl groups into carbonyl and carboxyl groups.

These considerations give an idea of the paper/environment interactions complexity; for this reason it was necessary to carry out this study on a simplified system,

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

based on a pure cellulose paper subjected only to oxidative degradation. Once achieved these results, it was necessary to compare them with really aged paper: to this purpose we performed thermal analyses also on paper from an old book.

Materials and methods

DTA and TG analyses were simultaneously performed by means of a Netzsch STA 409 apparatus.

DSC measurements were carried out by a Mettler Toledo DSC 821 apparatus.

The operative conditions were chosen on the basis of a preceding work [3], in which we stated that the heating rate of 1 K min^{-1}, under oxygen flow, was suitable in order to get in-phase DTA and DTG effects in a relatively short time.

The operative conditions were, therefore, the following: temperature range: 298–773 K; atmosphere: 100 mL min^{-1} O_2 flow; static air; heating rate: 1 K min^{-1}; sample amount: 12–25 mg for STA measurements, 4.0–5.5 mg for DSC experiments.

The study on paper oxidative degradation was performed on Whatman n. 1 chromatographic grade paper, made of pure cellulose. A further simplification was necessary for this process: oxidation was performed by means of $NaIO_4$, since it reacts preferably with the 2, 3 cellulose hydroxylic groups, while other oxidising agents, such as NaClO, H_2O_2, react randomly [4]. $NaIO_4$, 99% pure, was supplied by Aldrich, Germany.

The Whatman paper oxidation was carried out under the following conditions: $NaIO_4$ concentration=0.1 M; dried paper/oxidising solution ratio=1 g 100 mL^{-1}; temperature =295 K

Time of reaction, under magnetic stirring and light absence=6 h, 21 h, 96 h.
A Brucker FTIR IFS 66 infrared spectrophotometer was used to detect the occurrence of carbonyls on the oxidised paper.

X-ray diffractometry was carried out by means of a Philips PW 1830 X-ray generator, by using the CuK_α radiation, 2θ range=5.000–60.000, 2θ acquisition step=0.050, sampling time=2 s.

The really aged paper samples were drawn from a book, collecting poems by various authors, entitled 'I poeti di Ausonia'. This book was edited in Siena, Italy, by Editoriale Ausonia in 1948. As many other old books, its pages looked more brownished in the borders than in the centre; this behaviour was due to degradative oxidation, occurred formerly at the more exposed parts of the leaves. Several samples were drawn from different leaves: for each leave we drew two series of samples, one from the border and one from the central part. Inked parts were avoided.

Results and discussion

FTIR results for Whatman paper before and after 6 h of laboratory oxidation are shown, respectively, in Fig. 1 (A, B). The two spectra differ in the 1700–1750 cm^{-1} zone, where Fig. 1B shows the signal due to carbonyls occurrence. The FTIR spec-

trum shown in Fig. 2 is referred to the book paper: the bands originated by cellulose, such as in Whatman spectra, are visible. Figure 2 shows the C=O band at 1717.8 cm^{-1} and the band at 1506.6 cm^{-1}, typical of lignin; in this figure three bands due to kaolinite, present as an addictive, are also shown. The band of lignin indicated that the book paper was produced by wood pulp. The presence of kaolinite was confirmed also by X-ray diffractometry, as shown in Fig. 3.

Figure 4A shows DTA and TG curves for both non-oxidised and oxidated to different extents Whatman paper. DSC curves for analogue samples are reported in Fig. 4B; DSC measurements allowed us an upper accuracy in peak temperature determinations. Within the range 298–750 K paper degraded completely, until combustion

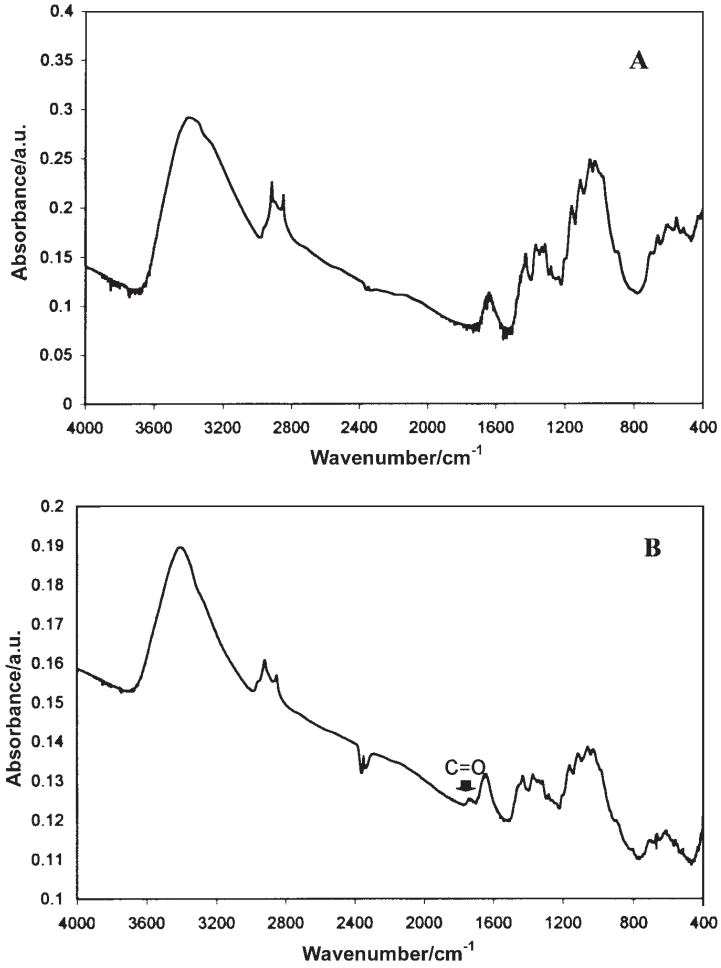

Fig. 1 FTIR spectra of n. 1, chromatographic grade Whatman paper: A – before oxidation; B – after 6 h of $NaIO_4$ laboratory oxidation; The C=O band due to carbonyls is visible in B

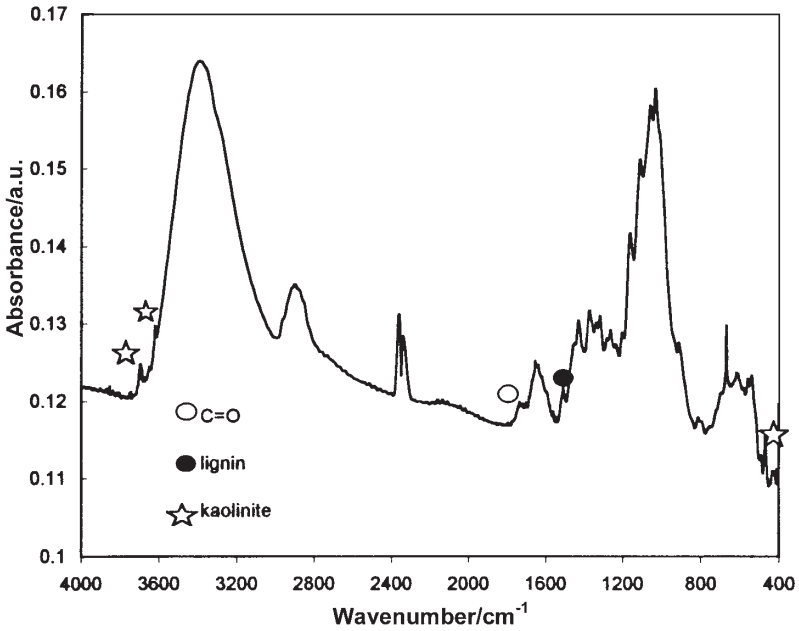

Fig. 2 FTIR spectrum of a leaf from the 1948's book. It is shown the presence of carbonyls, lignin, caolinite

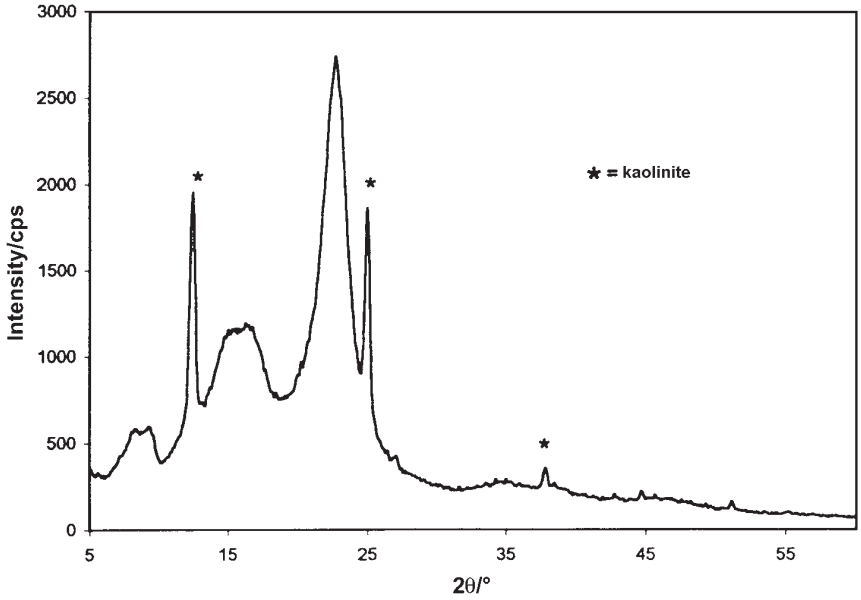

Fig. 3 X-ray diffractogram of a sample from the 1948's book: the presence of kaolinite was confirmed

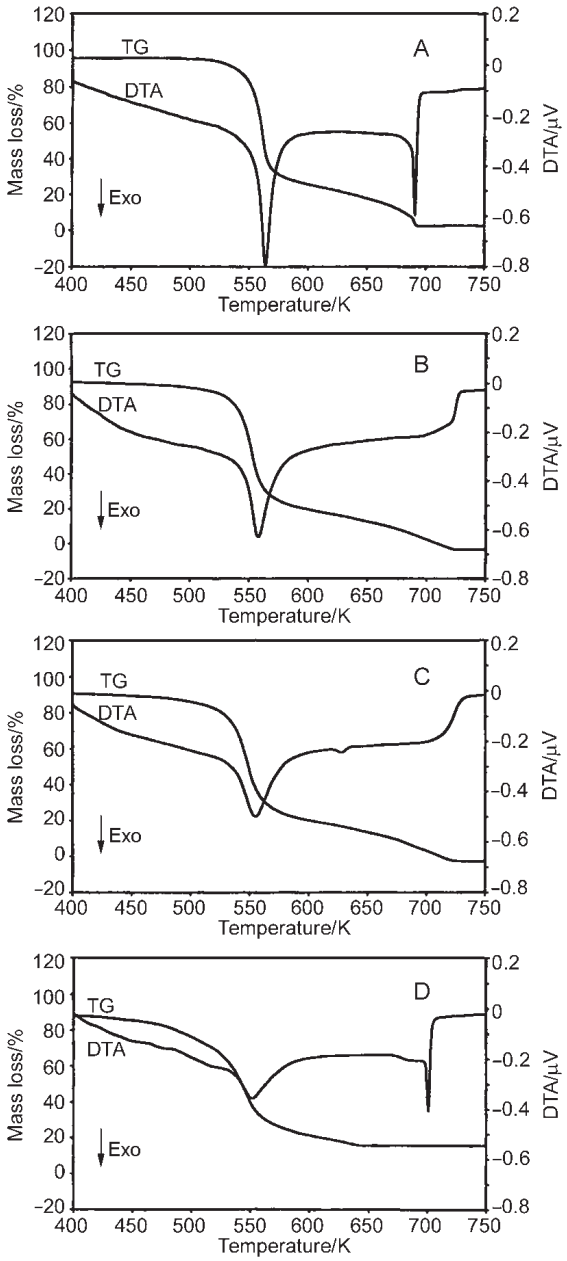

Fig. 4a DTA and TG curves of (from top to bottom): A – non-oxidised Whatman paper; B – Whatman paper oxidised by $NaIO_4$ for 6 h; C – Whatman paper oxidised by $NaIO_4$ for 21 h; D – Whatman paper oxidised by $NaIO_4$ for 96 h (Exothermal peaks downwards)

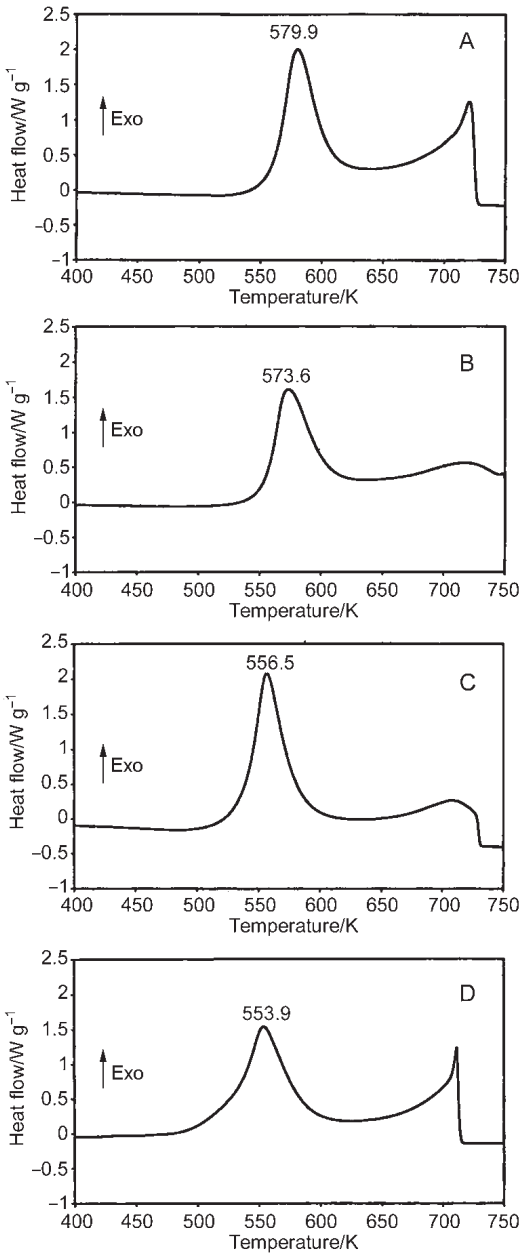

Fig. 4b DSC curves of (from top to bottom): A – non-oxidised Whatman paper; B – Whatman paper oxidised by $NaIO_4$ for 6 h; C – Whatman paper oxidised by $NaIO_4$ for 21 h; D – Whatman paper oxidised by $NaIO_4$ for 96 h (Exothermal peaks upwards)

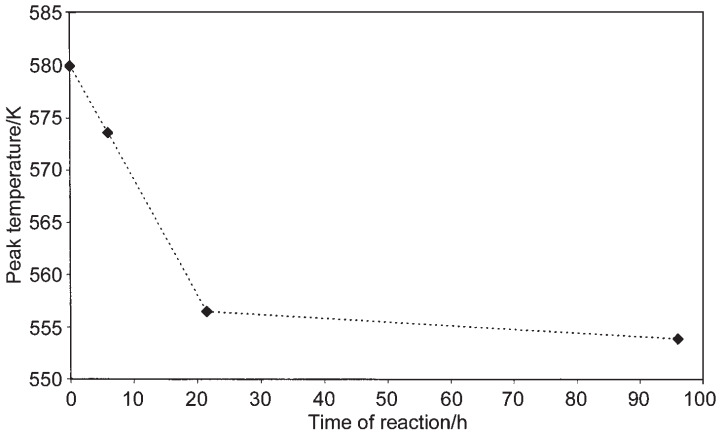

Fig. 4c Behaviour of the main degradation peak temperatures, measured by DSC, by increasing the time of paper oxidation

was achieved. Under our experimental conditions the process was globally exothermal. The comparison among the curves showed a gradual difference in the main degradation peak temperature, corresponding to the higher mass loss shown by TG curves: the DSC peak temperature corresponding to this thermal effect varied from 579.9 K for the non-oxidised sample to, respectively, 573.6, 556.5 and 553.9 K for the increasely oxidised samples. Figure 4C shows the behaviour of the DSC peaks *vs.* oxidation time. This difference is in agreement with an expected lower stability of oxidised paper.

It was interesting to compare the results on Whatman paper with a really aged paper. In Fig. 5 (A, B, C) the curves performed on internal points from the three leaves of the 1948's book are shown; Fig. 6 (A, B, C) represents the thermal behaviour of three samples drawn from the border of the same leaves. It was remarkable that each border sample showed a DTA peak temperature about 4–5 K lower than the samples drawn from the inner, less oxidised parts. This feature was in agreement with the results obtained on Whatman paper, althought in the real case, degradation could be caused also by several other factors (e.g. acid-catalysed hydrolysis).

Conclusions

The correspondence between the results on laboratory oxidised Whatman paper and on the book sheets showed that our experimentation was significative and our simplifications reasonable, even in the case of a more complex system, such as a real book sheet aged in a non-controlled environment.

It is furthermore remarkable that the differences between the DTA peak temperatures shown in Figs 5A–6A, 5B–6B, 5C–6C were constant, to confirm the suitability of thermal analyses as a tool of investigation in the studies on paper stability.

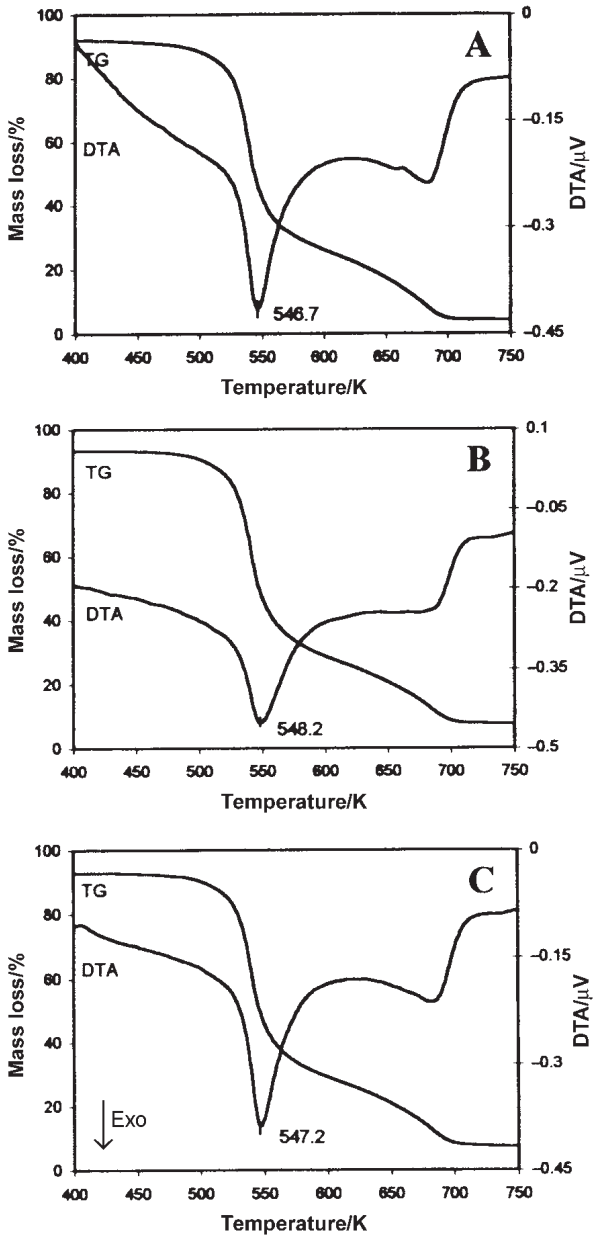

Fig. 5 DTA and TG curves of samples from the inner parts of three different leaves from the same 1948's book (Exothermal peaks downwards)

Further experiments are in progress, to ascertain the mechanical properties of differently aged papers.

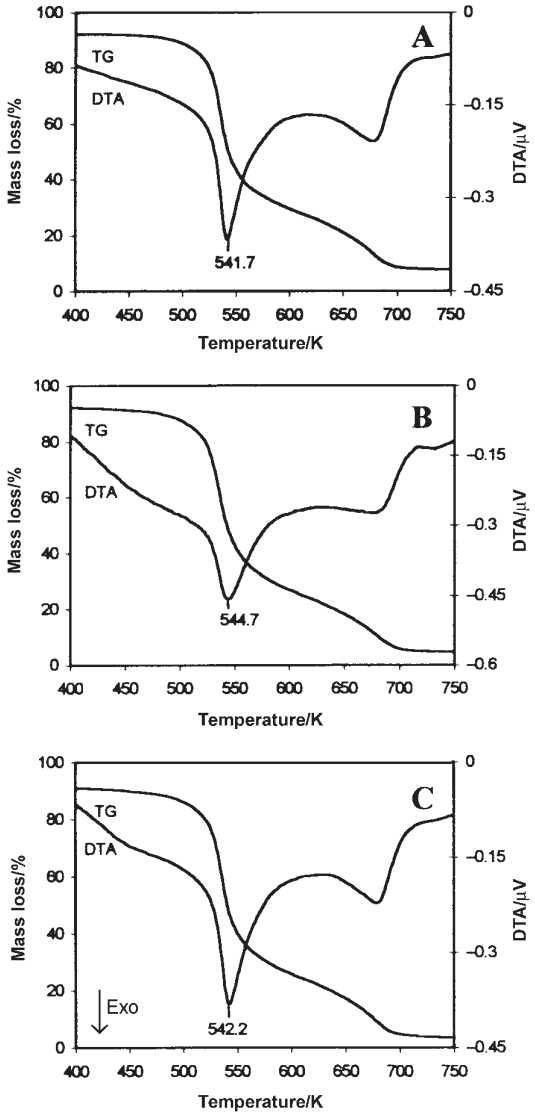

Fig. 6 DTA and TG curves of samples from the borders of three different leaves from the same 1948's book (Exothermal peaks downwards)

* * *

The authors thank the Italian MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), for the financial support to the research.

References

1 L. Santucci, Bollettino Ist. Centr. Patol. Libro, 38 (1982–83) 121.
2 H. A. Carter, J. Chem. Ed., 73 (1996) 1068.
3 P. Calvini, E. Franceschi and D. Palazzi, Sci. Technol. Cult. Herit., 5 (1996) 1.
4 P. M. Whitmore and J. Bogaard, Restaurator, 15 (1994) 26.