

THERMAL ANALYSIS OF NEW, ARTIFICIALLY AGED AND ARCHIVAL LINEN

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Abstract

The thermal degradation of new, and artificially aged fine Ulster linen and archival linen specimens from 19th century paintings were compared using thermogravimetric analysis and differential scanning calorimetry. Thermal degradation data from new and artificially aged linen were found to be similar in nature. Archival specimens showed a decreased major degradation temperature, an increase in char remaining at the end of the experiment and some evidence of a depressed glass transition temperature. These indicate natural ageing through chain scission. Evidence of a two-stage degradation process was observed in some archival specimens suggesting that an unknown additive was present.

Keywords: artificial ageing, linen, paintings, thermal degradation

Introduction

A recent research project has considered the chemical and mechanical degradation of 19th century English canvas paintings [1–2]. The work was based at Imperial College of Science Technology and Medicine in collaboration with The Courtauld Institute of Art, The Tate Britain and The National Gallery (all located in London). The project developed a physical model of a typical 19th century painting (consisting of linen, animal glue size and ground layers), which was used to investigate the failure mechanisms of 19th century paintings. This paper describes an investigation of the thermal degradation of new, artificially aged and archival linen.

Materials

Specimens for thermal analysis were prepared from the following materials:

i) New fine Ulster linen (style 3151 Ulster Weavers) – the linen was stretched, wetted and allowed to dry three times on a large loom.

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ii) Acid-aged fine Ulster linen (style 3151 Ulster Weavers) – the linen was firstly prepared as for specimens *i*). Then a 450×450 mm square of the linen was stretched onto a PVC stretcher, fastened with stainless steel screws and immersed in 10% sulphuric acid for 500 h with all light excluded. On removal, the linen was washed and neutralised with 5% ammonium hydroxide until the pH of the rinse water was neutral. The linen was allowed to dry before removal from the stretcher.

iii) Thermally aged, acid-aged linen – the linen was prepared as for specimens *ii*), and then thermally aged at 60°C and 55% R.H. for 214 days with all light excluded.

iv) Naturally aged specimens – linings** removed from a range of 19th century paintings (Table 1). Each lining had been previously subjected to mechanical testing and found to have similar selected mechanical properties to specimens prepared as in *ii*) [3].

All materials were pre-conditioned at 54±5% R.H. for a minimum of 72 h before thermal analysis commenced.

Thermogravimetric analysis

Table 1 Archival specimens

Specimen	Date	Artist	Painting title	Lining
L001	1840–1845	Turner	Sunrise, with Boat between Headlands	Loose
L002	1843–1900	Highmore	Equestrian portrait of King George II	Glue
L003	1882–1930	Romney	Lady Hamilton as Circe	Glue
L004	1856–1858	Frith	The Derby Day	Loose
L005	19th c.	Wright	Portrait of Lady Elizabeth Churchill	Glue
L006	1820–1870	Aken	An English Family at Tea	Glue
L007	1843	Turner	The Sun of Venice Going to Sea	Loose
L023	1840–1845	Turner	Landscape with Water	Loose
L024	1845	Turner	Venice, Evening, Going to the Ball	Loose
L025	1840–1845	Turner	Sunrise, a Castle on a Bay, Solitude	Loose

Experimental procedure

Approximately 5 mg of the specimen was placed in an open aluminium crucible. The specimens were heated in a Shimadzu TGA50 apparatus at a rate of 10°C min⁻¹ from room temperature to 500°C. A nitrogen atmosphere was used for all tests with a flow rate of 60 mL min⁻¹. Repeat scans were completed to determine data repeatability. The quantity of absorbed moisture, the temperature at which the maximum rate of degradation occurs, the initial and culmination temperatures of the major degradation process and the quantity of char remaining were calculated for each specimen.

** Secondary fabric mounted on a painting's stretcher to protect the rear of the painting and to improve structural integrity.

Experimental results

Excellent repeatability was achieved with all specimens. The data obtained compared favourably with previously published TG data in nitrogen for the degradation of cellulose [4–5], retted flax [6] and linen [7–9].

A comparison between typical TG scans obtained for new linen, acid-aged linen and thermally aged, acid-aged linen is shown in Fig 1. An initial mass reduction due to the loss of absorbed moisture of approximately 4% was observed between room temperature and 100°C for new and acid-aged linen. The absorbed moisture observed in acid-aged linen that had been thermally treated was approximately 2.6%. The major mass loss relates to the thermal degradation of the cellulose molecule. The detailed mechanism of this degradation is not clear, but it is generally accepted that the main reaction at temperatures between 300°C and 600°C is chain scission at the 1–4 glucosidic bonds [4, 9]. This mass loss was typically 75% for new linen, 79% for acid-aged linen and 82% for thermally aged, acid-aged linen. The initiation (~300°C) and culmination (~375°C) of the major stage of the degradation were similar for all specimens. The maximum rate of mass loss occurred at approximately 365°C for all specimens (obtained from the first derivative of the TG curves). The quantity of residual char at 500°C varied between 14–18%.

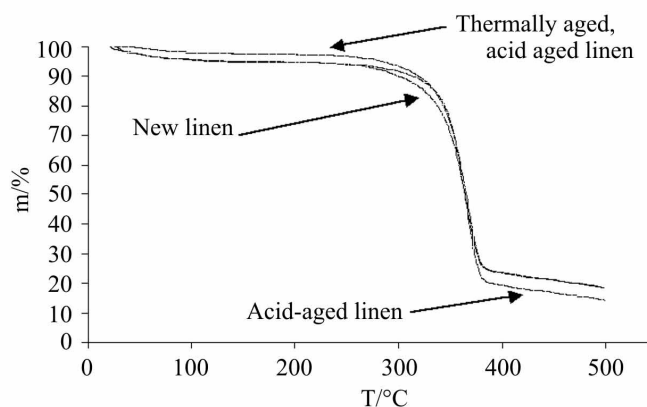


Fig. 1 TG data for new and artificially aged fine Ulster linen

Figures 2–3 show typical scans from the archival glue paste^{***} and loose^{****} linings respectively. Two distinct responses to heating were observed in both sets of specimens. Linings L001, L002, L004, L007 and L025 exhibited a thermal response similar to that observed for the specimens derived from modern linen: that is, loss of absorbed moisture below 100°C and then a one-stage major mass loss. However, the remaining archival specimens exhibited a two-stage degradation process above

^{***} Secondary fabric glued to the rear of the primary canvas using animal or starch glue.

^{****} Secondary fabric mounted on the painting stretcher to protect the rear of the primary canvas.

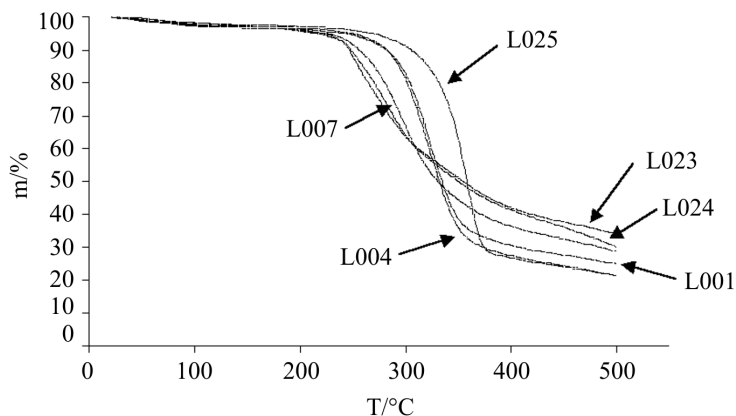


Fig. 2 TG data for 19th century glue linings

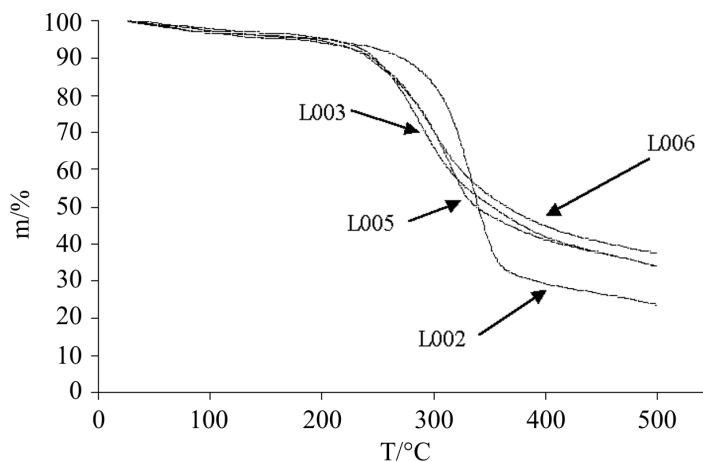


Fig. 3 TG data for 19th century loose linings

100°C. The differences observed in the data are reflected in the initiation temperature, the culmination temperature, the temperature at which the maximum rate of mass loss occurred, and in the total mass lost for the archival linings. The major mass loss in specimens found to undergo a one-stage process initiated at an elevated temperature (230–245°C) compared to those that possessed a two-stage process (190–205°C). The temperature range over which the major degradation occurred was increased for specimens undergoing a two-stage degradation process (culmination temperatures 425–450°C), compared to the remaining archival specimens (culmination temperatures 405–410°C). The maximum rate of mass loss occurred between 315–360°C for one-stage processes and between 250–300°C for two-stage processes. The total mass lost was decreased for a two-stage degradation (~65%) compared to that observed for a one-stage process (~76%).

It was initially assumed that the two-stage degradation process observed with some specimens was due to the presence of a size layer, for example, rabbit skin glue (RSG). Therefore, acid-aged linen specimens with two layers of 5% RSG applied, which were then thermally aged were analysed. A one-stage degradation process was observed, however; the amount of char remaining (~23%) was more similar to the archival specimens.

The archival specimens that had a two-stage degradation process were known to be more acidic in nature than those that had a one-stage degradation process [3]. Specifically, all archival specimens with a two-stage degradation process had a pH below 4.10. This increased acidity suggested increased chain scission and explains the lower initiation temperature observed during thermal analysis. Specimen L007 might be considered to have a degradation behaviour that is intermediate in nature and was found to have a pH of 4.14. However, L025 has a clear one-stage degradation but a pH of 4.19. Previously obtained TG data for de-acidified linen archival specimens [10] reported a two-stage degradation process indicating that the acidic nature of the specimen had not influenced the degradation process.

The thermal degradation of the archival linings (Figs 2–3) may be contrasted to that for the specimens originating from modern linen (Fig. 1). The initial loss of absorbed moisture between room temperature and 100°C was similar for all specimens (~4%). The initiation temperature of the major degradation process was reduced for all archival specimens compared to artificially aged materials. For specimens demonstrating a one-stage degradation process this reduction was typically 50°C, for specimens demonstrating a two-stage degradation process the reduction was approximately 100°C. The temperature at which the maximum rate of mass loss occurred was also decreased for the archival specimens compared to specimens originating from modern linen. The quantity of char remaining at 500°C was increased for all the archival specimens. The reduced initiation temperature and reduced temperature at the maximum rate of degradation was an indicator of a reduction in the mean molecular weight of the polymeric chains. The increased quantity of char observed in the archival specimens is likely to include a contribution from the non-volatile degradation products of the glue or size layers and was reflected in the artificially aged specimens containing size.

Differential scanning calorimetry

Experimental procedure

Specimens were heated in open aluminium crucibles from room temperature to 500°C at a rate of 10°C min⁻¹ in a Shimadzu DSC50 apparatus. The specimens were first heated from ambient to 150°C, allowed to cool and then heated from ambient to 500°C. This regime ensured the removal of any volatile substances. The mass of the specimen was approximately 4 mg. A nitrogen atmosphere was used for all experiments with a flow rate of 20 mL min⁻¹. The scans were baseline corrected. Repeat scans were completed to check data repeatability.

Experimental results

Good agreement with previously published DSC data for linen was obtained [6–7]. The general form of the DSC spectra for new, acid-aged and thermally aged, acid-aged linen was similar (for example Fig. 4 for new linen). A small endothermic peak or baseline shift occurred at approximately 240°C with all specimens and may be evidence of the glass transition temperature. A large endothermic peak then occurred at approximately 375°C in the new linen, 370°C in acid-aged linen and 369°C in thermally-aged, acid-aged linen: this was attributed to the major degradation process.

All archival specimens except L004 showed two or three endotherms between ambient temperature and 150°C (for example L005 Fig. 5). These endotherms typically occurred in the region 95–130°C and may be due to size or other additives. For specimens characterised by a two-stage TG degradation process, the major endotherm occurred at a lower temperature compared to specimens characterised by a one-stage degradation process (Table 2). Compared to specimens based on new linen the temperature at which the major endotherm occurred was decreased. In common with the specimens based on new linen, a small endotherm may identify the glass transition temperature. For archival spec-

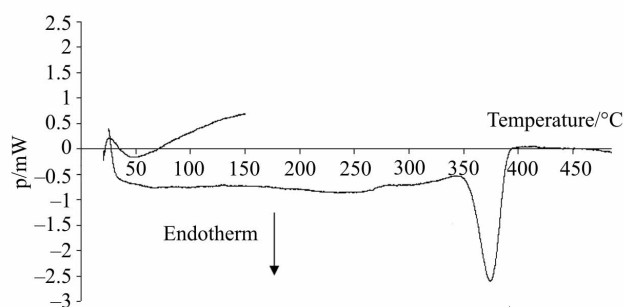


Fig. 4 Typical DSC data for new linen

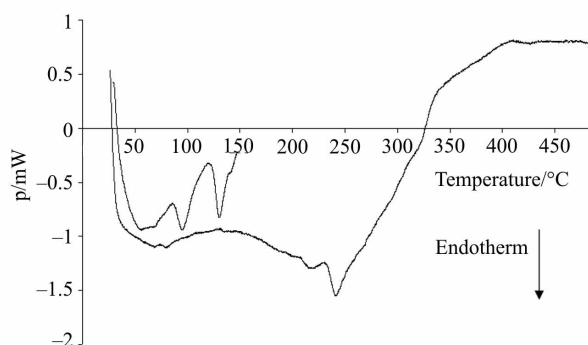


Fig. 5 Typical DSC data for L005

Table 2 Temperature at which the major endotherm occurred (DSC) and pH of archival specimens (from [3]).

Specimen	Temperature /°C	Mean pH
New linen	375	–
Acid-aged linen	370	–
Thermally aged, acid-aged linen	369	–
L001 - 1 stage	306	4.42
L002 - 1 stage	332	4.26
L003 - 2 stage	246	3.75
L004 - 1 stage	304	4.99
L005 - 2 stage	241	4.07
L006 - 2 stage	245	3.56
L007 - 1 stage	294	4.14
L023 - 2 stage	248	3.76
L024 - 2 stage	245	4.02
L025 - 1 stage	327	4.19

imens, this appeared to be slightly depressed compared to new linen specimens and typically occurred at approximately 230°C.

Conclusions

The following conclusions can be drawn from this comparison of the thermal degradation of new, artificially aged and archival linen:

- i)* Thermal analysis (TG and DSC) results for new linen and for artificially aged linen were generally similar. This finding was rather unexpected, since it had been thought that evidence of chain scission of the cellulose molecules would be observed in the artificially aged specimens corresponding with the reduction in selected mechanical properties of these specimens when compared to new linen [1–2].
- ii)* For the archival samples, TG and DSC data were different to both new and the artificially aged linen, although some of the archival samples show a similar one-stage TG decomposition process to new and artificially aged canvas. Interestingly, these one-stage archival samples have, at least among this group, a relatively high pH (above 4.10). All the two-stage samples have a pH below 4.10.
- iii)* There is evidence of a relationship between the one- and two-stage archival specimens and the temperature of the major endotherm observed with DSC: all the two-stage specimens have the endotherm around 250°C and the one-stage specimens around 300°C.

iv) For archival specimens, evidence of a decreased initiation temperature, a decreased temperature of the major degradation and a depressed glass transition temperature suggested that chain scission had occurred in these specimens.

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References

- 1 D. J. Carr, The Chemical and Mechanical Degradation of 19th Century Canvas Paintings, unpublished report, Department of Mechanical Engineering, Imperial College of Science Technology and Medicine, University of London, April 2001.
- 2 R. D. Hibberd, D. J. Carr and C. R. T. Young, The Failure Mechanisms of Model 19th Century Primed Canvases, poster presentation at the International Institute for Conservation of Historic and Artistic Works (IIC) 18th Congress, Melbourne, Australia, 10–14 October, 2000.
- 3 C. R. T. Young and R. D. Hibberd, A Comparison of the Physical Properties of 19th Century Canvas Linings with Acid-Aged Canvas, pre-prints of the 12th triennial meeting of the International Council of Museums – Committee for Conservation (ICOM-CC), Lyon, France 1999, (James & James, London), Vol. I, pp. 353–360.
- 4 C. J. Keatch and D. Dollimore, An Introduction to Thermogravimetry, Heyden and Son Ltd., London, UK 1975.
- 5 D. Dollimore and J. M. Hoath, *Thermochim. Acta*, 45 (1981) 87.
- 6 B. Wielage, Th. Lampke, G. Marx, K. Nestler and D. Starke, *Thermochim. Acta*, 337 (1999) 169.
- 7 S. Kokot and P. Yang, *Anal. Chim. Acta*, 304 (1995) 297.
- 8 P. Yang and S. Kokot, *Appl. Polym. Sci.*, 60 (1996) 1137.
- 9 M. Z. Sefain, M. H. Fadl, N. A. El Wakil and M. S. A. El-Salam, *Polym. Degrad. Stabil.*, 50 (1995) 195.
- 10 M. Odlyha, Characterisation of Cultural Materials by Measurement of their Physiochemical Properties, unpublished PhD thesis, University of London, 1998.