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# THERMAL DEGRADATION OF COLLAGEN-BASED MATERIALS THAT ARE SUPPORTS OF CULTURAL AND HISTORICAL OBJECTS

*P. Budrugeac* [1*], *L. Miu* [2], *V. Bocu* [2], *F. J. Wortman* [3] *and C. Popescu* [3]

[1]ICPE-CA-Research and Development Institute for Electrical Engineering, 313 Splaiul Unirii, Sector 3, 74204 Bucharest, Romania
[2]Leather and Footwear Research Institute, 93 Ion Minulescu, Sector 3, 74259 Bucharest, Romania
[3]DWI-Deutsches Wollforschungsinstitut an der RWTH Aachen e. V., Veltmanplatz 8, 52062 Aachen, Germany

## Abstract

The thermal analysis methods (TG, DTG and DTA) were used for the investigation of the thermal degradation of some recent manufactured tanned leathers, leathers that are supports of cultural or historical objects (leather from book covers (XVII–XIX centuries); leather from an Austrian belt (Franz Joseph period), Cordoba leather (XVII century), lining leathers), recent and patrimonial parchments and recent extracted collagen (sorts of collagen obtained from bovine leather at different pH-values, bovine collagen with different hydration degree). At progressive heating, all investigated materials exhibit two main successive processes, associated with the dehydration and thermo-oxidative degradation. Each analyzed material has a characteristic thermal analysis curve (TG, DTG and DTA) that can be considered a material 'fingerprint'. This result suggests the use of the thermal analysis methods to identify of leathers from which the patrimonial objects are manufactured. The rate of thermo-oxidation of recent manufactured tanned leathers is substantially higher than the rate of the same process corresponding to naturally aged leathers that exhibit values of the thermo-oxidation rate appropriate to those obtained for parchments and collagens. The rate of thermo-oxidation of leather can thus be used as a criterion to distinguish between recent manufactured leather and patrimonial one.

**Keywords:** collagen-based materials, 'fingerprint', historical objects

## Introduction

The use of leather products (light leather: tanned skin for footwear, garments, book-binding leathers; heavy leathers: for soles and belts; parchment, collagen, clay, etc.) is strongly dependent on the historical a cultural heritage. Most of the objects in a museum are produced on leather, leather derivations or parchments. Among the problems of the museum custodians, private collectors or antiquaries one may specify:

*a*) the identification of the cultural or historical object (author, period in which the object was manufactured, etc.);

* Author for correspondence: E-mail: bp@icpe-ca.ro

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*b*) the distinction between the original artifacts and the bootlegs;
*c*) the evaluation of museum environmental risk;
*d*) the restoration of the patrimonial objects;
*e*) the achievement of some suitable preservation treatments.

There is a long history of the procedures to identify the patrimonial objects and to evaluate the impact of environmental factor on them. The development of the analytical techniques improved these procedures. The techniques give information concerning the physical and chemical properties of a material using samples of 3–20 mg. As it is noticeable from literature, only during the last 10 years these methods were often used in the field of patrimonial objects. Some results obtained by thermal analysis methods (DSC, TG, dynamic mechanical thermal analysis (DMTA), thermomicroscopy), applied to leather, parchment and paper from patrimonial objects, were reported in several papers [1–6]. The [1–5] are from the volume 165 of the Thermochimica Acta Journal, dedicated to the recent works performed within the area of 'Research for Protection, Conservation and Enhancement of Cultural Heritage'. Very interesting results were also reported by Chahine [2] who used DSC technique in order to investigate the hydrothermal stability of new, naturally and artificially aged vegetable tanned leathers and parchments. The modifications of the parameters (temperature, enthalpy change) of the denaturation process, determined by DSC, were associated with those of other chemical and mechanical characteristics.

Recently, Marcolli and Wiedemann [6] used TG and DTG techniques to study the thermo-oxidative degradation of paper and paper-like materials for some decades. It was pointed out [6] that TG and DTG methods permits to distinguish between the original paper which was used by artist and possible forgeries.

The purpose of the investigation reported here is to characterize and compare recent manufactured leather, naturally aged leathers (patrimonial leathers), recent manufactured parchments, patrimonial parchments and some recent extracted sorts of collagen (sorts of collagen obtained from bovine leather at different pH-values, bovine collagen with different hydration degree), using the thermal analysis methods (TG, DTG and DTA). The modifications of thermo-oxidative degradation parameters as a result of the naturally aging will be discussed and a criterion to distinguish between recent manufactured tanned leather and patrimonial tanned leather will be suggested.

## Experimental

### *Materials*

Our experiments were carried out on the following samples:

• recent manufactured leathers: five sorts of sheep-leathers (NL1, NL2, V1, V2 and V3); two sorts of calf-leathers (CL1 and CL2) (All recent manufactured leathers were obtained using natural (vegetal) tannins (tara, mimosa or quebracho). The investigated sorts differ each other by the used tannin as well as by some conditions in which the tanning process takes place);

• naturally aged leathers extracted from the following patrimonial objects: Romania armor from XVI century (A); book covers of two Romanian Bible from XVII century (RB1 and RB2); Cordoba leather from XVII century (C); leather pieces from a Romanian bookbinding manufacture from XVII century (L17); German tobacco box from XVIII century (TGER); book cover of an Armenian Bible from XVIII century (AB); calf-leather from a chair tapestry from XVIII century (Tap18); lining leather of a Romanian chest from the beginning of XIX century (RCL); lining fur of a Romanian chest from the beginning of XIX century (RCF); Austrian belt from Franz-Joseph period – aprox. 1860 (FJ);

• recent manufactured parchments: seven sorts of sheep parchments (P1, P2, P3, P4, P5, S I and S II);

• naturally aged parchments extracted from the following patrimonial objects: Romanian document from XVI century emitted by the hospodar Simion Moghila (SM); Romanian armor from XVI century (PA);

• recent extracted collagen: five sorts of collagen obtained from bovine leather at different pH-values (AM1, AM2, AM3, AM4 and AM5); four sorts of bovine collagen with different hydration degree (col20, col30, col60 and col80) (The hydration of collagen matrices was accomplished with saturated water vapors, at 20°C, varying the hydration time from 17 to 202 h. For the thermal characterization of the hydrated matrices, samples of 21.7; 31.1; 60.3 and 80.0% humidity were selected).

The new leathers, parchments and the sorts of collagen were produced at ICPI – Leather and Footwear Research Institute – Bucharest – Romania.

Romanian National Museum of History and The Military Museum from Bucharest supplied the historical leathers.

*Thermal analysis*

The heating curves (TG, DTG, DTA) of samples were simultaneously recorded with a Q-1500D Derivatograph (MOM, Hungary), in static air atmosphere, in the temperature range 20–500°C, at a heating rate of 2.5 K $min^{-1}$. The mass of the analyzed samples was in the range 18.0–20.0 mg. The heating of the sample was performed in a cylinder shape platinum crucible and $\alpha$-$Al_2O_3$ was used as reference material.

## Results and discussions

Figure 1 shows the TG, DTG and DTA curves for the sample NL1. Similar plots have been obtained for all analyzed samples. These are similar with those previously reported for some sorts of leather [7] and the collagen [8, 9].

The thermal degradation of a sort of leather (recent manufactured or from patrimonial objects), parchment (new or aged) or collagen occurs through two successive processes accompanied by mass losses. The first process (denoted by I) is endothermic one and takes place in the temperature range of 25 to 125°C. This consists of the loss of water contained by each investigated material [7–9]. The second process (denoted by II) is exothermal one and consists of the decomposition and thermo-

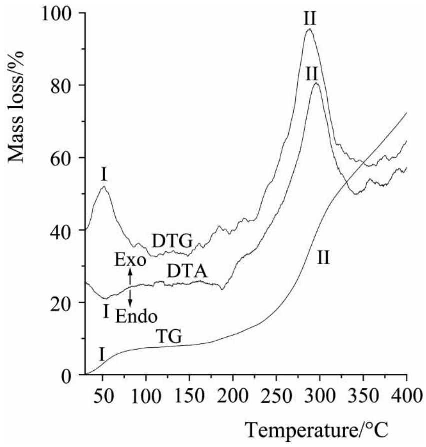


**Fig. 1** The TG, DTG and DTA curves of the sample NL1

oxidation of dry material. Some volatile products with low molecular mass are also released during this process. The characteristic temperatures of the processes II and I and the mass losses at 125 and 350°C are listed in Table 1. The inspection of this Table shows that: a) the parameters show specific values for each analyzed material; b) for process II, the new and patrimonial leathers exhibit well defined DTA peaks, while DTA curves are blunted in the cases of new and patrimonial parchments and collagens; c) a criterion of distinction between a recent manufactured leather and a patrimonial leather, based on the temperatures, cannot be suggested.

Figure 2 depicts comparatively the DTG curves corresponding to a recent manufactured leather (NL1), a naturally aged leather (RB2), a recent manufactured parchment (S I) and a sort of collagen (col20). One can note that each material exhibits specific values for the dehydration and thermo-oxidation rates. The maximum rate of process II has the highest value for NL1 and the smallest value for col20 (that is appropriate on the corresponding value for S I); RB2 exhibits an intermediate value of this rate. Similar statement results also from the DTA curves (Fig. 3).

**Table 1** The parameters of non-isothermal degradation of the investigated materials

| Material | $\Delta m_{125}$/% | $T^{I}_{max}$(DTG)/ °C | $T^{I}_{min}$(DTA)/ °C | $T^{II}_{max}$(DTG)/ °C | $T^{II}_{max}$(DTA)/ °C | $\Delta m_{350}$/% |
|---|---|---|---|---|---|---|
| New leathers | | | | | | |
| NL1 | 7.6 | 52.0 | 53.0 | 289.0 | 297.0 | 58.7 |
| NL2 | 11.1 | 55.1 | 59.2 | 298.3 | 307.3 | 61.0 |
| V1 | 7.4 | 51.0 | 60.0 | 286.0 | 293.3 | 61.2 |
| V2 | 6.7 | 49.3 | 57.2 | 288.0 | 289.1 | 53.6 |
| V3 | 10.8 | 46.4 | 53.0 | 282.3 | 290.0 | 67.8 |
| CL1 | 7.8 | 52.8 | 53.4 | 288.0 | 290.3 | 60.7 |
| CL2 | 10.2 | 51.1 | 56.2 | 305.0 | 309.4 | 60.1 |

**Table 1** Continued

| Material | $\Delta m_{125}$/% | $T^{I}_{max}$(DTG)/°C | $T^{I}_{min}$(DTA)/°C | $T^{II}_{max}$(DTG)/°C | $T^{II}_{max}$(DTA)/°C | $\Delta m_{350}$/% |
|---|---|---|---|---|---|---|
| Patrimonial leathers | | | | | | |
| A | 4.8 | 52.5 | 56.0 | 281.0 | 307.0 | 70.6 |
| RB1 | 10.6 | 56.0 | 56.0 | 293.0 | 300.0 | 55.1 |
| RB2 | 7.7 | 49.0 | 51.0 | 283.0 | 292.0 | 55.0 |
| C | 5.4 | 52.0 | 54.0 | 304.0 | 315.0 | 48.2 |
| L17 | 8.8 | 46.0 | 57.0 | 291.0 | 303.0 | 60.0 |
| TGER | 11.9 | 50.0 | 50.0 | 304.0 | 308.0 | 54.1 |
| AB | 8.6 | 51.0 | 50.0 | 264.0 | 296.0 | 49.5 |
| Tap 18 | 6.8 | 59.6 | 59.6 | 292.5 | 297.2 | 44.4 |
| RCL | 12.3 | 54.0 | 59.0 | 283.0 | 298.5 | 44.9 |
| RCF | 6.7 | 53.1 | 53.1 | 288.0 | 286.0 | 35.8 |
| FJ | 11.1 | 49.0 | 51.0 | 290.0 | 301.0 | 56.7 |
| New parchments | | | | | | |
| P1 | 7.1 | 49.6 | 53.2 | 283.0 | 238–292 | 51.6 |
| P2 | 6.4 | 49.0 | 56.0 | 265.0 | 240–310 | 53.1 |
| P3 | 8.4 | 55.5 | 59.6 | 252–319 | 245–307 | 49.8 |
| P4 | 10.8 | 50.2 | 59.8 | 269.0 | 263–294 | 43.0 |
| P5 | 9.8 | 50.8 | 50.0 | 291.4 | 260–305 | 38.4 |
| SI | 10.8 | 59.0 | 58.0 | 295.0 | 265–305 | 45.3 |
| SII | 12.0 | 52.0 | 50.0 | 284.0 | 272–310 | 51.6 |
| E | 13.6 | 57.0 | 58.0 | 281.0 | 270–303 | 63.8 |
| Patrimonial parchments | | | | | | |
| SM | 7.4 | 56.0 | 54.0 | 280.0 | 273–299 | 40.4 |
| PA | 6.8 | 55.0 | 57.0 | 290.0 | 265–310 | 48.5 |
| Collagens | | | | | | |
| AM1 | 15.1 | 49.0 | 50.0 | 273; 286 | 256; 300 | 55.3 |
| AM2 | 13.4 | 40.0 | 55.0 | 265; 305 | 259; 287 | 55.1 |
| AM3 | 15.7 | 44.0 | 52.0 | 257; 271 | 270; 292 | 58.0 |
| AM4 | 12.8 | 51.4 | 53.8 | 257; 280 | 263; 294 | 41.8 |
| AM5 | 9.4 | 48.5 | 54.0 | 274.0 | 270.0 | 42.9 |
| Col20 | 19.3 | 48.0 | 47.0 | ≈277.0 | 277–301 | 59.2 |
| Col30 | 18.5 | 50.0 | 50.0 | ≈273 | 255–300 | 50.3 |
| Col60 | 33.0 | 53.0 | 53.0 | ≈266 | 255–300 | 62.1 |
| Col80 | 38.1 | 56.0 | 56.0 | ≈263 | 253–300 | 62.9 |

$\Delta m_{125}$=the relative mass loss (until 125°C); $\Delta m_{350}$=(until 350°C)

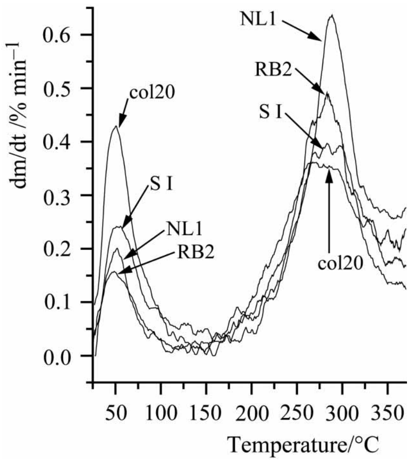


**Fig. 2** The DTG curves corresponding to: the recent manufactured leather (NL1); the books cover of a Romanian Bible from XVII century (RB2), the recent sheep-parchment (S I) and the collagen (col20)

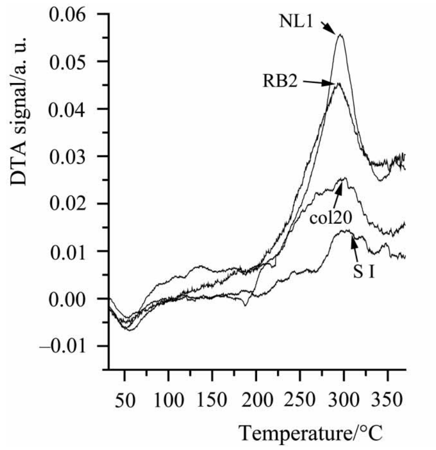


**Fig. 3** The DTA curves corresponding to: the recent manufactured leather (NL1); the books cover of a Romanian Bible from XVII century (RB2), the recent sheep-parchment (S I) and the collagen (col20)

As can be seen in Fig. 4, the order of the thermo-oxidation rate magnitudes (new leather>naturally aged leather>parchment~collagen) is followed by all the investigated materials. One may note that a similar hierarchy is obtained if the rate of process II at $T_{max}^{II}$ (DTG) is considered (for a given material, there is a small difference between the rate at 288°C and the rate at $T_{max}^{II}$ (DTG)).

The relative high values of the thermo-oxidative rate of new leathers could be due to the reactive sites introduced by tanning, which is mainly a cross-linking process. Similarly, the oxidative reactivity of polymeric materials carbon increases with the increased degree of substitution obtained by cross-linking [10, 11].

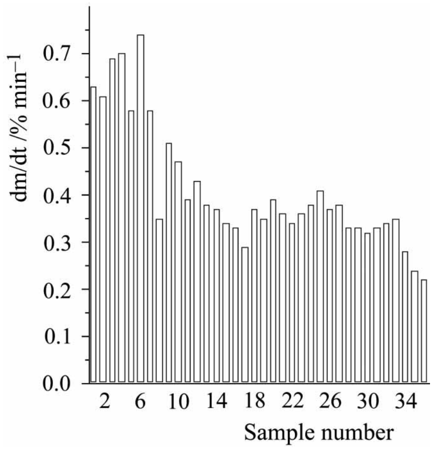


**Fig. 4** $\frac{d\%\Delta m}{dT}$ at 288°C for the analyzed samples: 1–7 correspond to recent manufactured leathers (1→NL1; 2→NL2; 3→V1; 4→V2; 5→V3; 6→CL1; 7→CL2); 8–18 correspond to patrimonial leathers (8→A; 9→RB1; 10→RB2; 11→C; 12→L17; 13→TGER; 14→AB; 15→Tap 18; 16→RCL; 17→RCF; 18→FJ); 19–25 correspond to recent manufactured parchments (19→P1; 20→P2; 21→P3; 22→P4; 23→P5; 24→S I; 25→S II); 26 and 27 correspond to patrimonial parchments (26→SM; 27→PA); 28–36 correspond to some sorts of colla-

The results presented in Fig. 4 show that aging changes the thermal behaviour of the leather. The thermal behaviour of degraded leather tends to that corresponding to parchments or collagens, which are not tanned materials. This suggests that the main result of the complex process-taking place at the naturally aging of tanned leather is the decrease of the cross-linking degree. This assumption has to be further checked by other analytical techniques.

From a practical point of view, the results presented in this paper show that the differences between the DTG curves recorded in air atmosphere can be used as a qualitative criterion for distinction between a recent manufactured leather and a naturally aged leather (patrimonial leather).

## Conclusions

• The thermal analysis (TG, DTG, DTA) of some recent manufactured vegetable tanned leathers, patrimonial leathers, recent manufactured parchments, patrimonial parchments and collagens were performed in static air atmosphere.
• It was pointed out that the group of TG, DTG and DTA plots is characteristic of each material and therefore can be considered its ‘fingerprint’.
• A criterion to qualitatively distinguish between recent manufactured leather and a patrimonial one was suggested.

## References


1 R. Larsen, Thermochim. Acta, 365 (2000) 85.
2 C. Chahine, Thermochim. Acta, 365 (2000) 101.
3 N. S. Cohen, M. Odlyha and G. Foster, Thermochim. Acta, 365 (2000) 111.
4 T. J. Wess and J. P. Orgel, Thermochim. Acta, 365 (2000) 119.
5 G. M. Nielsen-March, R. E. M. Hedges, T. Mann and M. J. Collins, Thermochim. Acta, 365 (2000) 129.
6 C. Marcolli and H. G. Wiedemann, J. Therm. Anal. Cal., 64 (2001) 987.
7 G. de Simone, B. Naviglio, M. Tomaselli, L. Bianchi, D. Sannino and P. Ciambelli, XXIII IULTCS Congress, Friedrichshafen, May 15–20, 1995, Part I, Paper 21.
8 J. J. Lim and M. H. Shannon, Biopolymers, 13 (1974) 1791.
9 A. Kaminska and A. Sionkowska, Polym. Degrad. Stab., 51 (1996) 15.
10 L. Slusarski, J. Thermal Anal., 29 (1984) 905.
11 C. Vasile, in ‘Handbook of Polyolefins’ (Eds C. Vasile and R. Seyrmour), Dekker, New York 2000, Chap. 12.