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IDENTIFICATION OF COLLAGEN-BASED MATERIALS THAT ARE SUPPORTS OF CULTURAL AND HISTORICAL OBJECTS

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Abstract

The TG, DTG, DTA methods were used for investigation of the thermal degradation in static air atmosphere of some collagen-based materials (some sorts of collagen, recent manufactured parchments and tanned leathers, patrimonial (historical) leathers). At the progressive heating, all investigated materials exhibit two main successive processes, associated with the dehydration and thermo-oxidative degradation. The patrimonial leathers were divided in two groups, namely: a group containing the majority of the analyzed materials, for which the rates of the thermo-oxidation process are substantially lower than those corresponding to the recent manufactured leathers, and a group for which the rates of thermo-oxidation process are closed to those corresponding to the recent manufactured leathers. Consequently, if by the thermal analysis in air atmosphere of a leather sample, a value of the rate of the thermo-oxidation process smaller than that corresponding to the recent manufactured leathers is obtained, then the analyzed leather is a patrimonial one. The reciprocal statement of this qualitative criterion for distinction between recent manufactured leather and patrimonial leather is not valid.

The DSC analyses of collagen-based materials were performed in air (DSC(air)) and in water (DSC(water)). The denaturation process takes place at lower temperatures in water than in air. Unlike recent manufactured leathers and parchments, each patrimonial leather exhibits on DSC(water) plot 2–4 peaks. Consequently, the number of peaks from DSC(water) curve could be another qualitative criterion for distinction between a recently manufactured leather and a patrimonial leather.

Keywords: leather, parchment, patrimonial objects, thermal analysis

Introduction

The leather products (light leathers: tanned skin for footwear, garments, bookbinding leathers; heavy leathers for soles and belts; parchment; collagen; clay; etc.) have

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been useful materials since the dawn of human history. For example, in Egypt vegetable tanned leather was used from the pre-historic period [1], while the use of parchment dates back to the Middle Kingdom [2].

Among the problems of the museum custodians, private collectors on antiquaries one may specify: a) the identification of the cultural or historical object (author, period in which the object was manufactured, etc.); 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.

The development of the analytical techniques improves the procedures to identify the patrimonial objects made from collagen-based materials as well as the methods to put in evidence the impact of the environmental factors on them. As it may be noticed from literature, the methods of thermal analysis (DSC, TG, dynamic mechanical thermal analysis (DTMA), thermomicroscopy) were used, only during the last 15 years, in the field of leather, parchment and paper from patrimonial objects [3–9]. [3–7] 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 [4] 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.

In a previous paper [9] we have used TG, DTG and DTA methods for investigation of the thermal degradation of: 7 sorts of recent vegetable tanned leathers (five sorts of sheep-leathers and two sorts of calf-leathers; natural vegetable tannins: tara, mimosa, quebracho); 11 sorts of patrimonial leathers (covers of some religious books, chair tapestries, lining leathers, etc.); 7 sorts of recent manufactured parchments (sheep parchments); 2 sorts of patrimonial parchments; and 10 sorts of collagen obtained by hydrophilization of type I collagen from bovine hides. It was pointed out that the thermal analysis curves (TG, DTG, DTA) can be considered a material 'fingerprint'. The following order of the rate of thermo-oxidation process was put in evidence: recent manufactured leathers>>naturally aged leathers (patrimonial leathers)≈recent manufactured parchments collagens.

The purposes of the works reported in this paper are:

- to check the conclusion of our previous work [9] for larger sorts of collagen-based materials (collagen, recent manufactured parchments and leathers, patrimonial leathers);
- to apply DSC technique for investigation of the thermal stability in air and in water of the collagen-based materials.

The suitability of the thermal analysis methods (TG, DTG, DTA, DSC) for distinguishing between a recent manufactured tanned leather and a patrimonial leather will be also discussed.

Experimental

Materials

Our experiments were carried out on the following collagen-based materials:

- 5 sorts of recent collagen obtained by hydrophilization of type I collagen gels, extracted from bovine hides at different pH values (3.5, 4.5, 5.5, 6.5, 7.2) according to a technology elaborated by the Leather and Footwear Research Institute – Bucharest, Romania;
- 9 sorts of recent manufactured parchments (sheep, kid, lamb, calf and pig parchments);
- 14 sorts of recent manufactured leathers (vegetable tanned leathers, and chrome+vegetable tanned leathers);
- 24 sorts of patrimonial (historical) leathers vegetable tanned from XVII to XIX century (book cover of some religious books, leather pieces from a bookbinding, Cordoba leathers, Austrian belt, leathers from Romanian armors, leathers from chair tapestry, lining leather and fur, leathers from hilts, leathers from some tobacco boxes).

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, the Military Museum from Bucharest and Cotroceni Palace – Bucharest Museum 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 α-Al_2O_3 was used as reference material.

The measurements of heat flow *vs*. temperature were performed using a Perkin Elmer DSC 7 calorimeter. For each sample, two DSC curves were recorded, namely, a DSC curve corresponding to denaturation in air (with the water absorbed by the sample from atmosphere) and another corresponding to denaturation in water. For investigating the denaturation in air, each sample was weighed (3–6 mg) and hermetically sealed in an aluminum pan. Thermal changes were measured with respect to a similar empty pan while flushing the chamber with nitrogen. The reference and sample pans were heated at the constant heating rate of 10 K min^{-1}. For investigation of denaturation in water, 35 μL water were added at each sample (of 3–6 mg), and the corresponding sample pan was hermetically sealed and stocked for 24 h. Thermal changes were measured with respect to a similar water sample (the same amount of water was used in reference and sample pans), while flushing the chamber with nitrogen. The heating rate was 10 K min^{-1} again.

Results and discussions

TG, DTG and DTA measurements

Figure 1 shows the TG, DTG and DTA curves for a recent manufactured leather (vegetable tanned calf leather). These are similar with those previously reported for some sorts of leather [9–11] and collagen [9, 12, 13]. All investigated collagens, parchments and leathers exhibit also similar TG, DTG and DTA curves.

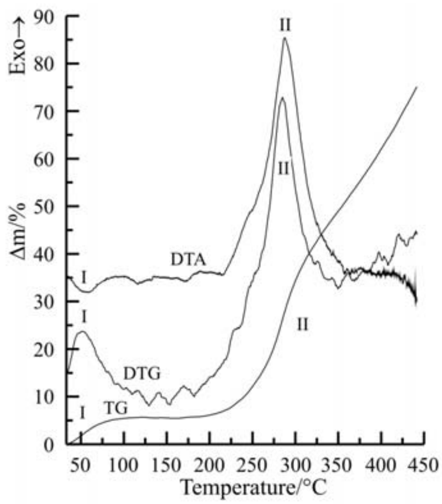

Fig. 1 The TG, DTG and DTA curves of a sort of recent manufactured leather (vegetable tanned calf leather)

The thermal degradation of a sort of leather (recent manufactured or from patrimonial objects), parchment or collagen occurs through two successive processes accompanied by mass losses. The first process (denoted by I) is an endothermic one and takes place in the temperature range of 25 to 125°C. It consists of the water loss contained by each investigated material [9–13]. The second process (denoted by II) is exothermal one and puts into evidence the pyrolytic decomposition and thermo-oxidation of dry material. Some volatile products with low molecular mass are released during this process.

The main characteristics of these two processes for the investigated collagen-based materials are listed in Table 1. For each characteristic, the range of variation, and, when this range is small, the average value, are given.

The patrimonial leathers were divided in two groups, namely: PL1 (18 sorts) for which the rates of thermo-oxidation process are substantially lower than those corresponding to the recent manufactured leathers, and PL2 (6 sorts) for which the rates of the thermo-oxidation process are close to those of recent manufactured leathers. PL1 group contains: book cover leathers (10 sorts), Romanian armor leathers (3 sorts), linings leather and fur (2 sorts), Cordoba leathers (2 sorts) and tobacco box

Table 1 The main characteristics of the non-isothermal degradation in air and the denaturation in air and in water of the investigated collagen-based materials

Method	Process	Characteristic parameter	Collagen	Recent manufactured parchments	Recent manufactured leathers	Patrimonial leathers(PL1)	Patrimonial leathers(PL2)
TG	dehydration	$\%\Delta m_{125}/\%$	9.4–15.1	6.4–10.8	6.6–11.1	4.8–12.3	4.5–8.5
	thermo-oxidation	$\%\Delta m_{350}/\%$	34–42	29–47	45.9–69.7	44.4–69.2	47.8–63.8
DTG	dehydration	T_{max}^{DTG}/°C	43–56(47)	49–59(54)	46–58(52)	44–58(51)	48–58(52)
		T_{i}^{DTG}/°C	213–232(223)	181–238(218)	242–255(250)	193–237(217)	218–255(240)
	thermo-oxidation	T_{max}^{DTG}/°C	260–279(268)	269–297(283)	279–290(286)	265–296(286)	275–291(285)
		$(d\%\Delta m/dT)_{288}$	0.22–0.38 (0.31)	0.34–0.41 (0.38)	0.58–0.82 (0.70)	0.23–0.55 (0.42)	0.58–0.79 (0.63)
DTA	dehydration	T_{min}^{DTA}/°C	49–55(53)	50–58(56)	51–62(58)	50–59(55)	49–61(530)
	thermo-oxidation	T_{i}^{DTA}/°C			242–268(256)	200–242(224)	229–264(243)
		T_{max}^{DTA}/°C	large exothermic peak	large exothermic peak	282–296(289)	285–305(297)	280–295(289)
		$(\Delta T/m)_{max}$ rel.unit.			5.0–7.9 (6.5)	1.0–4.5(2.9)	3.8–5.7(4.8)
DSC(air)	denaturation	No. of peaks	1	1	1	1	1
		T_{max}/°C	85–100(92)	120–127(125)	110–128(127)	110–128	110–128
		ΔH/J g^{-1}	18.2–21.4(19.8)	185–276(220)	175–216 (195)	5.5–210	5.5–210
DSC(water)	denaturation	No. of peaks	1	1	1	2–4	2–4
		T_{max}/°C	48–52(50)	54–71	88–92 (90)	62–97	62–97
		ΔH/J g^{-1}	28.9–39.7(33.8)	7.0–38.0	8.6–21.9	≈1.1–≈24	≈1.1–≈24

leather (1 sort), while PL2 group contains: hilt leathers (3 sorts), sandle leather (1 sort), sheep leather from a chair tapestry (1 sort), and book cover leather (1 sort). The differences among thermo-oxidative behavior of some collagen-based materials are illustrated in Figs 2–4.

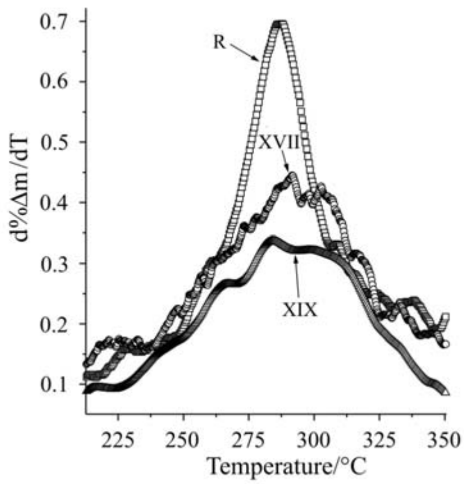

Fig. 2 DTG curves for: a recent manufactured leather (vegetable tanned sheep leather) denoted by R; leather pieces from a bookbinding from XVII century, denoted by XVII; lining leather of a chest from the beginning of XIX century, denoted by XIX

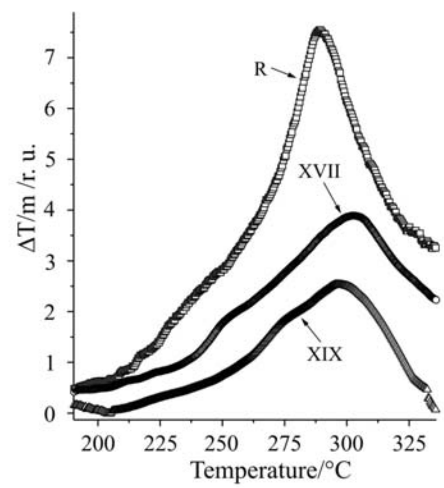

Fig. 3 DTA curves for: a recent manufactured leather (vegetable tanned sheep leather) denoted by R; leather pieces from a bookbinding from XVII century, denoted by XVII; lining leather of a chest from the beginning of XIX century, denoted by XIX

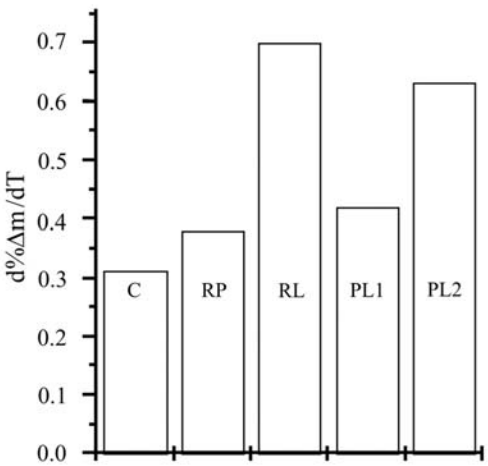

Fig. 4 The average rate of thermo-oxidative degradation: C – collagens; RP – recent manufactured parchments; PL1 and PL2 – patrimonial leathers

The following statements may be inferred from these figures and Table 1:

- DTG curves of patrimonial leathers are rougher than those recorded for recent manufactured leathers.
- T_i^{DTG} values corresponding to collagens, recent manufactured parchments and PL1 are close to each other and smaller than those identified on recent manufactured leathers and PL2.
- T_i^{DTA} values of recent manufactured leathers and PL2 are close to each other and higher than those recorded for PL1.
- The values of thermo-oxidizing rate for PL1, which are proportional to $(d\%\Delta m/dT)_{288}$, are close to those of collagens and recent manufactured parchments, and substantially smaller than those from recent manufactured leathers. One may note that similar hierarchy is obtained if the rate of thermo-oxidation process is considered at T_{max}^{DTG} (for a given material is a small difference between the rate at 288°C and the rate at T_{max}^{DTG}).
- All patrimonial leathers exhibit normalized DTA area, $(\Delta T/m)_{max}$, smaller than those corresponding to recent manufactured leathers.

The relative high values of the thermo-oxidation rate of recent manufactured 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 [14, 15].

The results listed in Table 1 and shown in Figs 2 and 4 indicate that the change of the thermal behavior of PL1 sorts of leather is a result of their naturally aging. The thermal behavior of these degraded leathers tends toward that corresponding to parchments and collagens, which are not tanned materials. This suggests that the main result of the complex process taking place at the naturally aging of the vegetable tanned leathers (PL1) is the decrease of the cross-linking degree. This assumption has to be further checked by other analytical techniques.

The different behavior of PL2 sorts of leather in respect with PL1 sorts of leather is probably due to the fact that the leathers were prepared in different ways, and coming from different collections, they had been exposed to various environmental conditions. The naturally degradation of hilt and saddle leathers could be due to the interaction of the leathers with perspiration. Of cause, this kind of degradation is not proper for other sorts of leathers like, for example, book cover leathers.

From the above mentioned results it appears that, if by thermal analysis experiments in air atmosphere of a leather sample, the values of thermo-oxidative process, $(d\%\Delta m/dT)_{288}$, and of normalized DTA area, $(\Delta T/m)_{max}$, are smaller than those corresponding to a recent manufactured leather, then the analyzed leather is a patrimonial one.

The reciprocal statement of this qualitative criterion for discrimination between recent manufactured leather and patrimonial leather is not valid.

DSC measurements

Both in air and in water, we have recorded endothermic processes corresponding to the denaturation of collagen contained in sample. The main characteristics of the denaturation in air (with water contained by material) and in water of the investigated materials are also listed in Table 1.

Figures 5–7 show comparatively the DSC curves, obtained in air and in water, for a recent manufactured parchment (sheep parchment), a recent manufactured leather (vegetable tanned sheep leather) and for a patrimonial leather (book cover of a Romanian Gospel, 1762).

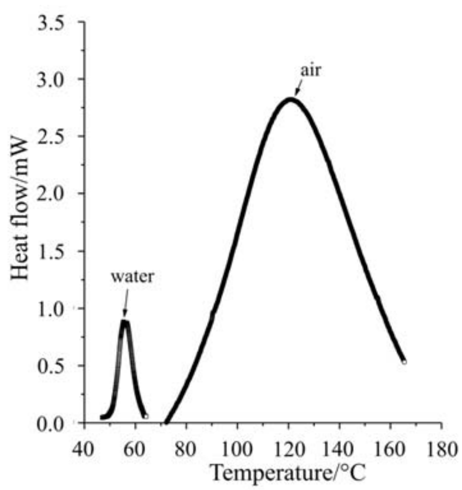

Fig. 5 DSC curves for denaturation in air and in water of a recent manufactured parchment (sheep parchment)

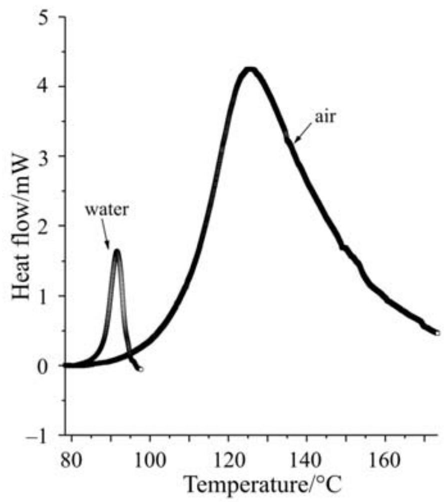

Fig. 6 DSC curves for denaturation in air and in water of recent manufactured leather (vegetable tanned sheep parchment)

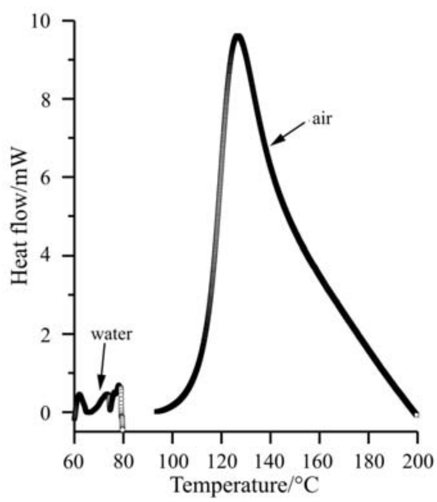

Fig. 7 DSC curves for denaturation in air and in water of a patrimonial leather (book cover of a Romanian Gospel from 1762)

The following statements result from the inspection of these figures and Table 1:

- The denaturation in air takes place in the temperature range 70–200°C and exhibits a single DSC peak with the maximum temperature in the range 85–100°C for collagens, and 110–128°C for the rest of the investigated materials.
- For the denaturation in air, ΔH values of recent manufactured parchments and leathers fall in the same range, and are approximately ten times higher than those

of the collagens. The ΔH values of the patrimonial leathers sweep a large range (5.5–210 J g^{-1}).

- The denaturation in water takes place in the temperature range 45–100°C. While collagens and recent manufactured parchments and leathers exhibit a single DSC peak, all patrimonial leathers (both PL1 and PL2) show 2–4 DSC peaks.
- For denaturation in water, collagens exhibit minimal values of T_{max}^{DSC}. The T_{max}^{DSC} values fall in a narrow range for collagens and recent manufactured leathers and in a relative large range for the rest of the investigated materials.
- The denaturation in water of all patrimonial leathers exhibits values of ΔH within a large range (≈1.1–≈24 J g^{-1}). Note that in these cases it is very difficult to define the baselines correctly. Therefore, we have relatively large errors in the evaluation of ΔH.

The results show that all investigated patrimonial leathers exhibit a high level of alteration, which determines a high heterogeneity of the materials and this is put into evidence easily by the shape of the DSC(water) curves.

The above mentioned results with DSC curves suggest that the number of peaks from DSC(water) curve could be a qualitative criterion for discriminate between a recent manufactured and a patrimonial (historical) leather.

Conclusions

We have recorded the TG, DTG, DTA in static air atmosphere and DSC curves in air and in water of some collagen-based materials: recent manufactured leathers and parchments, patrimonial (historical) leathers and collagens.

The non-isothermal parameters of thermo-oxidative degradation in air atmosphere and of denaturation process in air and in water were compared.

Based on the results obtained by TG, DTG and DTA analysis performed in air atmosphere, the patrimonial leathers were divided into two groups, namely: a group containing the majority of the investigated materials, for which the rates of thermo-oxidation process are smaller than those corresponding to recent leathers, and a group for which the rates of thermo-oxidation process are closed to those corresponding to recent manufactured leathers. It resulted the following criterion for qualitative discrimination between patrimonial and recently manufactured leather: If by thermal analysis in air atmosphere of a leather sample, a value of the rate of thermo-oxidation process smaller than that corresponding to the recently manufactured leathers is obtained, then the analyzed leather is patrimonial. The reciprocal statement of this qualitative criterion is not valid.

The results obtained by DSC analysis of collagen-based materials performed in water show that, unlike the recently manufactured leathers and parchments, each patrimonial leather exhibits 2–4 peaks. The number of peaks from DSC(water) curve could be another qualitative criterion for distinction between a recently manufactured leather and a patrimonial one.

The two suggested criteria could be used for distinction between an original artifact and a bootleg.

Work is in progress to understand the thermo-oxidative destruction process of leathers and leather-like materials for better supporting the proposed criteria.

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