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Application of thermal analysis methods for damage assessment of leather in an old military coat belonging to the History Museum of Braşov—Romania

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Abstract The aim of this work has been the assessment of the thermo-oxidative, hydrothermal and crystalline zone stabilities of several leather samples taken by the conservators from a military coat dated sixteenth–seventeenth centuries, belonging to the History Museum of Braşov—Romania. For this purpose, the thermo-gravimetry/derivative thermo-gravimetry (TG/DTG), differential scanning calorimetry (DSC) and micro hot table (MHT) methods have been employed. The thermo-oxidative damage of leather has been characterized by the rate of the first thermo-oxidation process highlighted in TG/DTG curves recorded in static air atmosphere. The hydrothermal denaturation of leather has been characterized by MHT method and DSC analysis in excess water conditions. The damage of crystalline zone of collagen in leather has been determined by DSC analysis in nitrogen flow. The qualitative damage for each leather sample and each kind of deterioration has been evaluated using the criteria resulted by thermal analysis of a large number of collagen-based materials (pure collagens, new and old parchments and leathers). The obtained results could facilitate the choice of the restoration and conservation procedures applicable for the investigated military coat.

Keywords Thermal analysis · Historical leather · Military coat · Damage assessment

Introduction

The animal skin products (clothing, footwear, furniture, upholstery, storage vessels, writing support, book bindings, etc.) have been useful materials since the dawn of human history. Tanning has been described as man's first manufacturing process [1].

Museums, libraries, archives and religious institutions preserve significant collections of leather and parchment objects with historic, artistic and documentary value. It is therefore vital to ensure their longevity.

Deterioration of collagen-based materials (parchment and leather) appears at all levels of structural hierarchy (from molecular to microscopic levels) and can be categorized as: chemical damage due to oxidation, environmental chemical pollutants such as NO_x and SO_2, hydrolysis, photochemical degradation; physical–mechanical damage due to frequent stretching and shrinkage of the material that appear when fluctuations in relative humidity occur; biological damage induced by bacteria, fungi, insects, molds. The investigation of collagen-based materials deterioration is very important for conservators involving some problems, including the achievement of suitable preservation and restoration of historical objects.

The development of the analytical techniques improves the procedure to identify the patrimonial objects made from leathers as well as the methods to highlight the impact of

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Table 1 Investigated properties, used methods and corresponding qualitative criteria of degradation level of vegetable tanned leathers

Type of degradation	Method	Property characteristic for degradation level	Measured quantity	HD	MD	C
Thermo-oxidative degradation	TG/DTG analysis in air atmosphere	First process of thermo-oxidation	V_{310}/ % min^{-1}	<3.86 or >4.71	–	Between 4.07 and 4.70
Hydrothermal degradation	MHT DSC analysis of samples immersed in water excess	Shrinkage	T_s/°C	<57	Between 57 and 64	>64
Degradation of crystalline (rigid) region	DSC analysis in N_2 flow, DMA	Melting of crystalline zone	T_m/°C	<227	Between 227 and 234	>234

The heating rates at which the thermal analyses were performed are: 10 K min^{-1} for TG/DTG and DSC analyses, and 2 K min^{-1} for MHT analyses

$V_{310} = -\left(\frac{d\%\Delta m}{dt}\right)_{310}$ = rate of the first process of thermo-oxidation at 310 °C (the average temperature of DTG minimum obtained for all analyzed collagen-based materials), T_s = shrinkage temperature, T_m = melting temperature, HD = high degree of degradation, MD = medium degree of degradation, C = good conservation

Note 1 The ranges of HD, MD and C were evaluated [2–5] by comparing the thermal analysis performed for 31 sorts of new parchments, 63 sorts of old parchments, 19 sorts of new vegetable tanned leathers and 76 sorts of old leathers

Note 2 The standard deviations of average values of measured quantities were considered for establishing the ranges corresponding to HD, MD and C

environmental factors on them. Among these techniques, the thermal analysis methods, especially thermo-gravimetry (TG) [2–7], differential thermal analysis (DTA) [5], differential scanning calorimetry (DSC) [2, 6–13], thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA) [2, 11, 12, 14–17], and micro hot table (MHT) [2, 6, 13, 18–22] are potentially useful to conservation scientists.

In this work, we will focus on the application of TG/DTG, DSC and MHT methods for assessment of hydrothermal stability, crystalline zone deterioration and thermo-oxidative deterioration of several leather samples taken by conservators from a military coat dated sixteenth–seventeenth century belonging to the History Museum of Braşov—Romania.

The applied criteria for the damage assessment of old leathers

In some previous papers [3–6, 10, 11], the results obtained by thermal analysis of some collagen-based materials (sorts of collagen, new and old parchments and leathers) were presented and discussed. The comparison of the results led to some qualitative criteria of degradation level of vegetable tanned leathers which will be briefly presented below.

Stability at thermo-oxidation

The TG/DTG analyses performed in air static atmosphere show [3–6] that the degree of thermo-oxidative degradation of a collagen-based material is characterized by the rate of the first process of thermo-oxidation put in evidence in non-isothermal conditions. The analysis of the obtained data shows that two main complex processes occur during the natural aging of leathers by decomposition, hydrolysis, oxidation and/or biological damage, namely the breaking of cross-linking bonds resulted by tanning of native leathers, and the splitting off of collagen macromolecules. When the breaking of cross-linking bonds is prevalent, the rate of the first process of thermo-oxidation of natural aged leather highlighted in DTG curve is between the rates corresponding to new and old parchments and those corresponding to new leathers manufactured by vegetable tanning. A higher deterioration of old leather consisting in splitting off of collagen macromolecules determines the increase in thermo-oxidative rate to a value higher than those corresponding to new leathers manufactured by vegetable tanning. These statements led to the qualitative criteria of degradation level of vegetable tanned leathers given in Table 1.

Hydrothermal stability

MHT and DSC analyses were performed in water excess [10] for determination of the shrinkage temperature (T_s). For natural aged leathers, T_s exhibits values comparable with those of parchments, but lower than those corresponding to new leathers manufactured by vegetable tanning. This could be explained by the process of breaking of cross-linking bonds, which occurs during natural aging. The obtained results led to the qualitative criteria of

Fig. 1 Military coat dated sixteenth–seventeenth centuries. The places from which the investigated samples were extracted are indicated

degradation level of vegetable tanned leathers listed in Table 1.

Crystalline zone stability

The DSC analyses of collagen-based materials, performed in nitrogen flow [10] show a melting process that occurs in the temperature range 200–240 °C. The temperature value of the DSC peak corresponding to this process (T_m) is the melting temperature of the crystalline zone and characterized the deterioration by natural aging of this zone [10]. For natural aged leathers, T_m exhibits values between those corresponding to parchments and to new vegetable tanned leathers. The obtained results led to the qualitative criteria of degradation level of vegetable tanned leathers listed in Table 1.

Experimental

Materials

Six leather samples were taken by conservators from different places of an oriental military coat dated sixteenth–seventeenth century belonging to the History Museum of Braşov—Romania (Figs. 1, 2). The leather coat is made of skins of different qualities. The collar is from sheep leather and exhibits orange ornaments made from lamb or untanned sheep leather. The sleeves are from bovine leather with thick structure that was tanned with vegetable extracts. The

Fig. 2 Military coat dated sixteenth–seventeenth centuries—ornamental details

front of coat is decorated with sheep leather and parchment. The cuffs are from sheep leather. The piece has undergone repair interventions during which the interior was almost completely doubled with goat leather pieces bound together and the heavily degraded areas were

Table 2 Samples extracted from the military coat

Samples	Name	Animal identification
1	Leather sample on the back of the collar	Sheep
2	Inner right sleeve sample	Bovine
3	Tails leather sample, inner right side corner	Goat
4	Inner tails patch	Goat
5	Front ornament sample, left side of the piece	Goat
6	Inner left side back lining sample	Goat

covered with pieces of leather of various qualities, using a yellow–brown adhesive which had degraded over time. Based on the visual assessment made by conservators, the military coat is well preserved.

The investigated leather samples of the military coat are presented in Table 2.

Thermal analysis

For thermal characterization of leathers, the following techniques were used: TG/DTG, DSC and MHT.

TG/DTG analyses were performed with STA 409PC Luxx apparatus produced by Netzsch, Germany, in static air atmosphere, in the 20–600 °C temperature range, at a heating rate of 10 K min^{-1}. The mass of analyzed samples was in the range 4–6 mg, and the heating of each sample was performed in a cylinder shape α-Al_2O_3 sample holder.

The following kinds of DSC measurements were performed by using DSC 204 F1 Phoenix apparatus produced by Netzsch, Germany:

- DSC analysis of the sample (1–5 mg) immersed in water (35 µL deionized water), hermetically sealed in an aluminum pan and stocked for 24 h. Each sample was heated from 25 to 110 °C, at a heating rate of 10 K min^{-1}.
- DSC analysis of the sample (1–5 mg) in nitrogen flow (nitrogen purity was 99.999 %; 20 mL min^{-1}), in an open aluminum pan, at the heating rate of 10 K min^{-1} and the temperature range 25–260 °C.

MHT analyses were performed with homemade equipment made of a CALORIS hot table controlled by a temperature processor and coupled with a Leica S4E stereomicroscope. The magnification used was 40×. A sample of about 10–15 fibers was thoroughly wetted with deionized water for 10 min on a microscope slide. The fibers were then separated under the microscope using needles, covered with a second microscope slide, placed on the hot table and heated with a 2 °C min^{-1} rate. A FLTK. 1.1.X homemade software was used for data collection. The shrinkage activity of collagen fibers is monitored, taking into account the following ranges [19, 20]:

- A_1 and A_2—shrinkage activity is noticed in individual fibers (T_{first} is the temperature at which the first contraction occurs and coincides with the start of A_1 interval, while T_{last} is the temperature to which the last contraction occurs and marks the end of the A_2 interval);
- B_1 and B_2—the contraction of a fiber is immediately followed by the contraction of another fiber;
- C—the main shrinkage interval during which most collagen fibers shrink (shrinkage temperature—T_s marks the beginning of this interval).

Shrinkage intervals occur in the following order:

No activity—A_1–B_1–C–B_2–A_2—full shrinkage.

Results and discussion

The thermo-oxidative deterioration, hydrothermal stability and crystalline zone deterioration of the leather samples taken from military coat mentioned in Table 3 were

Table 3 Characteristic parameters of the leather samples and their degradation level

	Thermo-oxidative degradation		Hydrothermal degradation					Degradation of crystalline (rigid) region		
Methods	TG/DTG		MHT		DSC analysis in water excess			DSC analysis in nitrogen flow		
Samples	V_{310}/% min^{-1}	D	T_{first}/°C	T_s/°C	T_{onset}/°C	T_{min}/°C	D	$T_m(1)$/°C	$T_m(2)$/°C	D
1	3.31	HD	52.4	60.2	60.4	64.4	MD	172.5	220.3	HD
2	3.40	HD	37.2	39.4	34.0	38.4	HD	–	190.0	HD
3	2.85	HD	49.0	63.7	67.5	72.9	C	171.0	223.7	HD
4	4.6	C	74.8	90.3	90.9	91.4	–	–	–	–
5	4.13	C	44.2	54.7	55.3	63.7	HD	–	212.1	HD
6	3.46	HD	54.2	64.0	66.1	70.4	C	169.7	205.8	HD

The heating rates at which the thermal analyses were performed are: 10 K min^{-1} for TG/DTG and DSC analyses, and 2 K min^{-1} for MHT analyses

determined by TG/DTG, DSC and MHT methods and the criteria given in Table 1 were applied for estimation of their qualitative deterioration levels.

Stability at thermo-oxidation

The TG and DTG curves obtained for the sample 3 extracted from military coat are shown in Fig. 3; similar curves were obtained for all analyzed samples as well as for all kinds' collagen-based materials which were analyzed for obtaining the deterioration criteria given in Table 1. The non-isothermal degradation of the leather occurs through three processes accompanied by mass losses. In the first process, denoted by I in Fig. 3, which occurs at <150 °C, the water contained by material was evolved. The next two steps, denoted by II and III in Fig. 3, consist in pyrolytic thermo-oxidation and decomposition of the material.

It was pointed out [3–6] that the main characteristic parameter, which could be correlated with the leather damage is the rate $(-\frac{d\%\Delta m}{dt})$ of the first process of thermo-oxidation (process II in Fig. 3), at 310 °C (the average temperature of DTG minimum obtained for the collagen-based materials, which were analyzed in air at 10 K min^{-1} for obtaining the qualitative degradation criteria given in Table 1). Table 3 lists also the qualitative degree of degradation of each analyzed sample. The inspection of this table shows:

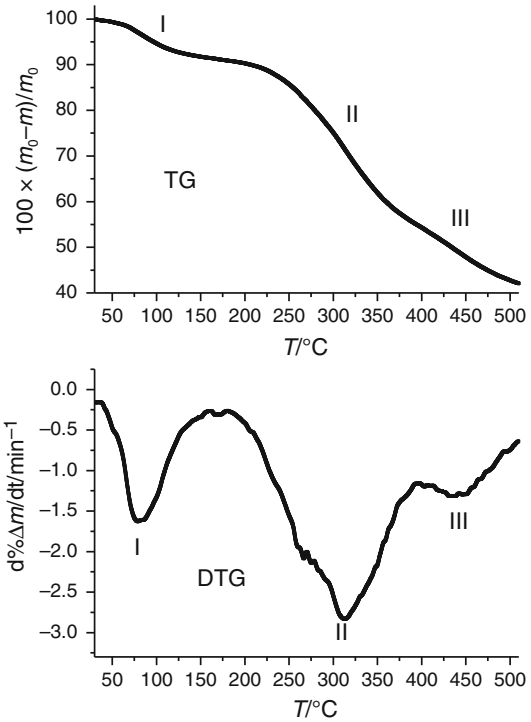

Fig. 3 TG and DTG curves obtained for sample 1 extracted from military coat

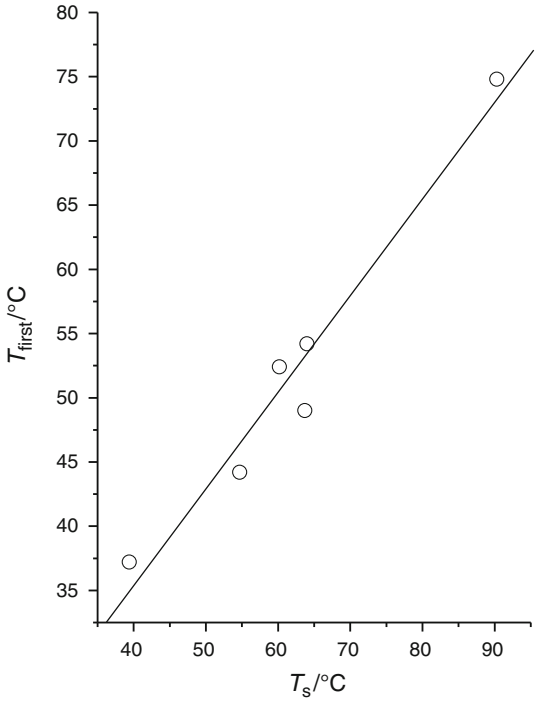

Fig. 4 Plot of T_{first} versus T_s

- Samples 1, 2, 3 and 6 exhibit high degree of thermo-oxidative degradation consisting mainly in splitting off of cross-linking bonds as a result of natural aging.

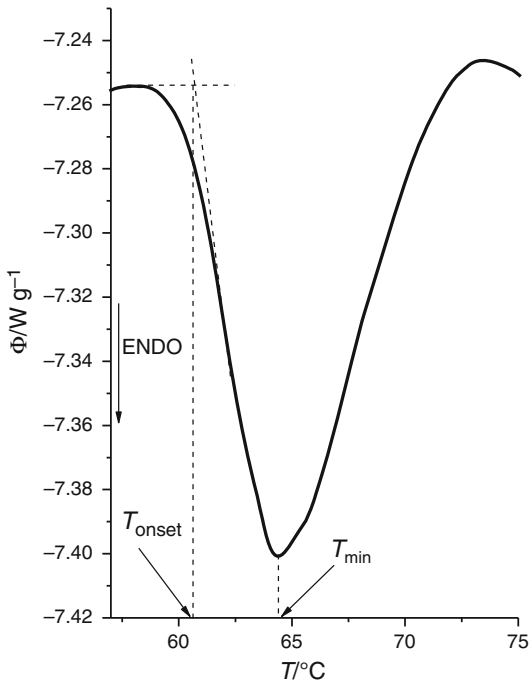

Fig. 5 DSC curve for sample 1 of leather extracted from military coat, obtained by analysis of sample immersed in water

- Sample 5 exhibits a good conservation. This means the natural aging of this sample does not determine the destruction of the sites of material that are active in oxidation.
- Sample 4 exhibits a relatively high value of V_{310}. This is recent vegetable tanned leather and has a relatively high cross-linking degree.

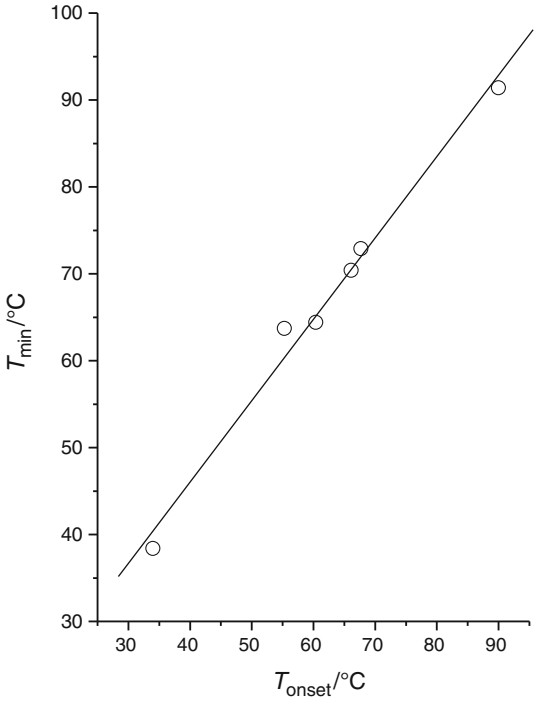

Fig. 6 Plot of T_{min} versus T_{onset}

Hydrothermal stability

The hydrothermal stability is characterized by the shrinkage temperature (T_s), which was determined by MHT and DSC methods.

The values of the temperature at which the first contraction occurs (T_{first}) and shrinkage temperature (T_s) determined by MHT method are listed in Table 3. A strong correlation between these temperatures was found (Fig. 4). A similar dependence was also obtained by Larsen et al. [21] for parchments.

Figure 5 shows the DSC curve for the sample 4 extracted from military coat, immersed in water, which exhibits an extrapolated onset temperature (T_{onset}) of 60.4 °C and a peak temperature (T_{min}) at 64.4 °C; similar DSC curves were obtained for all analyzed leather samples. Extrapolated onset temperature could be influenced by the base line applied to thermograms. However, the DSC curves obtained for numerous leathers and parchments [6, 10] exhibit a linear region in the temperature range T_{onset}–10 °C–T_{onset}, and therefore, T_{onset} can be determined with an accuracy of ±0.3 °C. On the other hand, it was pointed out [6, 10] that the value of T_{onset}, and not the value of T_{min}, is practically equal with the value of shrinkage temperature (T_s) that is a marker of deterioration. The linear correlation between T_{onset} and T_{min} (Fig. 6) shows that T_{min} could be also used as marker of deterioration. This linearity will be checked for some sorts of parchments and leathers in a future work. One notes that the value of enthalpy cannot be used as a marker of deterioration because the value of this quantity is reported to 1 g of leather that is a complex material for which we do know the quantitative composition. The values of T_{onset} and T_{min}

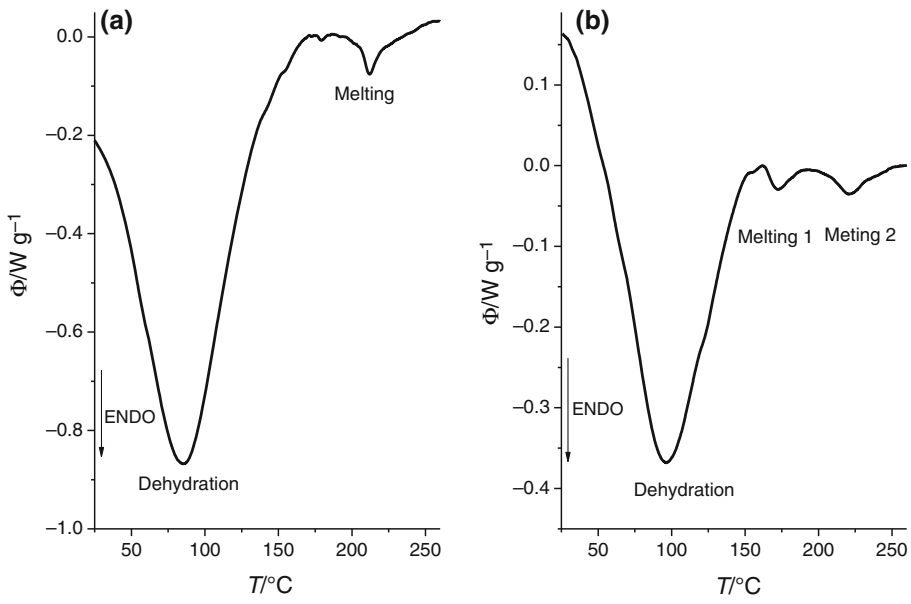

Fig. 7 DSC curve obtained in open crucibles and nitrogen flow for: **a** sample 5 and **b** sample 1

as well as the corresponding qualitative deteriorations of the analyzed samples are listed in Table 3.

The inspection of Table 3 shows:

- There is a good agreement between the values of T_s determined by MHT method and T_{onset} determined by DSC method.
- Different samples of old leathers (samples 1, 2, 3, 5 and 6) exhibit different deteriorations.
- As is expected, the sample 4 exhibits a relatively high value of shrinkage temperature.

Crystalline zone stability

DSC curves associated with thermal transitions which typically occur in parchment and leather samples measured in open crucibles and gas flow display a broad endothermic peak followed by one or two smaller endotherms (Fig. 7). The samples 2 and 3 exhibit DSC curves similar to those from Fig. 7a, while the samples 3 and 7 exhibit DSC curves similar to those from Fig. 7b. The broad peak in the temperature range (50–120) °C is associated with thermal dehydration. The first endotherm at $T_m(1) \approx 170$ °C was related to collagen matrix thermal denaturation [6, 10], whereas the second peak at $T_m(2) > 190$ °C was ascribed to melting of the crystalline collagen zone embedded in the amorphous matrix [10]. The temperature $T_m(2)$ is characteristic parameter for deterioration of the crystalline zone [6, 10]. The values of these temperatures as well as the corresponding qualitative deteriorations for the investigated samples are listed in Table 3.

The inspection of this table shows:

- The old leathers (samples 1, 2, 3, 5 and 6) exhibit high degree of deterioration of the crystalline zone.
- The DSC curve obtained for sample 4 does not exhibit a melting peak. This is explained by the high degree of cross-linking of this leather that determined the overlap of melting process with the first process of thermo-oxidation.

Conclusions

A multi-scale investigation was performed to characterize degradation and evaluate damage of a military coat dated sixteenth–seventeenth centuries belonging to History Museum of Braşov—Romania. The coat is a complex object with collar manufactured from sheep leather, the inner sleeve—from bovine leather, and front and back—from goat leather. Six different micro-samples of leather extracted from each of these parts of coat were analyzed by TG/DTG, DSC and MHT methods. The characteristic non-isothermal parameters of thermo-oxidation, denaturation in excess water and melting of crystalline zone were determined, and the qualitative criteria for assessment of thermo-oxidative deterioration, hydrothermal stability and crystalline zone deterioration were applied. Differences between the degradation levels of investigated old samples could be attributed to different degree of splitting of cross-linking bonds as a result of natural aging.

The obtained results could be used for finding the best possible procedures for preservation and/or restoration of the investigated heritage object.

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