The use of thermal analysis methods for authentication and conservation state determination of historical and/or cultural objects manufactured from leather

P. Budrugeac · Andrei Cucos · Lucreţia Miu

Abstract Leather products have been useful materials since the dawn of human history. Many leathers objects are valuable treasures due to the history they represent, and their preservation challenges museum custodians and private collectors alike. In this article, the applications of thermal analysis methods (Micro Hot Table (MHT), thermogravimetry/derivative thermogravimetry (TG/DTG), dynamic scanning calorimetry (DSC), differential thermal analysis (DTA), and dynamic mechanical analysis (DMA)) for the characterization of the recently manufactured and old leathers are presented. These methods can be used for the assessment of deterioration degree of leathers, and, therefore, the data obtained by these techniques could be useful for achievement of the suitable preservation procedures as well as the effects of conservation treatments. In addition, it was pointed out that these methods are suitable for qualitative distinction between the recently manufactured leathers and heritage items.

Keywords Thermal analysis · Leathers · Historical objects · Damage assessment

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Introduction

The leather products (light leathers: tanned skin for footwear, garments, bookbinding leathers, etc.; heavy leathers: for soles, and belts, etc.) have been useful materials since the dawn of human history. The tanning has been described as man's first manufacturing process. For example, in Egypt, tanned leathers were used from the pre-historic period [1].

Leather's natural degradation at all levels of structural hierarchy (from molecular to microscopic levels) can be categorized according to the cause and associated external manifestation in chemical, mechanical, and biological damage [2].

There are reviews [3–5] concerning the history of the interpretation of chemical deterioration of vegetable-tanned leathers according to which the degradation of tannin/collagen complex consists in two main processes, hydrolysis and oxidation. These reactions are both influenced by the environment within leathers, e.g., humidity, heat, light, pH, gaseous pollutants, etc.

Concerning the biological damage, the leathers are resistant to bacterial attack, but more than 50 species of fungi have been found growing on leather [6].

The investigation of these kinds of leather deteriorations is very important for solving the following problems of the museum custodians, private collectors, and restaurateurs: (a) the identification of cultural or historical object (manufacturer, period in which the object was manufactured, etc.); (b) the distinction between the original artifacts and bootlegs; (c) the evaluation of museum environmental risk; (d) the restoration of the patrimonial objects; and (e) the achievement of some suitable preservation treatments.

The analysis of a historical or cultural material raises two major problems, namely, the sample size and the

heterogeneity of the material. The quantity of material is limited and, therefore, it is frequently not possible to make more than one measurement on the actual sample. On the other hand, the heterogeneity of the investigated material does not allow the correlation of the results obtained independently by two different methods of analysis.

The development of the analytic techniques improves the procedure to identify the patrimonial objects made from leathers as well as the methods to put in evidence the impact of environmental factors on them. Among these techniques, the thermal analysis methods, especially thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), Micro Hot Table (MHT), thermo-mechanical analysis (TMA), and dynamic mechanical analysis (DMA), are potentially useful to conservation scientist (see, for example [7]). In this article, the results reported in the literature concerning the application of these methods in the investigation of leathers from some historical and/or cultural objects will be presented and discussed.

Thermo-analytical techniques used in leather investigation

In this article, the nomenclature in thermal analysis based on the articles of the Nomenclature Comity of ICTA published by Mackenzie [8, 9] and discussed by Hemminger et al. [10, 11] will be used. The main thermal analysis techniques which have been used in the investigation of leathers from some historical and/or cultural objects are thermomicroscopy (MHT method), TG, DTA, DSC, and DMA.

Thermomicroscopy

Thermomicroscopy is the technique in which the sample is observed by means of a microscope while it is the subjected to a temperature regime. For the investigation of collagen-based materials (pure and modified collagen, parchment, leather etc.), a simple thermomicroscopy technique, known as Micro Hot Table (MHT) method, has been used. A hot table with wet leather fibers is placed between a microscope glass and coverslip. The temperature of the heating element is increased with a constant heating rate (usually 2 K min^{-1}). The fibers are examined using magnification of 100 times as they are heated. For the observation of the sample and, especially for the registration of dynamic events, a video camera may be attached to the microscope.

Thermogravimetry

Thermogravimetry (TG) consists in the measurement of the mass change of the sample while it is subjected to a temperature regime. Modern electro-balances have resolution for mass change better than 2 μg, and allow performing measurements under defined gas atmosphere in isothermal and non-isothermal (usually linear heating rate) conditions. Modern instruments need samples of few mg, even less than 1 mg for an accurate determination, and therefore the TG method is suitable for investigation of materials from a patrimonial object. These instruments allow also the numerical differentiating of TG curves. As it will be shown in "Simultaneous TG/DTG + DSC or DTA analysis" section, the DTG curves so obtained give us information concerning the deterioration of old leathers.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)

Both DTA and DSC techniques measure the thermal effect of some processes (phase transitions, crystallization, decomposition, thermo-oxidation, etc.). In DTA technique, the difference in temperature between the sample and a reference sample (ΔT_{SR}) is monitored against time while the samples are subjected to a temperature regime. On the other hand, DSC technique consists in the measurement of the difference in the heat flow rate (or power) to the sample and to a reference sample while they are subjected to a temperature regime. Obviously, DSC and DTA signals are proportional. The modern DTA and DSC apparatus allow using samples of few mg, and in some favorable cases, even less than 1 mg. Therefore, these thermal analysis methods are also suitable for investigation of materials from a patrimonial object, particularly the old leather.

Simultaneous TG/DTG + DTA (or DSC) analyses

The heterogeneity of the investigated material does not allow the correlation of the results obtained independently by different methods of analysis. This difficulty can be overcome using simultaneous thermal analysis (STA) technique, such as TG/DTG + DTA or DSC. The main advantages of using such techniques are the following [12]: (a) STA measurements need much less time to perform all required measurements; (b) accuracy correlation of the observed different events is assured; (c) the same sample (size, mass, surface, morphology, composition, etc.) is monitored by different techniques, but under identical external factors (heating or cooling rate, gas-flow, gas-composition, type of furnace, …).

Dynamic mechanical analysis (DMA)

Dynamic Mechanical Analysis (DMA) is a method that is used to acquire useful information about viscoelastic properties of materials. With this technique, the sample is

exposed to a sinusoidal mechanical force (or deformation) at fixed frequency over a specific temperature range (in this case, it is called dynamic mechanical thermal analysis, DMTA) or isothermally as a function of time, and the corresponding deformations (or forces) measured. This can be done in tensile, compression, shear, flexural, and bending modes of operation. The DMA data are used to determine the storage modulus (E'), which is an indication of elastic behavior and reveals the ability of the material to store elastic energy, the viscous or loss modulus (E''), which is an indication of energy absorbed that is not returned elastically, and the loss tangent (tan δ) or mechanical damping which is given by the ratio of the viscous modulus to the elastic modulus. This viscoelastic property is a measure of the mechanical energy dissipation or "loss" within the material in the form of heat. DMA can be also used in TMA mode, when it measures the changes in displacement under a static load. DMA has the advantage that it is much more sensitive than other techniques in detecting thermal transitions corresponding to subtle molecular changes [13].

Applications

Hydrothermal stability

Hydrothermal structural stability of collagen-based materials is characterized by shrinkage of the material when it is heated in water. The temperature at which fully hydrated material shrinks under definite conditions is called the shrinkage temperature (T_s) [5]. The reason of hydrothermal shrinkage of collagen-based materials is the weakening or dislocation of the triple helix configuration at heating, caused by breakdown of intermolecular and intramolecular forces (i.e., hydrogen bonding, hydrophobic bonding and crosslink bridges). Although the shrinkage process is irreversible, sometimes this has been linked to melting. The endothermic effect of shrinkage put in evidence by DTA and DSC techniques [14–17] supports the above association. T_s value depends on the raw material, the methods of tanning, and the deterioration degree which the leather has undergone during its lifetime [18]. The last dependence of T_s shows the importance of the determination of this in the study of historical and/or cultural collagen-based materials.

The standardized method for determination of the shrinkage temperature is described in TEST IUP 16 ("Measurement of shrinkage temperature up to 100 °C") of the International Union of Leather Technologists and Chemists Societies [19]. This Standard is equivalent to SLP 20 and EN ISO 3380. According to this method, T_s is determined by immersing a strip of leather in a mixture of water and glycerin subjected to a slow temperature increase. The shrinkage temperature is taken as the temperature when a contraction of the sample by about 0.3% of its length has occurred. This method recommended for Leather Industry requires a sample of 50×3 mm, which cannot be cut from any historic or cultural artifact. Therefore, in such cases, for determination of T_s, the MHT method and DTA or more recently DSC techniques, which need smaller samples (few fibers for MHT and few mg for DTA or DSC), have been used.

As was mentioned in "Thermo-analytic techniques used in leather investigation" section, MHT method consists in optical observation of few fibers of collagen-based material immersed in water when the water–fiber system is heated at a constant heating rate. On heating, the fibers will deform over a distinct temperature interval. Leather collagen fiber shrinkage can be described in the temperature range as follows [20]:

$$T_{\text{initial}} \rightarrow \mathbf{A1} \rightarrow \mathbf{B1} \rightarrow \mathbf{C} \rightarrow \mathbf{B2} \rightarrow \mathbf{A2} \rightarrow T_{\text{final}}$$
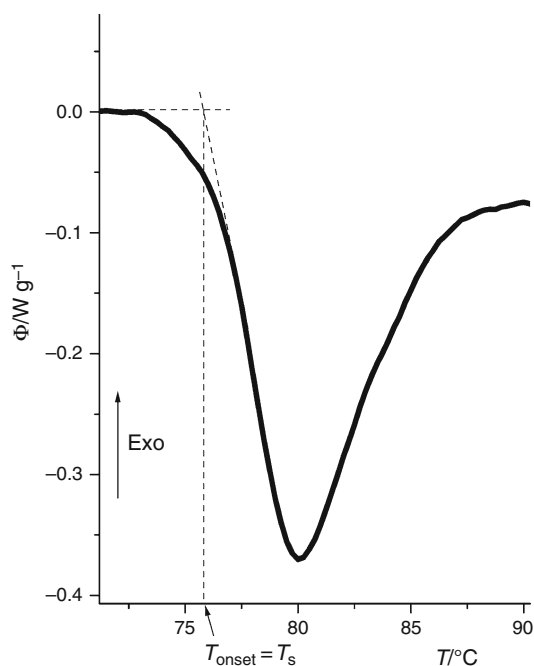
where T_{initial} corresponds to the temperature at which the material fibers are inactive; **A1** corresponds to the temperature at which the first shrinkage of individual fibers is noticed; **B1** corresponds to the temperature at which a fiber shrinkage is immediately followed by another fiber shrinkage (consecutive shrinkages); **C** corresponds to the contraction temperature at which most fibers experience simultaneous shrinkage (shrinkage temperature); **B2** corresponds to the temperature at which the last fibers experience simultaneous shrinkage; **A2** corresponds to the temperature at which the shrinkage of the last individual fibers noticed; and T_{final} stands for temperature at which fibers shrinkage is complete.

For example, for a new leather vegetable-tanned with Quebracho, $T_{\text{initial}} = 24.3$ °C; **A1** $\rightarrow$ 29.6 °C; **B1** $\rightarrow$ 50.8 °C; **C** $\rightarrow$ 69 °C; **B2** $\rightarrow$ 76.2 °C; **A2** $\rightarrow$ 78.8 °C; and $T_{\text{final}} = 82.9$ °C [21].

In a very recent article [22], the precision and accuracy of MHT method were investigated taking the official IUP 16 method as reference. For the samples of commercial leathers and leather artifacts provided by the Leather Museum of Igualada–Barcelona–Spain, a good agreement between T_s values determined by both methods was obtained.
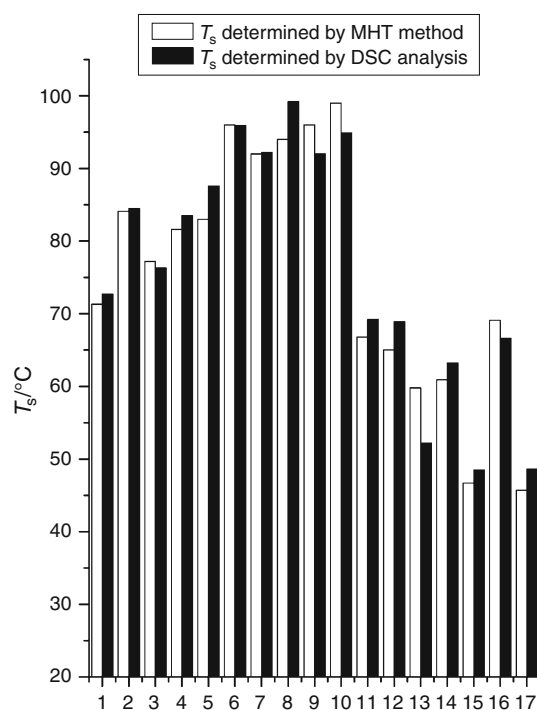
The MHT method has demonstrated to be a very good technique to help in the conservation work of different skin and leather artifacts, like museum skins subjected to freezing treatment [23], archeological seal skin [24], antique bookbinding and gilded leather [25], skins of vertebrate research collections of museum [26], historical parchment [27], bookbinding white tawed leather, [28] and ethnographic leather objects [29].

The DTA technique was first used by Witnauer and Wisnewski [14] for examination of shrinkage of collagen.

Fig. 1 DSC curve for a new vegetable-tanned leather immersed in water [30]

Fig. 2 T_s values determined by MHT method and DSC analysis. 1–4 new vegetable-tanned leathers; 5–10 new combined tanned leathers; 11–17 naturally aged leathers extracted from Romanian objects (XV–XIX centuries)

The DSC and DTA signals are proportional, but in comparison with the DTA technique, the DSC technique also allows for the direct and highly accurate determination of enthalpy of denaturation in water of a collagen-based material. Therefore, Chahine et al. [15–17] and Budrugeac et al. [30–33] had applied the DSC technique for evaluation of the shrinkage temperature of new and aged parchments and leathers. When the DSC method is applied, the sample pan is obtained by hermetically sealing into aluminum crucible of a collagen-based material piece of around 3 mg that was previously kept in water for several hours [17], or by hermetically sealing of a material piece of around 3 mg together with 35 µl deionized water and stoking this for 24 h [30]. In both procedures, each sample pan together with a reference pan are heated from room temperature to 110 °C with a heating rate of 10 K min^{-1}. Figure 1 shows the DSC curve for a new vegetable-tanned leather immersed in water with an extrapolated onset temperature of 76.3 °C, a peak at 80.1 °C, and $\Delta H = -11.45$ J g^{-1}. This extrapolated onset temperature is close to the shrinkage temperature evaluated by MHT method (72.2 °C). Figure 2 shows comparatively the values of T_s obtained by the DSC and MHT methods for some new vegetable-tanned leathers, new combined tanned (vegetable + Cr) leathers, and naturally aged leathers extracted from Romanian patrimonial objects [30, 32]. For a given leather, the reasonable differences between T_s values determined by the DSC and MHT methods could be due to heterogeneity of the investigated material.

One notes that according to the results shown in Fig. 2, the increasing order of the shrinkage temperature is old leathers < recent leathers manufactured by vegetable-tanning < recent leathers manufactured by combined (vegetable + Cr) tanning. Budrugeac et al. [30, 32] pointed out that old leathers exhibit T_s values higher than pure collagens and new and old parchments. On the other hand, Larsen et al. [20, 25] using the MHT method found that T_s values of old leathers were lower than those corresponding to new vegetable-tanned leathers. All these results led to the following sequence order of T_s collagen-based materials: fresh collagen (30–45 °C) < mature collagen (≈ 65 °C) < new vegetable-tanned leathers (70–90 °C) < new combined tanned (vegetable + Cr) leathers (92–97 °C). These results could be explained by structures of collagen-based materials and the change of leather structure as a result of natural aging. The collagens and parchments are untanned materials with a low degree of cross-linking. On the other hand, the new tanned leathers, since they include many cross-links between protein chains in the collagen fibers, invariably have a shrinkage temperature higher than the collagens and parchments. The obtained order of T_s values shows that the first stage of natural degradation of leathers consists in breaking of the cross-linking bonds, which is followed by splitting of collagen macromolecules. It appears that T_s value is a measure of degradation of leather during its
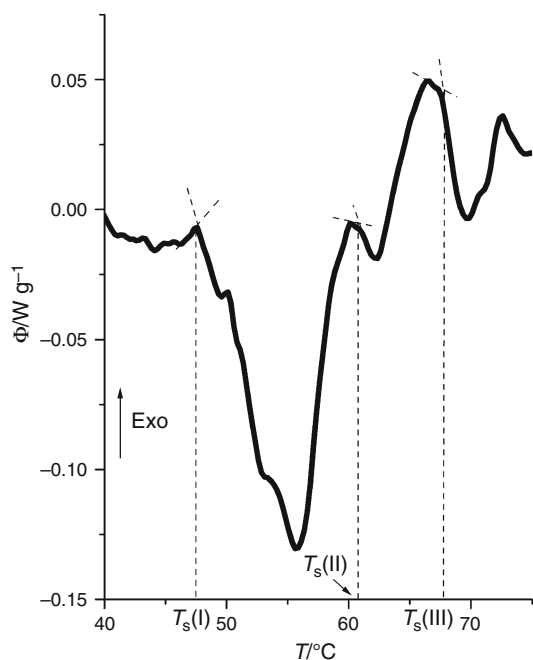
Fig. 3 DSC curve for a sample of leather extracted from the tomb of Hagi Gherai Khan [34]

lifetime. For a quantitative determination of the degradation degree of naturally aged leather, it is necessary to have reference leather manufactured by the same method as applied for the old one. The difference between the two values of T_s could be proportional with the degradation degree. However, the procedure of obtaining of old leather is not completely known, and therefore such quantitative evaluation is not possible.

The DSC curves of some old leathers immersed in water exhibit several peaks in the temperature range 20–100 °C [33, 34]. One such DSC curve is shown in Fig. 3. The existence of many peaks in the DSC curve indicates various deterioration levels within the material.

Melting of crystalline (rigid) region of leathers

Collagen is the major protein from which skin is formed, and is fundamental to the leather-making process. Therefore, the properties of leathers are expected to be similar, but not identical, to those of collagen. We begin with a brief discussion concerning the amorphous–crystalline structure of collagen as was put in evidence especially by the DTA and DSC methods.

In order to investigate the phase changes of collagen (purified steer Achilles tendon, and dried with phosphorus pentoxide), Okamoto and Saeki [35] used the following methods: dynamometry, DTA, and X-ray diffraction. By the DTA method, the following successive processes have been put in evidence on progressive heating of collagen

from room temperature to 225 °C: an endothermic process occurring between room temperature and 120 °C, and a second endothermic process that begins around 170 °C and exhibits a minimum at 215 °C. The first process consists in the vaporization of the adsorbed and absorbed residual water. The correlation of the results obtained by the DTA method and X-ray diffraction leads to the conclusion that the second process consists in the melting of stable crystalline region of collagen. Okamoto and Saeki [35] considered that the investigated collagen is a mixture of three regions of different structures: the amorphous region, the less-oriented unstable crystalline region, and the stable crystalline region.

A few other studies [36–38] performed by the DTA and DSC methods put in evidence similar behavior of some sorts of collagen. Nguyen et al. [36] and Samoillan et al. [37] considered that the second endothermic peak having the minimum around 220 °C corresponds to a first order transition, while Pietrucha [38] associated this peak with the evaporation of residual strongly bond water and continued conformational changes of superhelix. Samoillan et al. [37] specified that the collagen transition occurring around 220 °C consists in the denaturation of dry collagen and corresponds to the helix—coil transition induced by thermal disruption of hydrogen bonds. In solution, this collagen-gelatin transition occurs between 20 and 80 °C and is a measure of the thermal stability of collagen (see "Hydrothermal stability" section). This remark suggested that the value of the melting temperature depends on the cross-linking degree of collagen-based materials as well as on the degradation of these materials. The verification of this was the main objective of a recent study [30] that presented and discussed the results obtained by the DSC analysis in some gas (nitrogen, oxygen, and synthetic air) flow of a sort of pure collagen with $\overline{M} = 130{,}000$; 14 sorts of new parchments; 16 sorts of naturally aged parchments; new leathers (five sorts of vegetable-tanned leathers and six sorts of combined (vegetable + Cr) leathers); and 30 sorts of naturally aged leathers. Figure 4 shows the DSC curve obtained by analysis in nitrogen flow of a new vegetable-tanned leather.

On progressive heating of the leather, the following successive processes occur: an endothermic process, denoted by I, corresponding to the loss of absorbed water, and another endothermic process, denoted by II. This DSC curve is similar to those obtained [35–38] for some sorts of collagen, and therefore the second peak II could be attributed to melting of crystalline region of the investigated material. Very recently [39], the data from Proton solid-state NMR, obtained for pure collagen, new and old parchments and leathers, have led to a three-phase model (rigid, interface, and mobile phases) of collagen-based
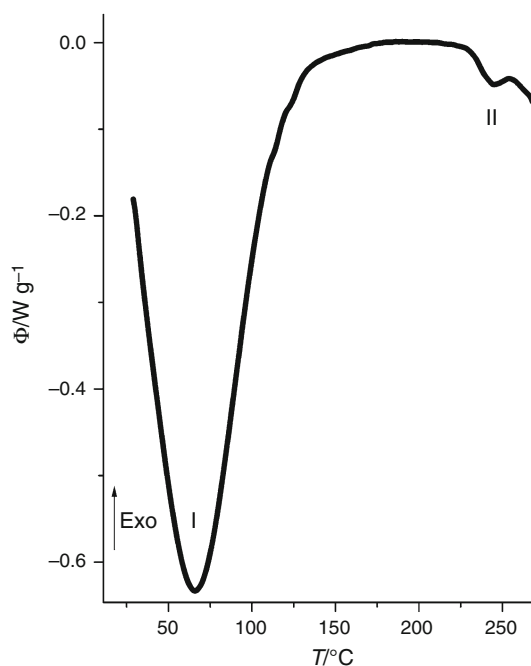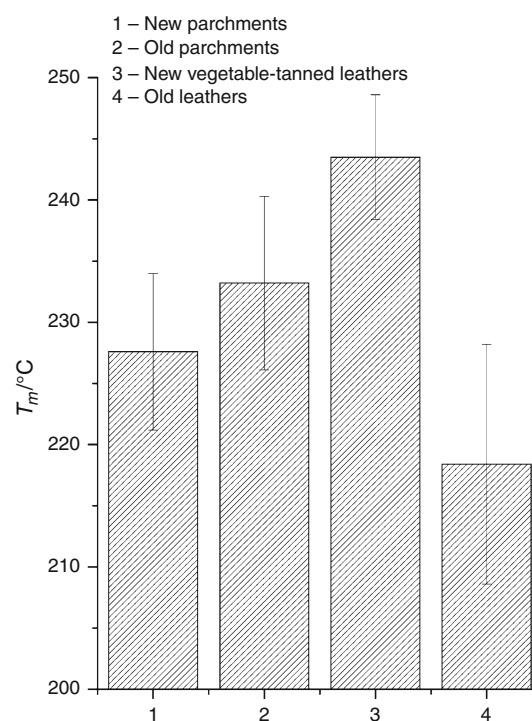
Fig. 4 DSC curve obtained by analysis in nitrogen flow and 10 K min^{-1} of a new vegetable-tanned leather [30]

Fig. 5 The average values of T_m for melting of collagen-based materials [30]

materials. According to this model, the process II might be related to softening of the rigid part of collagen-based materials. Except the new leathers manufactured by combined tanning and seven old leathers, the analyzed materials exhibit an endothermic peak II with the temperature (T_m) in the range 205–245 °C [30]. The old leathers could be classified in terms of number of endothermic peaks put in evidence after dehydration in old leathers that exhibit two endothermic peaks, one with T_m in the temperature range 125–141 °C, and another with T_m in the temperature range 208–228 °C; old leathers with a single endothermic peak with T_m in the temperature range 125–141 °C; and old leathers with a single endothermic peak with T_m in the temperature range 208–228 °C. The supplementary peak with T_m in the temperature range 125–141 °C could be due either to a different deterioration level, or to a common component of the leather that exhibits a melting process at relatively a low temperature.

Figure 5 [30] shows the average values of T_m for melting peak with $T_m > 200$ °C. It appears that (a) the new vegetable-tanned leathers exhibit the highest values of T_m, and (b) the old leathers have T_m values comparable with those for new and old parchments, but lower than those corresponding to the new vegetable-tanned leather.

These results were explained [30] by above mentioned amorphous-crystalline structure of collagen-based materials, according to which the melting of the crystalline region is hindered by rigidity of amorphous matrix. The tanning process by inducing cross-linking stabilizes the crystalline region. Therefore, T_m values in the case of recent

vegetable-tanned leathers are higher than those corresponding to new and old parchments. The lower values of T_m obtained for old leathers could be mainly caused by the decreasing of the cross-linking degree as a result of naturally aging process of the material. The processes of decrease in cross-linking and fragmentation are influenced by different leather preparation procedures and by various environmental conditions of stoking and exposure. Therefore, the temperature related to melting process cannot be used for dating of patrimonial objects, but be used only as a qualitative criterion to discriminate between new and old leathers. This criterion may be used for distinction between an original artifact and a bootleg.

Unlike the results obtained by DSC analysis in nitrogen flow, the values of melting temperature of the samples heated in oxidative atmosphere (oxygen or synthetic air) cannot be correlated with the damage of the leathers. This statement could be due to the oxidation of the new and old leathers during progressive heating in oxidative atmosphere.

Simultaneous TG/DTG + DSC or DTA analysis

In some recent articles [32, 40–42], the results obtained by simultaneous TG/DTG + DSC or DTA analysis in static air atmosphere of some collagen-based materials (collagens, new and old parchments, and leathers) were comparatively presented and discussed. Figure 6 shows the TG/DTG + DSC or DTA curves for a leather sample extracted
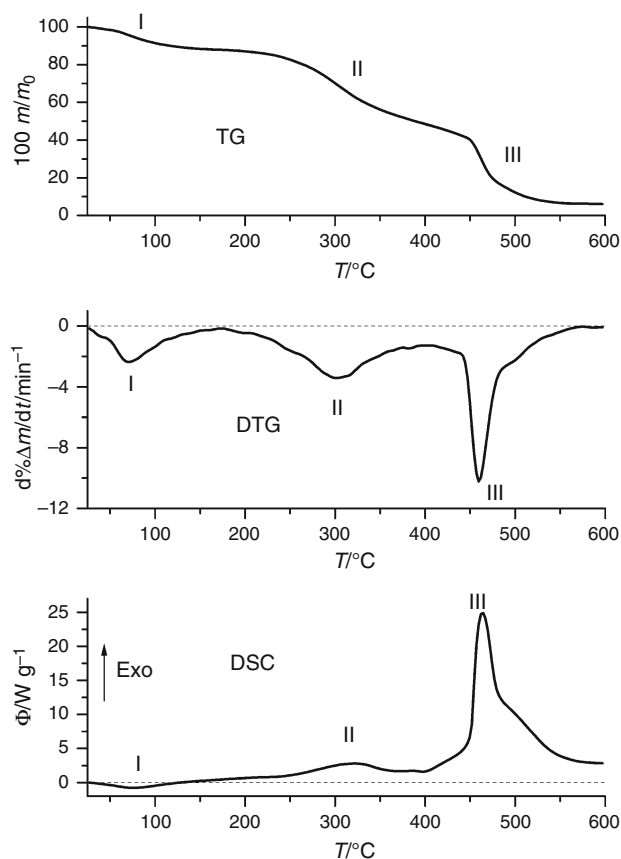
Fig. 6 TG, DTG, and DSC curves of a patrimonial leather (book cover of a Romanian Breviary published in the eighteenth century) recorded in static air atmosphere and at the heating rate of 10 K min^{-1}

from a book cover of Romanian Breviary published in XVIII century. Similar plots have been obtained [32, 40–48] for recently extracted collagens, recently manufactured parchments, naturally aged parchments, recently manufactured vegetable-tanned leathers, naturally aged leathers extracted from some patrimonial objects.

The non-isothermal thermo-oxidative degradation of a sort of collagen-based material occurs through three successive processes accompanied by mass losses. In the first endothermic process, denoted by I in Fig. 6, which occurs at less than 150 °C, the water contained by material is lost. The next two steps, denoted by II and III in Fig. 6, are exothermal and consist in the pyrolitic thermo-oxidation and decomposition of the material. The values of characteristic parameters of these processes depend on the conditions in which the thermal analysis were performed; e.g., for experiments performed at heating rate of 2.5 K min^{-1}, the maximum rate of process II occurs around 288 °C [40], while at the heating rate of 10 K min^{-1}, this temperature is around 310 °C [32]. It was pointed out [32, 40–42] that the main characteristic parameter that could be correlated with cross-linking of collagen-based materials and their damages

is the rate, $\frac{d\%\Delta m}{dt}$, of the first process of thermo-oxidation (process II in Fig. 6). For a given heating rate, all the investigated collagen-based materials exhibit values of temperature corresponding to maximum rate of process II in a narrow range (<10 °C) [32, 40–42]. Therefore, the values of $\frac{d\%\Delta m}{dt}$ for average temperature of this peak, as well as the rate values corresponding to the maximum II of DTG curves were compared. For the new and old parchments and new leathers, the following order of increasing of these rates was obtained [32, 40–42]: new parchments $\approx$ old parchments < new vegetable-tanned leathers < new combined (vegetable + Cr) tanned leathers. The patrimonial (old) leathers are divided in two groups, namely, PL1 for which the rates of thermo-oxidation process II are lower than those corresponding to new leathers manufactured by vegetable tanning, and PL2 for which the rates of the process II are close to or higher than those of new vegetable-tanned leathers (see Fig. 7 in which data given in ref. 32 were used).

The relatively high rate of thermo-oxidation process II observed for new leathers manufactured by combined tanning could be due to reactive sites introduced by cross-linking. Similarly, the oxidative reactivity of polymeric materials carbon increases with the increasing degree of substitution obtained by cross-linking, see for example, [49]. The following two main complex processes occur
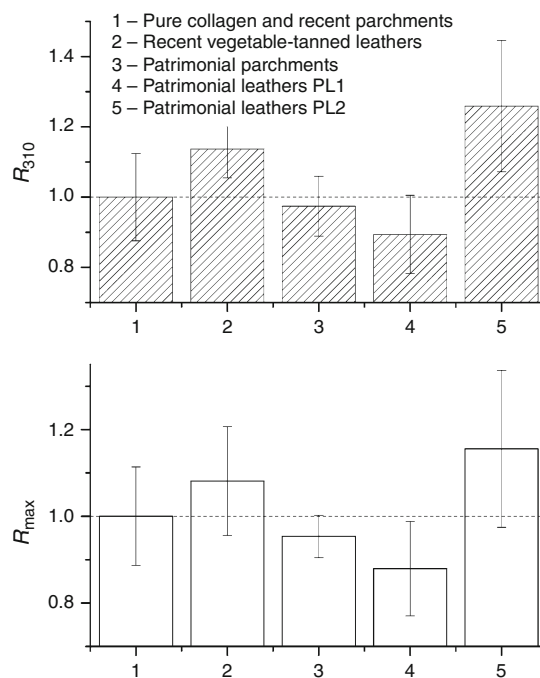
Fig. 7 R_{310} and R_{max} corresponding to the investigated collagen-based materials. The TG/DTG curves were recorded in static air atmosphere and the heating rate 10 K min^{-1}. R_{310} and R_{max} are the values of $\left(\frac{d\%\Delta m}{dt}\right)_{310^0}$ and $\left(\frac{d\%\Delta m}{dt}\right)_{T_{max}}$ respectively, normalized by corresponding average values of collagen + new parchments

during the natural aging of collagen-based materials: the breaking of the cross-linking bonds and the splitting off of collagen macromolecules by hydrolysis with water vapors, followed by the oxidation of the lower macromolecules. The thermal behavior of PL1 leathers tends toward that corresponding to parchments and collagen, which exhibit a low degree of cross-linking. This suggests that, for these leathers, the breaking of cross-linking bonds is predominantly of naturally degrading process. On the other hand, the PL2 leathers exhibit an advanced degree of degradation which determines their high reactivities in oxidation processes.

From the practical point of view, the results obtained by TG/DTG method could be used for distinction between recently manufactured leather and one naturally aged (patrimonial) leather. If for a leather sample one obtains values of rate of the first process of thermo-oxidation lower than those corresponding to recent vegetable-tanned leathers, 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 because the very high degradation of this material could lead to the fragmentation of collagen macromolecules. This criterion could be used for distinction between an original artifact and a bootleg. As was mentioned in previous section, the results obtained by thermal analysis, particularly by TG/DTG method, cannot be used for dating of patrimonial object because the characteristic parameters of an old material depend on the environmental conditions of stoking and exposure.

Application of DMA technique

The DMA studies on leathers are recent, and they initially characterized the drying and shrinkage behavior. Cohen et al. [50] have studied the shrinkage behavior in tensile mode of leather and parchment immersed in water and heated while measuring the changes in sample displacement as a function of time. Thus, for a sample of unaged leather, a rapid shrinkage was observed as a sharp decrease in sample length at a specific temperature step (Fig. 8). This behavior was found quite similar to that of unaged parchments.

Odlyha et al. [51] have performed DMTA in tensile and TMA mode on wet leather samples. In tensile mode, it was found that an aged calf leather sample has its tan δ peak at lower temperature (52 °C) than an unaged calf leather (70 °C) and is less viscoelastic (Fig. 9a). Also, for the aged sample, the initial modulus is higher and on heating through the shrinkage temperature it shows a smaller increase than the unaged leather, which becomes significantly stiffer (Fig. 9b).
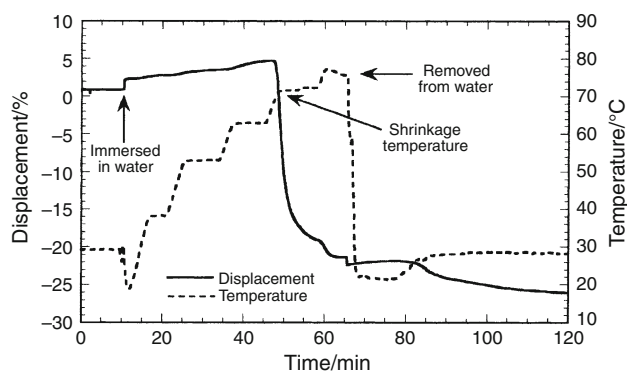

Fig. 8 Percentage displacement on immersion in water and on heating plotted as a function of time for modern (unaged) leather [50]
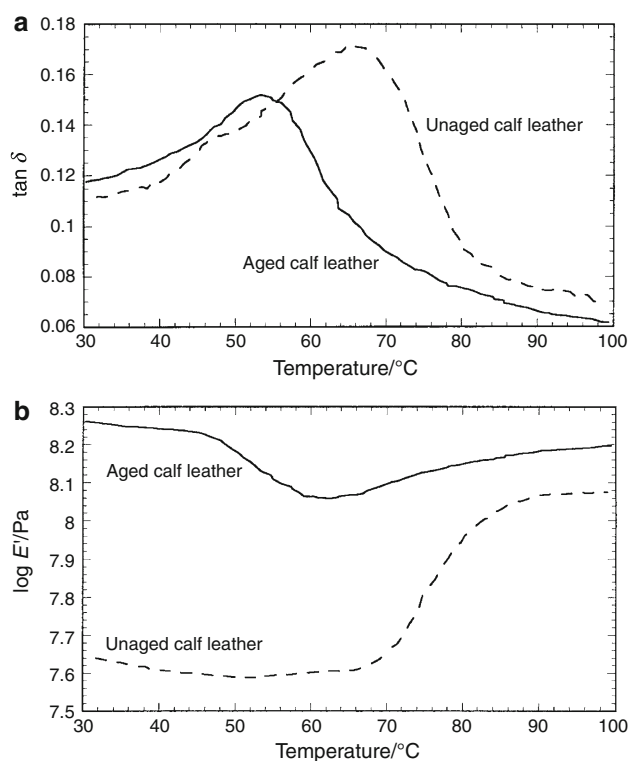
Fig. 9 Tan δ curves for unaged and aged calf leather (**a**), log (E'/Pa) curves for unaged and aged calf leather (**b**) [51]

The DMTA experiment in the TMA mode also revealed differences in behavior between the aged and unaged samples and between the goat and calf leather. The unaged sample showed a longer shrinkage and drying time than the aged sample and a smaller initial displacement. Goat leather samples had less distinct changes and took longer to dry than the calf leather. From values of displacement recorded as a function of temperature (Fig. 10b), it was possible to calculate values for the shrinkage temperature and the amount of shrinkage (in terms of percentage displacement change).
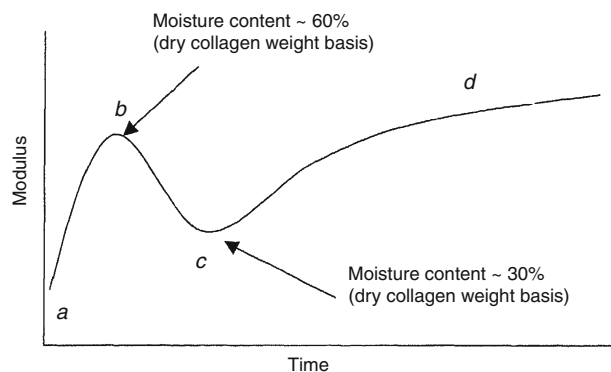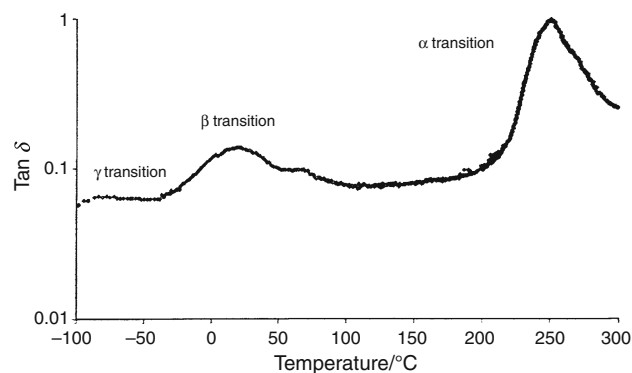
a

b
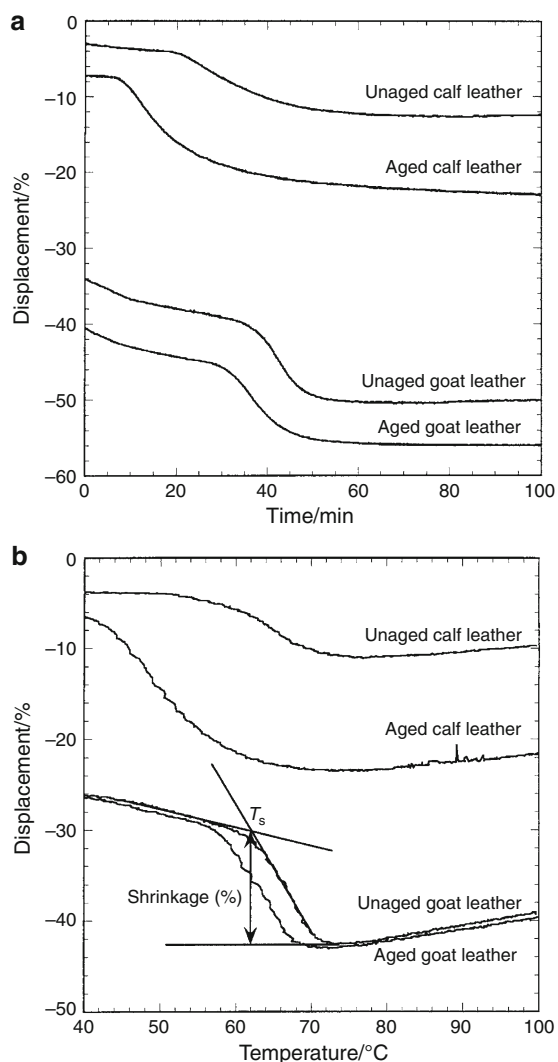
Fig. 10 Displacement (%) versus time (**a**) and temperature (**b**) for unaged and aged goat and calf leathers [51]

Fig. 11 Generic curve of changes in bend modulus during drying of leather [52]

Fig. 12 A typical DMTA thermogram of a vegetable tanned leather [53]

Jeyapalina et al. [52, 53] have reported two articles concerning DMTA studies in bending mode on new (unaged) leathers. The first article [52] investigates the drying profile of leathers in terms of monitoring the stiffness as a function of time at different temperatures. It was found that the changes in modulus are related to the moisture content of the samples and not to the drying temperature. A generic master curve for drying of leather shows two inflexions points **b** and **c**, corresponding to critical moisture contents of ∼ 60 and ∼ 30% (Fig. 11). The authors suggest that each stage of drying is attributed to different states of water molecules within leather and suitable explanations are given.

The second article reports the DMTA behavior of leather within the temperature range from −100 to 300 °C [53]. Three major viscoelastic transitions were identified (Fig. 12), whereby the α and β peaks are suggested to be

the shrinking-related transition and the glass transition, respectively. DMTA properties exhibited by chrome-tanned leather were found quite different from the untanned and vegetable-tanned leather, as it shows an additional β' peak. The authors found that tanning agents act as plasticizers and depress the glass transition β to a lower temperature. However, the same effect was observed with increasing moisture content, and complicated leather–water relationship was put in evidence and discussed.

Very recently, DMTA studies were performed by Cucos et al. [54, 55] on new and historical parchments and leathers from room temperature to 260 °C and in tensile mode. In [54], a preliminary comparison was made, among others, between the dynamic mechanical behaviors of a new and old leather. It is found that the behavior of the old leather is closer to that of parchments than to the new leather's one, and exhibits a major melting process above 200 °C. A more exhaustive series of DMA, DSC, and XRD studies are presented in [55] on a large number of samples, including 31 historical/heritage leathers such as old bookbindings, covers of religious books, chair tapestries, etc. Their DMA behaviors on heating were found quite different, from those similar to parchments and collagen,
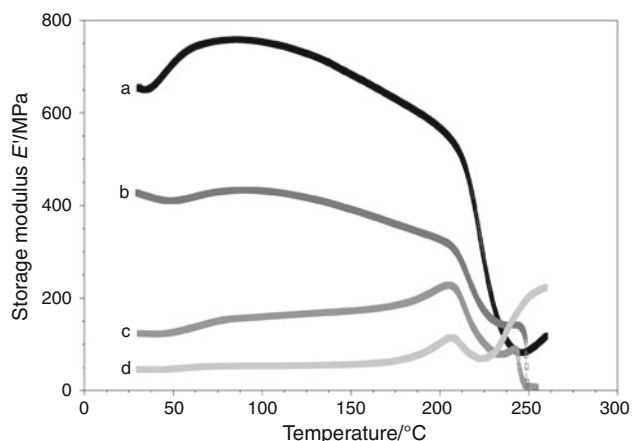
Fig. 13 Examples of E' versus T curves for historical leathers (adapted from [55])
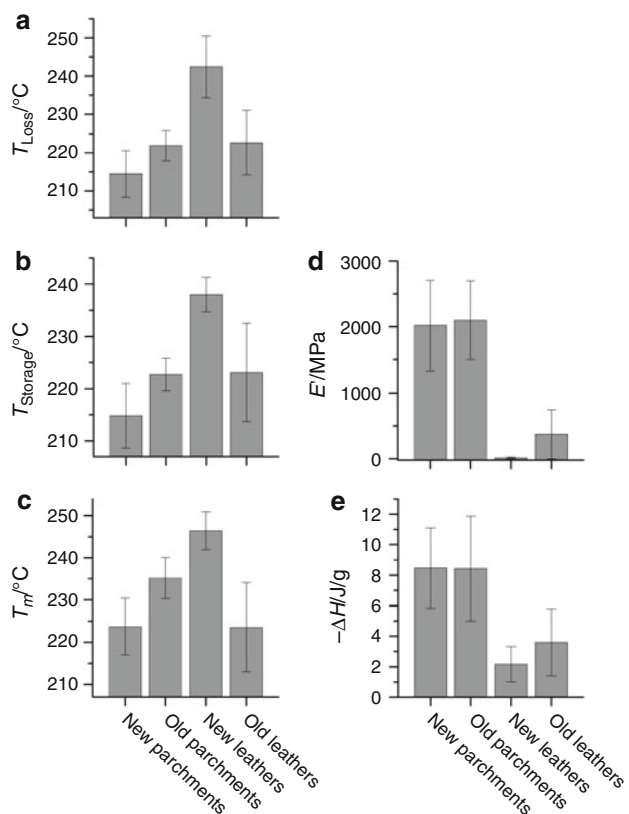
Fig. 14 Average melting temperatures determined by DMA (T_{Loss} (**a**), T_{Storage} (**b**)) and DSC (T_m (**c**)); average values of initial E' (**d**) and enthalpy of melting, $-\Delta H$, **e** for new and historical parchments and leathers [55]

characterized by an abrupt decrease of modulus at high temperatures due to the melting of the collagen crystalline phase (Fig. 13a), to those similar to new leathers, characterized by an increase in stiffness (Fig. 13d). The authors make the supposition that these behaviors represent various levels of degradation and could be used for a qualitative

assessment of heritage leathers. For these collagen-based materials, a good correlation was found between the average melting temperatures determined by DMA and DSC (Fig. 14a–c). A good agreement was also found between the average values of initial E' and the enthalpy of the melting (Fig. 14d, e), both related to the relative content of collagen crystalline phase determined by XRD [55].

Conclusions

The results presented in this review clearly establish that thermal analysis methods (MHT, DSC, DTA, TG/DTG, and DMA) are applicable to the characterization of leathers from some historical and cultural objects (patrimonial leathers). These methods can be used for assessment of deterioration degree of leathers at mesoscopic level. Therefore, the data obtained by thermal analysis techniques could be used for achieving the suitable preservation procedures applicable for patrimonial leathers as well as for monitoring the effects of conservation treatments.

In addition, several criteria to discriminate patrimonial leather from a newly prepared one are based on the results obtained by thermal analysis methods. These criteria may be used for distinction between an original artifact and a bootleg.

Future developments of thermal analysis techniques, the correlation of results obtained by these methods with those obtained by other analytic techniques, and research into material science will improve the understanding of degradation processes of leathers and their procedures of conservation.

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