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THE DAMAGE IN THE PATRIMONIAL BOOKS FROM ROMANIAN LIBRARIES
Thermal analysis methods and scanning electron microscopy

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The thermal analysis methods (TG, DTG, DSC, methods for shrinkage temperature evaluation) and scanning electron microscopy (SEM) were used for investigation of the thermal behaviour and surface morphology of some recent manufactured parchments and vegetable tanned leathers, patrimonial parchments and leathers proceeded from Romanian libraries. At the progressive heating in static air atmosphere and in the temperature range of 20–600°C, all investigated materials exhibit three main successive processes, associated with the dehydration and thermo-oxidative degradations.

The rate of the first thermooxidative process, temperatures corresponding to the maximum rate of the second thermooxidative process and shrinkage temperature were associated with the damage of the investigated materials due to environmental impact. Parchments and leathers surfaces were characterized by SEM, and specific morphological criteria were suggested for damage assessments. These criteria were correlated with the results obtained by thermal analysis methods.

Keywords: *DSC, DTG, leathers, parchments, patrimonial books from Romanian libraries, SEM, shrinkage temperature, TG*

Introduction

There is a long history of the procedures to identify the patrimonial objects and the evaluation of environmental factor on them. The investigation procedures were improved by the development of the analytical techniques like, X-ray diffraction, IR spectroscopy, Raman spectroscopy, gas-chromatography, scanning electron microscopy (SEM), thermal analysis methods (TG, DTG, DTA, DSC, DMTA, methods for shrinkage temperature determination, etc.). These techniques allow obtaining information concerning the physical and chemical properties of a material using samples of 1–5 mg. As it is noticeable from literature, only during last 15 years these methods were used in the field of patrimonial objects.

The thermal analysis methods were used to characterize some materials from patrimonial objects, like: sorts of parchments and leathers [1–11], paper and paper-like materials [12], pigments [13–19], glasses [20], ceramic materials [21–23], soil from China tombs [24], lime wood supports of old paintings [25], plasters [26], mortars [27], historic tapestries [28] and heritage stones [29].

In some previous papers [6, 8, 9] we have used TG, DTG and DTA methods for investigation of the degradation of some new and old parchments and leathers, in static air atmosphere, and in the temperature range of 20–500°C. The discussion was focused only on the first thermo-oxidative process for which the rate was correlated with the natural damage of the collagen-based materials.

In this paper, the results obtained by thermal analysis methods (TG, DTG, DSC, methods for shrinkage temperature evaluation) in the investigation of non-isothermal thermo-oxidative degradation of some recent manufactured parchments and leathers, patrimonial leathers and parchments proceeded from Romanian libraries will be presented. The conclusions of our previous works [6, 8, 9] will be checked and other possible correlation between the degradation degree and non-isothermal parameters will be advanced and discussed. In addition, the morphological alterations induced by natural aging of parchments and leathers have been monitored by SEM.

Experimental

Materials

Our experiments were carried out on the following samples:

- recent manufactured leathers: 6 sorts of vegetal tanned leathers (calf+quebracho, calf+mimosa,

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calf+chestnut, goat+chestnut, sheep+quebracho, sheep+mimosa); 7 sorts of combined tanned leathers (leather (calf, goat or sheep)+Cr+a vegetal tanner (quebracho, mimosa, chestnut, oak));
- a sort of pure collagen ($\overline{M}\approx130000$, produced by Riedel-de Haen AG);
- 10 sorts of recent parchments manufactured from sheep, calf and lamb skins;
- 4 sorts of naturally aged parchments extracted from patrimonial books published in XVII century and stored in the libraries of Romanian museums;
- 18 sorts of naturally aged leathers extracted from the covers of patrimonial books stored in the libraries of Romanian museums (3 sorts from XV century, one sort from XVII century, 10 sorts from XVIII century, 4 sorts from XIX century).

The new leathers and parchments were produced by ICPI-Leather and Footwear Research Institute, Bucharest, Romania.

Romanian Museum of History (Bucharest), The Central Military Museum (Bucharest–Romania), Bucharest City Museum and Moldova Museum (Iasi–Romania) supplied the patrimonial leathers and parchments.

Methods

Simultaneous TG/DTG and DSC analysis

The heating curves (TG/DTG and DSC) of samples were simultaneously recorded with STA 409PC 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 the analyzed samples was in the range of 4–6 mg and the heating of each sample was performed in a cylinder shape α-Al_2O_3 sample holder. For recent manufactured materials 2–3 measurements per sample were performed. Not more than 2 measurements were made on the old samples because very few were available.

Determination of the shrinkage temperature (T_s)

The shrinkage temperature was determined by the following methods:
- classical method (CM), using Giuliani–Italy apparatus, according to which the sample is immersed in a water bath and the temperature of water bath is gradually increase until T_s is reached, when the contraction of the material causes displacement of a pointer;
- micro hot table (MHT) method, using a Mettler FP900 Thermosystem and/or a MHT apparatus produced by Caloris–Romania;
- DSC analysis of each sample (2–5 mg), immersed in 35 mL of deionised water, hermetically sealed in an aluminium pan and stocked for 24 h [3, 30]. The DSC curve was recorded using DSC 204 F1 Phonix apparatus produced by Netzsch–Germany. Each sample was heated from 25 to 130°C at a heating rate of 10 K min^{-1}. The extrapolated onset temperature of the endothermic peak, which indicated denaturation of collagen-based material, was recorded as the shrinkage temperature.

The application of the first method needs a relative large amount of material. Therefore, this method was used only for T_s determination of recent manufactured materials. For these materials all methods of T_s determination were applied, while for old leathers and parchments only MHT and/or DSC methods that need small amounts of material were used.

Scanning electron microscopy (SEM)

SEM observations were made with a TESLA BS 301 apparatus. This method was used to inspect the general features of the surface of samples, the shape of the fibre patches, and the structure of individual fibres.

Results and discussion

Simultaneous TG/DTG and DSC analysis

Figure 1 shows the TG/DTG and DSC curves for a leather sample extracted from a book cover of a Romanian Breviary published in XVIII century. Similar

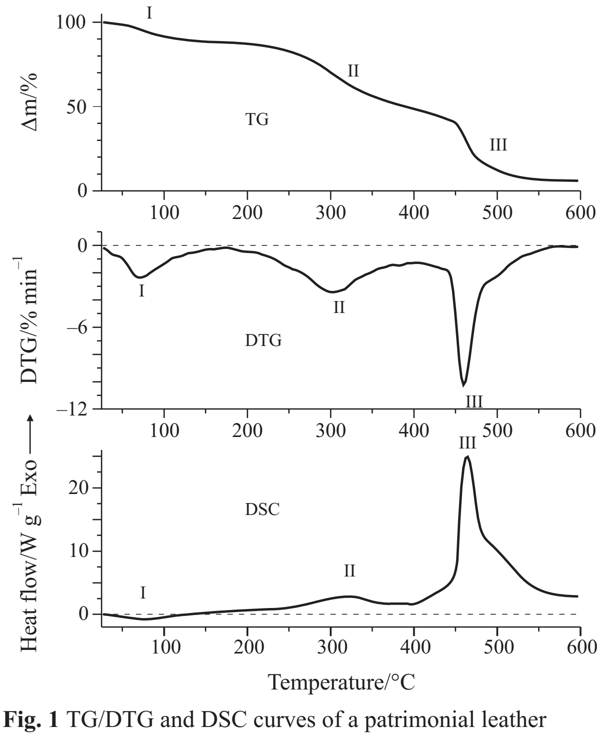

Fig. 1 TG/DTG and DSC curves of a patrimonial leather (book cover of a Romanian Breviary published in XVIII century)

plots have been obtained for all analyzed samples. These are in agreements with the results previously reported for some sorts of leather [6, 8, 9, 31], and collagen [6, 8, 9, 32–34].

The non-isothermal thermooxidative degradation of a sort of parchment or leather occurs through three successive processes accompanied by mass losses. In the first endothermic process (denoted by I), which occurs before 200°C, the water is completely lost. The next two steps (denoted by II and III) are exothermal ones and consist in the pyrolytic decomposition and thermo-oxidation of the collagen-based material.

In actual conditions of thermal analysis, the temperature corresponding to the maximum rate of process II is around 310°C, and, therefore we will compare the values of $d\Delta m/dt$ obtained at this temperature (Figs 2–4). The inspection of Figs 2–4 shows that:

- the pure collagen, and the recent manufactured and patrimonial parchments exhibit close values of $(d\Delta m/dt)_{310}$ or $(d\Delta m/dt)_{max}$;
- for the new leathers manufactured by combined tanning, $(d\Delta m/dt)_{310}$ or $(d\Delta m/dt)_{max}$ are higher than those corresponding to the new leathers manufactured by vegetal tanning;
- the patrimonial leathers are divided in two groups, namely: PL1 (13 sorts) for which the rates of thermo-oxidation process II are lower than those corresponding to new leathers manufactured by vegetal tanning, and PL2 (5 sorts) for which the rates of the process II are close or higher to those of new leathers manufactured by vegetal tanning.

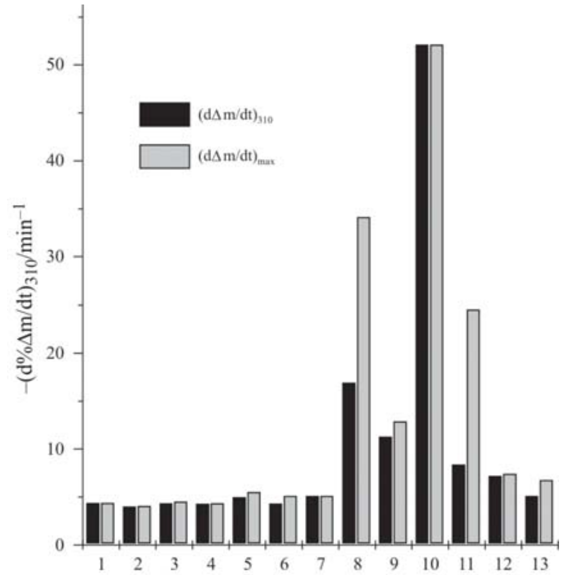

Fig. 3 The values of $(d\Delta m/dt)_{310}$ and $(d\Delta m/dt)_{max}$ for recent leathers manufactured by vegetal tanning (1–12) and by combined tanning (7–13)

Similar statements result by analysis of DSC curves.

Figure 5 shows the average values of $(d\Delta m/dt)_{310}$, $(d\Delta m/dt)_{max}$ and temperature corresponding to maximum rate of the thermo-oxidative process III (T_{max}(III))). One can see that $\overline{T}_{max}$ (III) has minimum value for PL2 leathers. However, for this kind of patrimonial leather, $\overline{T}_{max}$ (III) has a relative high standard deviation. The values of the considered parameters cannot be correlated with the ages of the an-

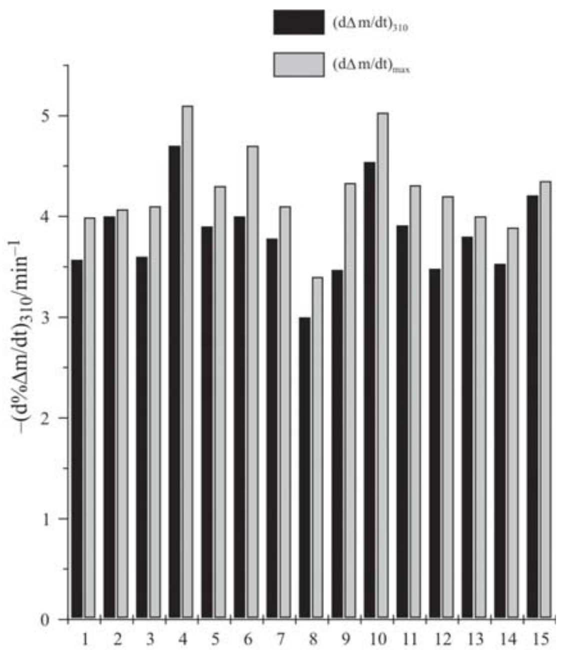

Fig. 2 The values of $(d\Delta m/dt)_{310}$ and $(d\Delta m/dt)_{max}$ for pure collagen (1), recent manufactured parchments (2–11) and patrimonial parchments (12–15)

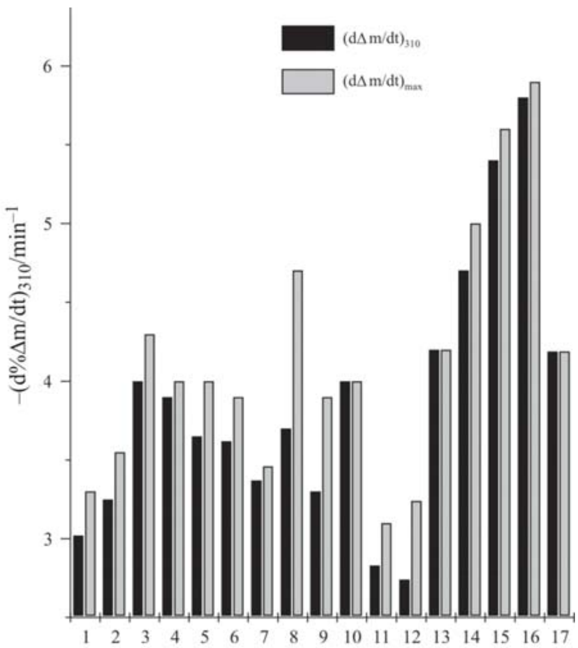

Fig. 4 The values of $(d\Delta m/dt)_{310}$ and $(d\Delta m/dt)_{max}$ for patrimonial leathers. 1–12: PL1; 13–17: PL2

alyzed materials because the degree of natural degradation depends not only on the duration of stocking, but also on the environmental conditions like humidity, heat, irradiation, polluants.

The relative high rate of thermo-oxidation process II observed for recent leathers manufactured by combined tanning could be due to the reactive sites introduced by cross-linking. Similarly, the oxidative reactivity of polymeric materials carbon increases with the increased degree of substitution obtained by cross-linking [35, 36]. The following two main complex processes occur during the natural aging of collagen-based materials: (1) the breaking of the cross-linking bonds and (2) the splitting off of the collagen macromolecules by hydrolysis with water vapors, followed by the oxidation of the lower macromolecules. The thermal behaviour of PL1 sort of leathers tends toward that corresponding to parchments and collagen, which are not tanned materials. This suggests us that, for these leathers, the breaking of the cross-linking bonds is the predominant degradation process. On the other hand, the PL2 sort of leathers exhibits an advanced degree of degradation, which determines their high reactivities in oxidation processes.

Shrinkage temperature (T_s) measurements

Figure 6 shows the average values of T_s determined by the mentioned methods. Practically identical values of T_s were obtained by CM and MHT methods. Therefore, the results obtained by these methods were not shown separately in Fig. 6.

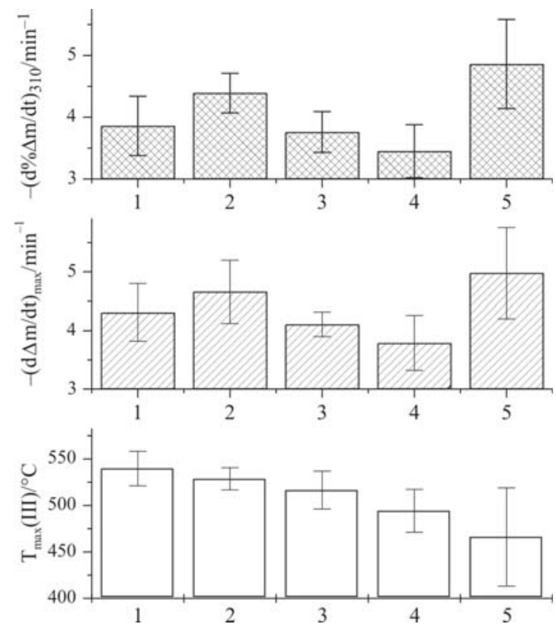

Fig. 5 The average values of $(\mathrm{d}\Delta m/\mathrm{d}t)_{310}$ and $(\mathrm{d}\Delta m/\mathrm{d}t)_{max}$ and T_{max}(III) for: 1 – collagen and recent manufactured parchments, 2 – recent leathers manufactured by vegetal tanning, 3 – patrimonial parchments, 4 – PL1, 5 – PL2

The inspection of this figure shows that:

- the T_s values obtained by CM and MTH methods are close to those obtained to those obtained by DSC method;
- the increasing order of T_s values is: PL1≈PL2≈new and old parchments<recent leathers manufactured by vegetal tanning<recent leathers manufactured by combined tanning;
- the higher scattering of T_s values was obtained for PL1 and PL2.

T_s is a measure of the collagen-based material strength and quality, and damage extent. The parchments that are untanned materials usually shrink near 60°C when heated in water. On the other hand, the new tanned materials, since they include many cross-links between protein chains in the collagen fibres, invariably have a shrinkage temperature higher than the parchment. The obtained order of T_s values confirms the above assumption according to which the first stage of natural degradation of leathers consists in the breaking of the cross-linking bonds, which is followed by splitting of the collagen macromolecules. One can note also that the investigated old parchments, which are maximum 350 years old, exhibit values of T_s close to those of new parchments. This result is in agreement with that reported by Reed [37], who obtained that for parchments a significant T_s change appears after a natural aging longer than ≈1000 years.

Scanning electron microscopy (SEM)

SEM technique was applied with the purpose of assessing the damage extent in collagen fibres in the

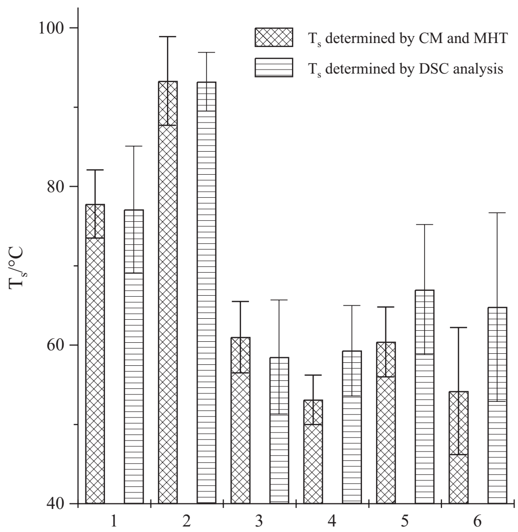

Fig. 6 The average values of T_s. 1 – recent leathers manufactured by vegetal tanning, 2 – recent leathers manufactured by combined tannin, 3 – recent manufactured parchments, 4 – patrimonial parchments, 5 – PL1, 6 – PL2

leather and parchment 3D structure as a result of natural aging. In order to put in evidence the changes of the surface morphology due natural aging, the fibres structures and their packing were comparatively investigated for new and old collagen-based materials.

Figure 7 shows comparatively the SEM pictures of a new calf parchment and an old calf parchment (book cover of 'Ton Basilicon' from 1647). The new calf parchment consists of a network of well individualized, delimited and outlined collagen fibres, while the SEM picture of the old book cover parchment reveals melted areas with some gel formations, no fibrilar network, and some cracks and fractions.

Figure 8 shows comparatively SEM pictures of a new goatskin (chestnut extract tanned) and old leather ('Acts of the Apostles' from 1746). The new goatskin reveals a fibre network as well individualized as in the new parchment but with some larger interfibrilar gaps, specific for the material. The SEM picture of the old leather exhibits a compacted structure with narrower interfibrilar gaps, thickened and shrunk fibres, and areas with adhered and segmented fibres.

Unlike recent manufactured materials, the patrimonial leathers and parchments exhibits: adherent fibres with no interfibrilar gaps; thickened and torn fibres; sections showing weakened, flattened fibrilar structure with no differentiation between reticular and papillary layers. Taking into account these differences, the damages of the collagen-based materials can be qualitatively estimated. SEM pictures show that the surfaces of PL2 leathers have a greater heterogeneity than those corresponding to PL1 leathers. It means that PL2 leathers exhibit major-severe damages greater than those of PL1 leathers. This damage ranking based on SEM results is in good agreement with the results obtained by applying thermal analysis methods.

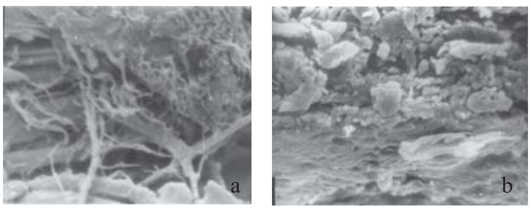

Fig. 7 SEM pictures of a – a new calf parchment and b – an old parchment (Ton Bazilicon –1647)

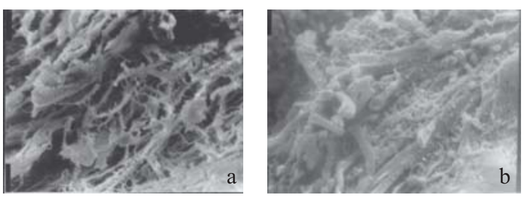

Fig. 8 SEM pictures of a – a recent manufactured leather (goatskin tanned with chestnut extract) and b – an old leather (Acts of the Apostles – 1746)

Conclusions

The results presented in this paper show that the thermal analysis methods (TG/DTG, DSC, and methods for shrinkage temperature evaluation) and scanning electron microscopy (SEM) are suitable for determination of the damages of patrimonial parchments and leathers as a result of natural aging.

The natural degradation of leathers, mainly consisting in the breaking of the cross-linking bonds, and the splitting off of the collagen macromolecules by hydrolysis with water vapors, followed by the oxidation of the lower macromolecules, determine changes in the thermo-oxidation rate (put in evidence in DTG and DSC curves), the decreasing of shrinkage temperature and important changes in surface morphology.

The thermal curves (ensemble of TG/DTG and DSC curves) and SEM picture of each collagen-based material is characteristic and therefore can be considered its 'fingerprint'.

The used analytical techniques and SEM have provided a set of criteria to qualitatively distinguish between recent manufactured leather and a patrimonial one as well as for the assessment of deterioration of the parchments and leathers as a result of natural aging. Therefore, the data obtained by these methods could be used for the achievement of the suitable preservation treatments of patrimonial leathers and parchments.

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