EFFECT OF TEMPERATURE AND RELATIVE HUMIDITY ON VEGETABLE TANNED LEATHER STUDIED BY THERMAL ANALYSIS

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The present paper reports the results obtained by Differential Scanning Calorimetry (DSC) and Micro Hot Table method (MHT) for new vegetable tanned leathers exposed to 80°C and 80% RH for 1 to 32 days. DSC measurements were carried out both in water excess (heating rate 10 C•min^{-1}, temperature range 25 to 110°C), and under nitrogen flow (heating rate of 10 K•min^{-1}, temperature range 25 to 280°C). MHT method was used to measure the shrinkage temperature of collagen fibres. The results on hydrothermal stability obtained using these two techniques were compared. In general, collagen denaturation and shrinkage temperature decreased with time exposure, whereas the melting temperature of collagen crystalline fraction, obtained by DSC analysis in dry nitrogen flow, remained practically constant.

Keywords: vegetable tanned leather, DSC, MHT.

INTRODUCTION

The chemical degradation of vegetable tanned leather is mainly caused by acid hydrolysis and oxidation induced by environmental deteriorative factors such as air pollutants, heat and light. The type of tannin highly influences both the pattern and rate of deterioration of leather.

In the last two decades, great attention has been dedicated to the heritage materials, objects, and artefacts made of leather and parchment through several research projects (PERGAMO, PELRESTAURO, PN STEP, ENVIRONMENT, IDAP and MEMORI). One of their main aims has concerned with identification of physical-chemical changes that occurred in historic and naturally aged leathers and better understanding the relation between degradation observed at different levels, from macroscopic to molecular level. The effects of temperature and humidity on hydrothermal stability of collagen can assist in providing adequate microclimate conditions for the collagen-based collections. Degradation in parchment was more extensively studied by comparing with leather using various physical-chemical techniques such as optical microscopy and collagen fibre shrinkage measurement by Micro Hot Table (MHT) method (Larsen *et al.*, 1993), thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) (Badea *et al.*, 2011; Budrugeac and Miu, 2008; Budrugeac *et al.*, 2010; 2011; Badea *et al.*, 2008), infrared spectroscopy (FTIR) (Badea *et al.*, 2008; Odlyha *et al.*, 2009), Raman spectroscopy (Bicchieri *et al.*, 2011), X-ray diffraction, X-

ray scattering and Micro-X-ray fluorescence (Mozir *et al.*, 2012), nuclear magnetic resonance (NMR) (Badea *et al.*, 2008; Odlyha *et al.*, 2009; Bicchieri *et al.*, 2011; Mozir *et al.*, 2012; Mašić *et al.*, 2012), scanning electron microscopy (SEM) (Badea *et al.*, 2008) and atomic force microscopy (AFM) (Odlyha *et al.*, 2009).

In this paper we present the results obtained for artificially aged vegetable-tanned leathers using Differential Scanning Calorimetry (DSC) and Micro Hot Table method (MHT).

MATERIALS

New vegetable tanned leather from sheep and calf hides, each tanned with mimosa, quebracho and chestnut extracts (Table 1) were prepared at the Leather and Footwear Research Institute Bucharest according to traditional recipes.

Table 1. List of the new manufactured leathers

New leathers		
Animal species	Tannin type	Symbol
sheep	Mimosa	SM
sheep	quebracho	SQ
sheep	Chestnut	SC
calf	Mimosa	CM
calf	quebracho	CQ
calf	Chestnut	CC

ARTIFICIAL AGEING TREATMENT

The artificial ageing treatment consisted in heating the samples at 80°C in a thermo-controlled oven for 1, 2, 4, 8, 16 and 32 days. A controlled 80% RH was maintained by keeping samples in a desiccator over a saturated KCl solution. Samples were treated in the Institute for Science and Technology in Art, Academy of Fine Arts,Vienna, Austria.

METHODS

Differential Scanning Calorimetry

DSC measurements were made with a DSC 204 F1 Phoenix (Netzsch, Germany) instrument. Samples of about 1-5 mg were measured in:

i. *excess water conditions,* using hermetically sealed aluminum pans in which samples were stocked with 30 µl distilled water for 24 h. Samples were heated from 25 to 110 °C at 10 C·min^{-1} heating rate.

ii. *in dry conditions, using* open aluminum pans and nitrogen flow (20 mL·min^{-1}, gas purity: 99.999%). Samples were measured from 25 to 280 °C at 10·C min^{-1} heating rate.

Micro Hot Table Method (MHT)

MHT measurements were performed with an easy-to-use equipment composed of a stereo microscope Leica S4E with a camera and a hot table Caloris equipped with a

FP90 temperature processor and a home-made software F.L.T.K. 1.1.X for temperature regulation and data collection. Magnification used was x40.

Micro-samples of 10-15 fibres from the flesh side were thoroughly wetted and separated in demineralised water, placed on a microscope slide with a concavity and left 10 min for homogeneous hydration. Hydrated fibres were separated as much as possible under a light microscope using a pair of fine needles and then covered with a cover glass, placed on the hot table and heated at $2°C \cdot min^{-1}$. The shrinkage process was digitally recorded and shrinkage temperature determined.

RESULTS

Collagen Denaturation in Hydrated State

The thermal denaturation of collagen in water can be characterized by both the MHT method and DSC analysis in excess water conditions. The shrinkage temperature T_s of collagen fibres is determined by MHT method, whereas the extrapolated onset temperature T_{onset} of the DSC peak associated with collagen thermal denaturation is measured by DSC.

The DSC peaks of new vegetable tanned leathers measured in excess water conditions displayed sharp and symmetrical shapes, with an onset temperature ranging from 80°C (chestnut tanned sheep leather) and 86°C (quebracho tanned calf leather). These values are in good agreement with those in the literature (Budrugeac *et al.*, 2011). The symmetrical shape of the peaks suggests a uniform distribution of the collagen populations with different thermal stabilities (Larsen *et al.*, 1993) and, hence, a homogeneous tanning process. With ageing time, the DSC peaks shifted gradually to lower temperatures and became shorter and broader by comparison to the new, untreated sample, indicating an increasing heterogeneity due to the formation of collagen populations with distinct thermal stabilities (Figure 1).

DSC analysis of artificially aged leather samples showed that thermal behavior depends on both animal species (i.e. calf leather is more thermostable than sheep leather) and tannin type (i.e. mimosa and quebracho tanned leather are more thermostable than chestnut tanned leather).

The onset temperature T_{onset} measured by DSC and shrinkage temperature T_s measured by MHT are generally very close as they characterise the same proces, e.g. thermal denaturation of collagen at mesoscopic and macroscopic levels, respectively. Figure 2 shows the comparison between T_{onset} and T_s for mimosa tanned sheep leather exposed to artificial ageing. The small diference between these values can be related to the different heating rates used for the two types of measurement and to the measurement quality. In fact, T_{onset} is a bulk material property, while T_s reflects the hydrothermal stability of a few collagen fibres from surface (Budrugeac and Miu, 2008; Budrugeac *et al.*, 2010; 2011).

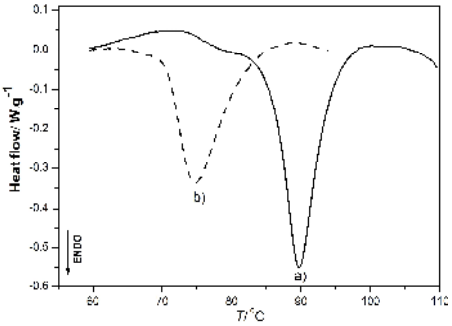

Figure 1. DSC curves obtained in sealed crucible for quebracho tanned sheep leather a) new, untreated and b) exposed to 80°C and 80% RH for 32 days

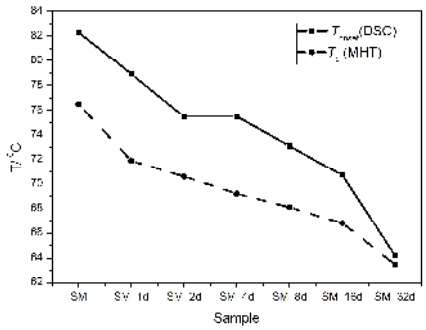

Figure 2. Comparison between the values of T_{onset}, measured by DSC in excess water conditions, and those of T_s, measured by MHT method, for mimosa tanned sheep leather during ageing

Collagen Denaturation in Dry State

DSC curves associated to the thermal transitions which tipically occur in parchment and leather samples measured in open crucibles and gas flow display a broad endothermic peak followed by one or more smaller endotherms (Figure 3). The larger DSC peak in the temperature range (50–110)°C corresponds to thermal dehydration of the sample. The first endotherm at about 129°C (T_{d1}) is related to denaturation of dehydrated collagen matrix, whereas the second peak at T > 220°C (T_{d2}) represents the thermal denaturation (or softening) of the crystalline collagen embedded in the amorphous matrix (Budrugeac *et al.*, 2011).

According to the literature (Budrugeac *et al.*, 2011), the tanning process stabilises the crystalline region by inducing cross-linking. The denaturation temperature of collagen crystalline fraction T_{d2} for the new vegetable tanned leathers showed to generally decrease on natural ageing and deterioration suggesting a progressive decrease of cross-linking degree (de-tanning process) (Budrugeac *et al.*, 2011). In our experiment, however, this value did not significantly change during the artificial ageing treatment, but a rather constant value of (245±5)°C was obtained for all investigated leathers.

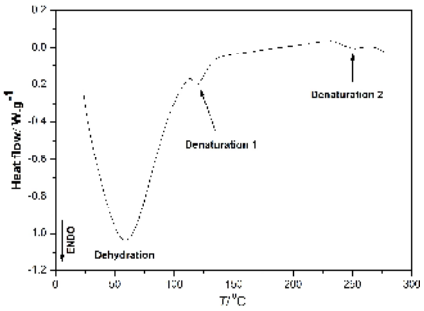

Figure 3. DSC curves obtained in open crucibles and nitrogen flow for new, untreated mimosa tanned sheep leather

T_{d1} values e.g. (122.0±2.9)°C were reported for new vegetable tanned leathers, while slightly high values, e.g. (125.7±2.9)°C were found for historical leathers (Budrugeac and Miu, 2008). In our experiment, this peak was observed for mimosa (113°C) and chestnut (104°C and 116°C) tanned leather only. Accelerated ageing did not induced significant variations of these values. The two DSC signals at 104°C and 116°C (Figure 4) may be ascribed to the presence of two collagen population with slightly distinct thermal stability.

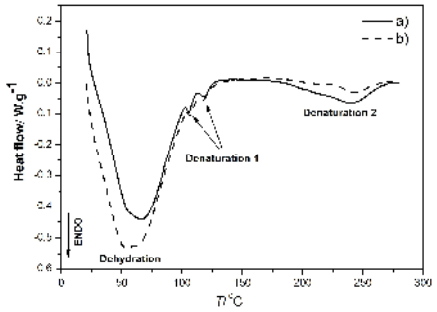

Figure 4. DSC curves obtained in open crucibles and nitrogen flow for chestnut tanned sheep leather a) new, untreated leather and b) leather exposed to 80°C and 80% RH for 32 days

CONCLUSIONS

The use of DSC and MHT method provides useful parameters as temperature of collagen denaturation in both hydrated and dry states, softening temperature of rigid, crystalline collagen and shrinkage temperature. The variations of these parameters enable us to evaluate the effect of accelerated ageing at 80°C and 80% RH for the vegetable tanned leather investigated.

In summary we observed:

(i) Temperature of denaturation measured in excess water, as well as shrinkage temperature decrease for all vegetable tanned leathers with time exposure.

(ii) Hydrothermal stability depends on both the animal species and tannin agent.

(iii) Softening temperature of crystalline collagen fraction does not significantly change during artificial ageing.

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