Journal of Analytical and Applied Pyrolysis 115 (2015) 419–427

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Thermal characterization of new, artificially aged and historical leather and parchment

Zoltán Sebestyén[a,*], Zsuzsanna Czégény[a], Elena Badea[b,c], Cristina Carsote[d], Claudiu Şendrea[b], Eszter Barta-Rajnai[a], János Bozi[a], Lucretia Miu[b], Emma Jakab[a]

[a] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok körútja 2, 1117 Budapest, Hungary
[b] Advanced Research for Cultural Heritage (ARCH) Group, National Research and Development Institute for Textiles and Leather (INCDTP), ICPI Division, 93 Ion Minulescu Street, 031215 Bucharest, Romania
[c] Department of Chemistry, Faculty Mathematics and Natural Sciences, University of Craiova, 13 A.I. Cuza Street, 200585 Craiova, Romania
[d] National Museum of Romanian History, Victoriei Street 12, 030026 Bucharest, Romania

ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 26 August 2015
Accepted 27 August 2015
Available online 29 August 2015

Keywords:
Parchment
Leather
Vegetable tannins
Artificial and natural aging
Py-GC/MS
TG/MS
Principal component analysis

ABSTRACT

The aging mechanism of leather and parchment was studied by thermoanalytical methods to understand the effect of the environment on the historical manuscripts and the heritage of libraries and archives. Alkaline and acidic treatments followed by thermal dehydration were applied to achieve chemical changes in the structure of new leather and parchment similar to the slow natural aging of historical samples. Chemical and structural changes during both natural and artificial aging processes were characterized by thermoanalytical techniques. The thermal stability and the evolution profile of the decomposition products under slow heating were studied by thermogravimetry/mass spectrometry (TG/MS). The distribution of the decomposition products of these collagen-based materials under fast pyrolysis was characterized by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). It was found that the maximal rate of the thermal decomposition (DTG_{max}) significantly decreases by aging in case of both leather and parchment samples indicating the degree of deterioration. Py-GC/MS has been found to be a suitable technique to sensitively monitor the degradation of the polyphenolic components of the vegetable tannins under natural or artificial aging. It was established that the tannin content of leather is more significantly affected by natural aging and alkaline treatment than the main structure of the polypeptide chains. Principal component analysis (PCA) has been used to find statistical correlations between the experimental data for leather samples. The results of the PCA confirmed that the alkaline treatment and the natural aging processes similarly modify the tannin content of the vegetable tanned leather.

1. Introduction

The skin is composed of three primary layers: epidermis, dermis and hypodermis. The epidermis, the keratin-rich outer layer of the skin, and hypodermis, the subcutaneous fatty tissue, are removed during the fabrication of both parchment and leather [1–3]. The dermis, the collagen and elastin rich inner layer, is the main component of both parchment and leather. The keratin, collagen and elastin are structural proteins built of polypeptide chains whose primary blocks are the amino acids.

The skin processing into leather involves a number of preparatory stages, which are identical to the first stages of parchment preparation, as well as tanning and crusting. The purpose of tanning is to achieve more durable materials suitable for a variety of applications, i.e., clothing, footwear, gloves, bookbindings, furniture pieces, military garments, tapestries, boxes, vessels, etc. The tanning procedure permanently alters the chemical structure of the collagen. The tannin molecules stabilize the collagen matrix by linking to the amino acid chains *via* hydrogen and/or covalent bonding, depending on the tannin type. The oldest system of tanning relies on the chemical action of vegetable extracts containing tannins, while tanning with chromium salts, was introduced at the end of the 19th century. The vegetable tannins are natural polyphenols;

* Corresponding author.
E-mail address: sebestyen.zoltan@ttk.mta.hu (Z. Sebestyén).

http://dx.doi.org/10.1016/j.jaap.2015.08.022
0165-2370/

the chemical structure of this group of compounds was described by HPLC–ESI-MS/MS method [4].

The parchment is made of animal skin by liming, scraping and drying under tension, but it is not tanned; hence it contains about 95% collagen [5], whereas the vegetable tanned leather has about 67% collagen [6]. While leather has always a wide range of applications parchment was mainly used as writing material. It was the unique writing support for both library and then archival documents since the 5th century to the Middle Ages when it was replaced by the cheaper paper.

The collagen-based materials like leather and parchment are sensitive to the environment and especially to sudden and large variation of the storage parameters (e.g., temperature, relative humidity) as well as to pH and atmospheric pollutants. All these factors, alone or synergistically, have generated different types of deterioration of parchment and leather objects during time. Oxidation, hydrolysis and gelatinization are the main mechanisms of their deterioration [7].

The amino acid sequence of collagen is known in detail [8] and it shows a distinctive domain structure. It is dominated by the amino acid glycine (roughly 1/3 of all residues) and mainly based on the repetition of tripeptides of the type of glycine-X_1-X_2, where proline and hydroxyproline are the most frequent amino acids (around 30%) occupying the X_1 and X_2 sites. The amounts of alanine, arginine, and glutamic acid are also significant [9].

Applying thermal degradation techniques to analyze different collagen-based materials is not a new idea [10–15]. Budrugeac et al. [14,16] studied the thermal behavior of leather and parchment under different atmospheres by differential scanning calorimetry (DSC). They exposed the materials to high concentrations of chemical pollutants (SO_2 and NO_x) and observed that the DSC peak was shifted to lower temperature with the aging time and became smaller and broader. It was also reported applying pyrolysis-mass spectrometry (Py-MS) [17] that the major pyrolysis products of peptides and proteins are 2,5-diketopiperazines, which are cyclic dimers of amino acids. Fabbri et al. [18] studied the formation of 2,5-diketopiperazines during the pyrolysis of linear dipeptides, tripeptides and proteins (e.g., collagen) using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) system. They established that the most intense 2,5-diketopiperazine (DKP) peaks in the chromatogram correspond to cyclo(proline–glycine), cyclo(proline–proline) and cyclo(proline–hydroxyproline). Marcilla et al. [19] studied the effect of NaOH treatment on the thermal decomposition of leather wastes tanned using various tanning agents. They found decreased thermal stability and wider temperature range of decomposition on the NaOH-treated samples by TGA method. Higher amounts of nitrogen-containing products, the occurrence of 1-vinylaziridine and decreased formation of aromatic compounds were detected among the thermal decomposition products by Py-GC/MS technique. Moreover, correlation was found between the electrical properties and the age of the human skin [20].

In this work, the natural aging and the effects of alkaline and acidic aging treatments on leather and parchment were studied by thermoanalytical techniques to understand the aging mechanisms and the response of parchment and leather to the environmental impact. TG/MS and Py-GC/MS were applied to characterize the changes in the structure of new, naturally and artificially aged leather and parchment samples.

2. Experimental

2.1. Materials

The new parchment was obtained at INCDTP–ICPI, Bucharest from goat skin, while calf skin and vegetable tannin (extract from chestnut-wood) were used for producing leather. The historical parchment samples were taken from a bookbinding dated 1832, generously offered by the Historical Archives of the University of Turin (Italy). This was the original parchment binding of an examination register at the Arts and Humanities Faculty that was replaced in the 90s by a new bookbinding. The historical leather samples analyzed by TG/MS and Py-GC/MS, were taken from an old gospel from Blaj (Romania) dated 1765 and belonging to the Central University Library C̆arol I" of Bucharest (two subsamples H/1 and H/2 from parts showing different degradation condition), and from a sermon dated 1505 (two subsamples H/3 and H/4 from two different parts). The goat parchment and the calf leather were artificially aged by two methods as summarized in Table 1. The artificial aging treatments consisted of acidic and alkaline treatments followed by thermal dehydration at 120 °C. The new collagen-based materials were soaked in alkaline or acid solutions for 2 days. After the soaking the acid or alkaline treated samples were rinsed with aqueous solutions of $(NH_4)_2SO_4$ or NaCl, respectively. The residual inorganic ions were removed by washing the samples with ion-exchanged water until neutrality tested by an indicator paper. Then the samples were heated at 120 °C in a ventilated oven for 4 days.

2.2. Methods

2.2.1. TG/MS

The TG/MS system consists of a modified PerkinElmer TGS-2 thermobalance and a quadrupole mass spectrometer (Hiden Analytical Ltd., Warrington, UK, model: HAL 2/301 PIC). About 3 mg samples were measured in argon atmosphere at a flow rate of 140 ml min^{-1}. The samples were heated in a platinum sample pan at a rate of 20 °C min^{-1} from 25 to 1000 °C. The evolved products were introduced through a glass lined metal capillary heated at 300 °C into the ion source of the mass spectrometer which was operated at a 70 eV electron energy.

2.2.2. Py-GC/MS

Approximately 0.8 mg samples were pyrolyzed at 600 °C for 20 s in helium atmosphere using a Pyroprobe 2000 pyrolyzer interfaced to an Agilent 6890A/5973 GC/MS. The pyrolysis products were separated on a DB-1701 capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The GC oven was programmed to hold at 40 °C for 4 min then increase the temperature at a rate of 6 °C min^{-1} to 280 °C with a hold for 5 min. The range of m/z 14–500 was scanned by the mass spectrometer in electron ionization mode at 70 eV. The identification of the pyrolysis products was based on NIST mass spectral library and literature data [18,21]. The peak areas of the total ion chromatograms were normalized to the sample mass and the normalized data were subjected to principal component analysis (PCA) using Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA).

Table 1
Conditions of aging treatments of leather and parchment.

Treatment type	Conditions	Neutralizing	Drying
Alkaline	4% $Ca(OH)_2$ + 0.5% NaOH, 25 °C, 48 h	1% $(NH_4)_2SO_4$	120 °C, 96 h
Acidic	0.5 M acetic acid, 4 °C, 48 h	0.7 M NaCl	120 °C, 96 h