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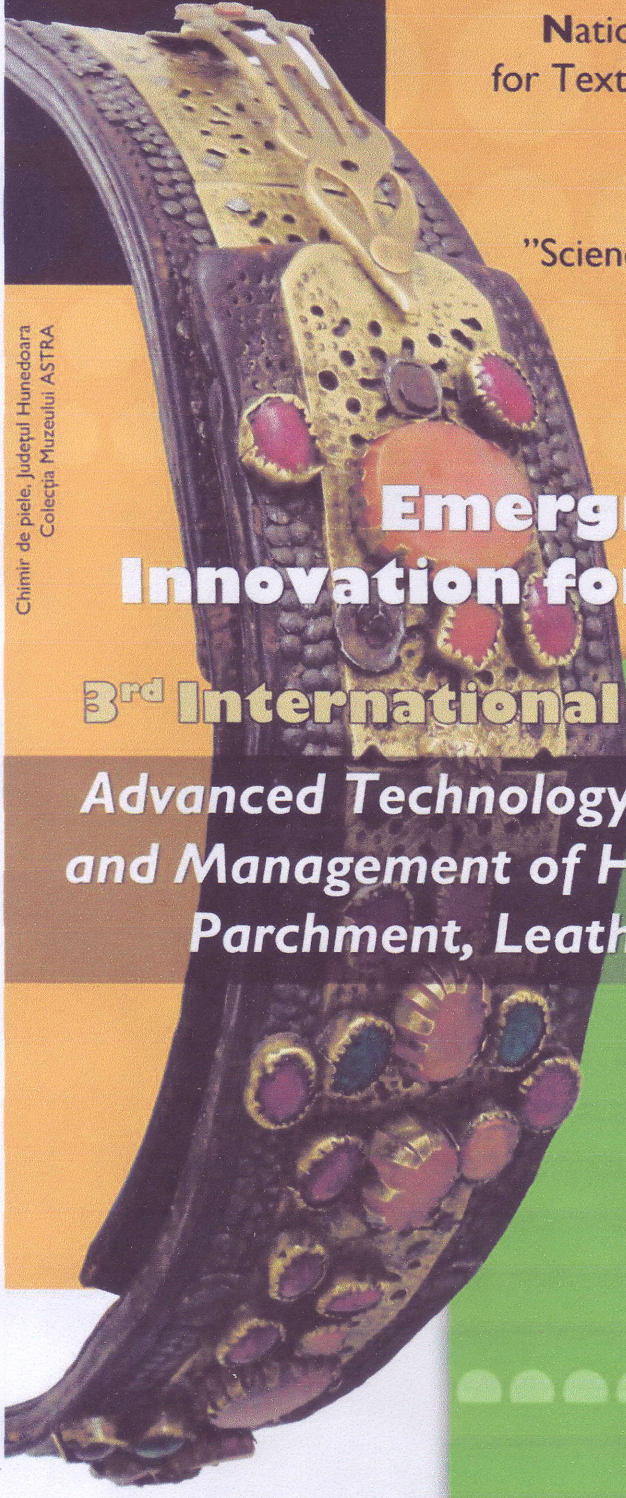

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Emerging Technology and Innovation for Cultural Heritage

3rd International Seminar & Workshop

Advanced Technology for Diagnosis, Preservation and Management of Historical and Archaeological Parchment, Leather and Textile Artefacts

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BOOK OF ABSTRACTS

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ORAL PRESENTATION

THERMAL CHARACTERIZATION OF NEW, ARTIFICIALLY AND NATURALLY AGED LEATHER AND PARCHMENT SAMPLES

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Introduction

Handwritten books, codices and letters stored or displayed in historic buildings are vulnerable to changes in the outdoor environment due to the limited climate control. Understanding the degradation mechanisms and changes in the structure of leather and parchment could help to find a proper way to protect these pieces from the aging and the environmental effects. In order to identify the aging mechanisms different analytical methods, among them thermoanalytical methods were used [1,2].

In this work natural aging mechanisms were modeled by acid and alkaline pretreatments. Structural changes of the samples during the aging were explored using thermoanalytical methods, in order to understand the response of parchment and leather to the environmental effects.

Materials

The new parchment was made from goat and the leather from calf skin. The leather was tanned by natural plant tanning agents. The aging modeling pretreatment conditions are given in Table 1. The historical parchment is from the Historical Archives of the University of Turin (Italy) from 1832. The historical leather sample originated from an old gospel Blaj (Romania) dated 1765.

Table 1. Pretreatment types and conditions of new leather and parchment

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

Methods

Thermogravimetry-Mass spectrometry (TG/MS)

About 3 mg sample was measured in argon atmosphere at a flow rate of 140 ml min^{-1} using the TG/MS system. The samples were heated at a rate of 20°C min^{-1} from 25 to 1000°C in a platinum sample pan. The evolved products were introduced through a glass lined metal capillary heated at 300°C into the ion source of the mass spectrometer.

Pyrolysis-Gas chromatography/Mass spectrometry (Py-GC/MS)

Approximately 0.8 mg samples were pyrolyzed at 600°C for 20 s in helium atmosphere using the pyrolyzer interfaced to the GC/MS. The pyrolysis products were separated on a DB-1701 capillary column. The GC oven was programmed to hold at 40°C for 2 min then increase the temperature to 280°C (hold for 5 min) at a rate of 6°C min^{-1}.

Results and discussion

TG/MS experiments

Leather and parchment behave differentially during the linear heating in TG/MS. More char yield was observed from leather samples then parchments, due to the cross-linked collagen structure of the tanned leather. Figure 1 shows the TG and DTG curves of new, artificially and naturally aged leather and parchment samples. The main decomposition process starts at the same temperature of all four examined parchment samples, however their maximum rate of decomposition are slightly different. The DTG curve of alkaline treated parchment is more similar to the naturally aged historical sample. There is a peak on the DTG curve of the alkaline pretreated parchment samples at about 690°C, indicating the decomposition of inorganic carbonate content.

Py-GC/MS experiments

Pyrolysis-gas chromatography/mass spectrometry has been applied to reveal the changes in the pyrolysis product distribution of leather and parchment samples after the pretreatment and after the natural aging.

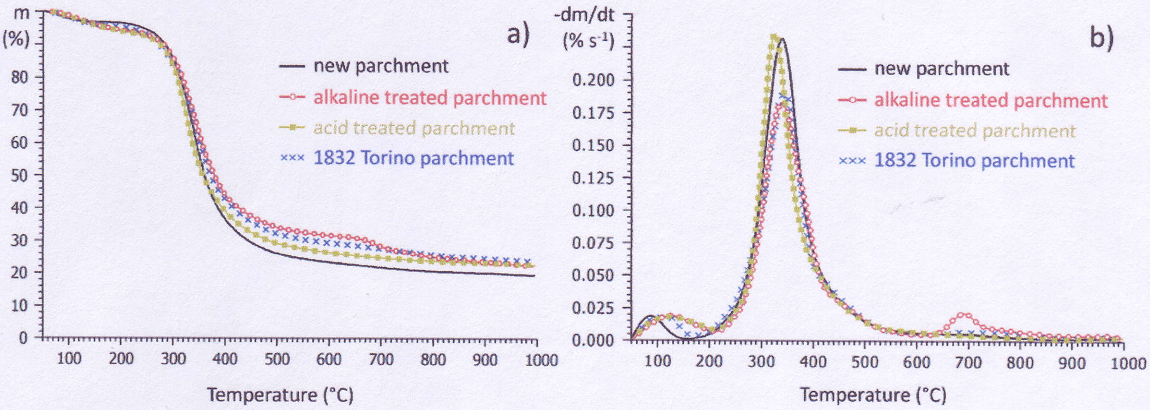

Figure 1. Thermogravimetric (a) and derivative thermogravimetric curves (b) of new, treated and naturally aged parchment samples

The peaks at lower retention time correspond to the lower molecular mass products of the collagen. SO_2 was formed mainly from the CH_3-S- and CH_2-SH- groups of the sulfur containing amino acids. The main decomposition products of the leather and parchment samples are the aromatic compounds and the diketopiperazines (DKP), which are cyclic dipeptides formed from the amino acids (Figure 2) [3,4].

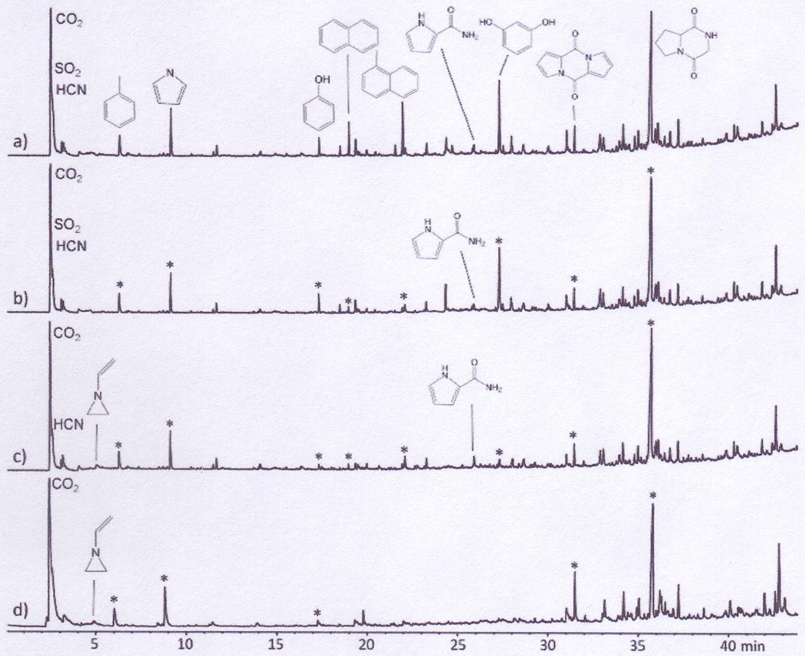

Figure 2. Pyrolysis chromatograms of new (a), acid treated (b), alkaline treated (c) and historical leather (d) samples. Some of the main decomposition products are represented.

According to the results, the evolution of the aromatic compounds decreased after the artificial aging as well as the natural aging. The yield of DKP's did not change. 1H-pyrrole-2-carboxamide (retention time: 26 min) can be seen on the pyrolysis gas chromatograms of new, acid and alkaline treated leathers as well as the parchments. The small peak disappears from the pyrograms of the historical samples so the amount of the peptide bonds decreased under the aging process. At lower retention time (5 min) can be found the 1-vinylaziridine, which was only formed during the pyrolysis of the alkaline treated and historical sample [2].

Conclusions

The decomposition of the naturally aged leather starts at lower temperature than that of the new sample. The thermal stability of parchment samples did not change after the treatments. The main decomposition products are aromatic compounds and diketopiperazines (DKP), which are cyclic dipeptides formed from the amino acid content of the samples. According to the TG/MS and Py-GC/MS, the evolution of the aromatic compounds decreased after the artificially aging as well as the natural aging. The yield of the DKP's did not change. The results show that after the alkaline treatment the thermal behavior of the leather is very similar to the naturally aged leather's. Modeling of the aging process using organic acids wasn't effective. The alkaline treated leather can model the 300 years old leathers and parchments during the thermal experiments, thus avoiding the application of the destructive analytical methods on the precious samples.

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