EFFECT OF LASER CLEANING ON THE FLUORESCENCE CHARACTERISTICS OF PARCHMENTS

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Au fost evidenţiate efectele radiaţiei laser (λ = 1064nm şi armonica acesteia de la 532nm la 2Hz) asupra caracteristicilor fluorescente ale mostrelor de pergament, în scopul stabilirii modului de declanşare a procesului de îmbătrânire accelerată. Caracteristicile fluorescente care reflectă modificările structurale ale catenei peptidice au fost corelate cu datele spectrale obţinute în domeniile IR şi UV-VIS.

The effects of the laser radiation (λ = 1064nm and its 532nm harmonics at 2Hz) on the fluorescent characteristics of the parchment samples have been rendered evident with the aim of establishing the onset of the accelerated ageing process. The fluorescent characteristics pointing to the structural changes in the peptide chain were correlated with the spectral data from the IR and UV-VIS domains.

Keywords: parchment, laser technique, fluorescence.

1. Introduction

The aim of our study consists in the appraisal of the restoration scenario development opened by the adaptation of the laser technology in art conservation. Laser cleaning is a modern technique that applies with high accuracy to organic and inorganic materials substrates [1, 2]. The physical-chemical methods applied to the parchment using absorption spectral techniques (IR and UV-VIS, RMN), thermal analysis, optical microscopy and SEM provide qualitative and quantitative data about the visual and structural changes of the polypeptide chain [3 – 5].

This paper describes the behaviour of new parchments subjected to laser cleaning (at λ = 1064nm and its first harmonic at λ = 532nm) by means of the fluorescence spectral (FP) characteristics.

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2. Experimental

Goat, lamb, and kid new parchment samples, produced by National Institute for Textile and Leather – Bucharest, were subjected to artificial soiling using natural charcoal. The laser cleaning was carried out using Q – switched YAG: Nd laser at λ = 1064nm and its first harmonic λ = 532nm, at a frequency of 2 Hz and different energy regimes. The fluorescence characteristics of the treated and untreated samples were examined using FP – 6500 JASCO fluorescence spectrometer.

3. Results and Discussion

Previous studies on the parchment samples from different animals showed small changes of the hydrolysis degree at irradiations at λ = 1064nm (from FT-IR data) [3, 4] and a weak hypochromic shift of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition bands (from UV-VIS data) [5] without denaturation effects of the peptide chain [1, 6]. We also noticed the batochrome shifts of up to 26nm of the 1470 – 1505nm band (νOH), which point to the involvement of the inter / intra-molecular hydrogen bonds in the formation of new associations [7].

The analysis by fluorescence provided new information regarding the changes induced by the laser radiation in the molecular structure of the peptide. The fluorescence characteristics of the same parchment samples are presented in Table 1.

Table 1

Parchment characteristics

λ_{ex} * nm	Initially λ_{laser} (nm)/ Fluency (mJ/cm^2)	Goat, $\lambda_{emission}$ / I**	Lamb, $\lambda_{emission}$/ I**	Kid, $\lambda_{emission}$ / I**
		Initially		
260 - 280		G_0 = 309/592	L_0 = 311/216	K_0 = 306/598
340 – 380		G_0 = 428/942	L_0 = 430/652	K_0=438/920
460		G_0 = 504/176	L_0 =513/160	K_0 =519/110
260 - 280	After Laser Irradiation			
	1064/90	G_1 = 320/870	L_1= 324/231	K_1 = 309/377
	1064/30	G_2 = 320/818	L_2 = 325/320	K_2 = 309/353
	532/23	G_3 =322/633	L_3 = 310/297	K_3 = 310/375
	532/6	G_4 = 320/621	L_4 = 325/314	K_4 =324/549
340 - 360	1064/90	G_1=412/953	L_1=432/788	K_1 = 414/570
	1064/30	G_2 = 412/904	L_2 = 431/941	K_2 = 412/663
	532/23	G_3 = 414/906	L_3= 428/596	K_3 = 412/820
	532/6	G_4 = 414/905	L_4 = 431/983	K_4 = 410/763

*λ_{ex}= fluorescence excitation wavelength (nm); **$\lambda_{emission}$/I = fluorescence emission wavelength (nm)/intensity (arbitrary units).

The data follow the evolution at excitation (in the 260 – 460nm domain) of some emission bands attributed to the aromatic amino-acids (phenylalanine, tyrosine and tryptophan) found in the structure of the collagen substrate from the parchment [8, 9].

For all types of parchment, the excitation at λ = 260 – 280nm produces an initial band at 306 – 311nm which, after exposure to laser radiation, has a batochrome shift of 11 – 18nm due to the association processes with the involvement of tyrosine [8, 9]. By excitation at λ = 340 – 380nm the initial band has a hypsochrome shift of 15 – 26nm only in the case of goat and kid parchments; in the case of lamb parchment, the initial emission band do not change. We also examined their intensity in the fluorescence spectra (fig. 1, 2) because in this emission domain the bands are given by association and / or reticulation processes in the polypeptide chain [10, 11].

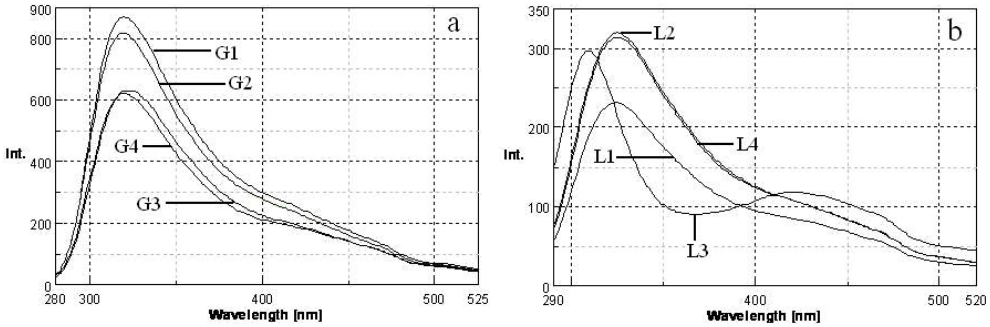

Fig. 1. FP spectra at λ_{ex} = 270nm: a – goat parchment; b – lamb parchment (*Table 1*)

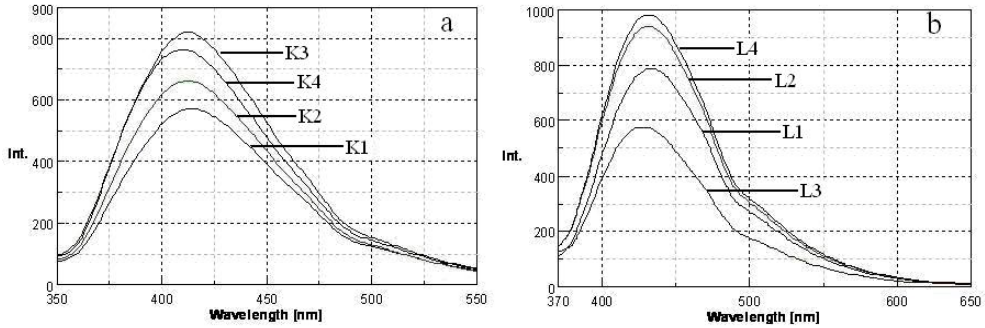

Fig. 2. FP spectra at λ_{ex} = 340nm: a – kid parchment; b – lamb parchment (*Table 1*)

For the goat parchment, at excitation in the 260 – 280nm range, an accelerated increase of the bands intensity with maximum 47% at λ = 1064nm and 7% at λ = 532nm was noticed. For the lamb there is also an increase of 48%, while for the kid there is a diminishing of 38%. These aspects point to changes with the involvement of tyrosine and, eventually, tryptophan traces from the same chain.

The excitation at 340 – 360nm leads to lower intensity variations for the goat parchment, to a high increase of the emission bands intensity for the lamb parchment (max. 51%), and to a decrease with 26 – 38% of the intensity for the kid parchment (fig. 3, 4).

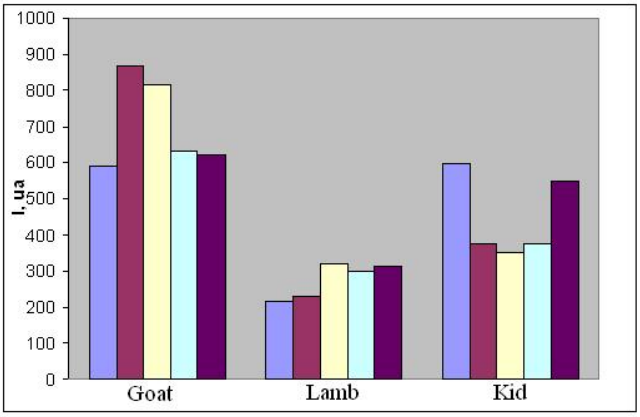

Fig. 3. Variation of the intensity at λ_{ex} = 260 – 280nm with the laser characteristics (in the order: 1064/90, 1064/30,532/23,532/6).

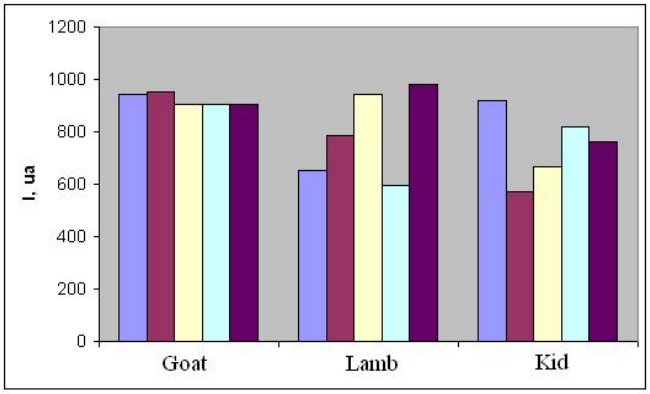

Fig. 4. Variation of the intensity at λ_{ex} = 340 – 380nm with the laser characteristics (in the order: 1064/90,1064/30,532/23,532/6).

The intensity of the fluorescent signal at 340-360nm was correlated with the association and / or reticulation degree of the collagen support. In the case of the kid parchment, at a laser irradiation of λ = 532nm, the reticulation degree is higher than at the laser irradiation of λ = 1064nm, irrespective of the applied energy. The opposite situation was found for the goat parchment, but only at excitation of 270nm. For the lamb parchment the reticulation degree varies with the applied energy. It is higher at 6 and 30mJ/cm^2 than in the case when the applied energy was of 23 and 90mJ/cm^2.

The change of the emission band intensity at 340-360nm was also correlated with the variation of the 1465 – 1510nm bands (νOH associated due to hydrogen bonds) from the NIR domain (fig. 5).

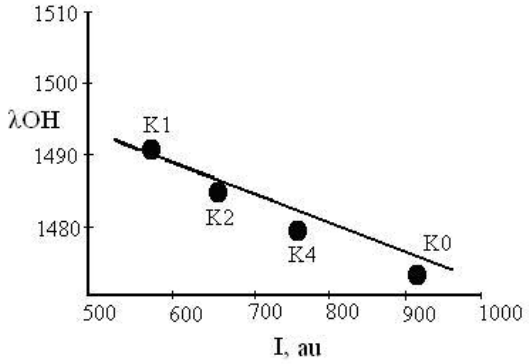

Fig. 5. Variation of λOH (NIR) for the kid parchment with the intensity (in arbitrary units, au) at λ_{ex} = 340 – 380nm

The emission bands from 504 – 519nm (λ_{ex} = 460nm) of the initial parchments not exposed to laser radiation are due to different compounds existing in the parchment beside the collagen (glucides, unsaturated fatty acids, etc.) [3]. The intensity diminished by exposure to laser radiation, and consequently they were not taken into consideration.

4. Conclusions

The spectral analysis by fluorescence of the new parchments exposed to laser radiation at λ 1064 and 532nm, with different energies, put in evidence some structural changes in the polypeptide chain of their collagen substrate. Bato- and hypsochrome shifts of the emission bands from 306 – 311nm and 428 – 438nm were registered. The latter aspect was attributed to the effect of the laser radiation on the reticulation degree of the polypeptide, and it was correlated with the variation of the band wavelengths from 1475 – 1510nm (associated νOH) from the NIR domain.

R E F E R E N C E S

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