Materials supports for cultural heritage objects treated in cold plasma

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Plasma treatment represents a non-destructive method applicable in decontamination and etching of cultural heritage objects. In this work high frequency plasma was applied on cellulose- and protein-based reference materials (cotton, paper, silk, wool and leather) similar in composition with those of historical materials. FT-IR (ATR) spectroscopy, ESCA (XPS) measurements, elemental analyses, X-ray diffraction and scanning electron microscopy (SEM) have been used to study plasma treatment effect on the materials, both in bulk and at surface level.

(Received October 24, 2007; accepted November 26, 2007)

Keywords: Plasma treatment, Materials, Restoration-conservation

1. Introduction

This work is devoted to restoration and conservation of cultural heritage objects by applying of high frequency plasma implying decontamination, etching and formation of polymeric protective and consolidate layers. Evaluation criteria for a physico-chemical method to be employed in restoration-conservation purposes have on its basis the fundamental principles of restoration of cultural objects. Concurrently the real possibilities and conditions for implementation in a museum laboratory are envisaged [1]. The conservator scientist is naturally tempted to apply new characterization techniques and new products [2,3]. Each of the cultural object represents a particular and complex case, to be carefully analyzed and demands an optimum solution for a long-lasting preservation. Previously we have been applied successfully high frequency plasma on historical objects [4] and we have also applied it on polymeric materials [5].

2. Experimental

Experiments related to this research work have been done on a reference materials collection (cotton, paper, silk, wool and leather) similar in composition to cultural heritage objects. A high frequency plasma has been applied: sequential application during 1 h at low pressure 2.1×10^{-1}mbar, intensity of the electric field 100 V/cm, frequency 13.5 MHZ. The untreated and treated samples were submitted to investigation through FT-IR (ATR), XPS, SEM, X-ray diffraction and elemental analyses.

FT-IR analyses have been done on VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000 cm^{-1}, resolution 2 cm^{-1}.

ESCA (XPS) spectra has been collected from Perkin Elmer PHI-1600, anode 350 W, detector (180°), vacuum 5×10^{-9} Torr; signal C 1s (284,8 eV) was used as reference and it was deconvoluted in multiple peaks corresponding to C-X groups (X=H, OH, O, C, etc.) by using Gauss-Lorentz function; sum area is equal to the area of C 1s signal.

Elemental analyses have been done on Perkin Elmer 2400 Series II CHNS/O System.

X-ray diffraction analyses of the samples have been done on an X-ray diffractometer Bruker Advance D8: geometry Bragg-Brentano 36 kV, 30 mA, radiation $Cu_{K\alpha}$, λ=1.5406 Å.

SEM analyses have been performed using a scanning electron microscope TESLA BS 301, at an accelerating tension of 10 kV.

3. Results and discussion

FT-IR (ATR) analysis

The FT-IR (ATR) spectra for untreated and plasma treated cotton samples (Figs. 1 and 2) evidence minor chemical changes appeared at the surface of the textile sample due to remanent air present in the plasma reaction chamber.

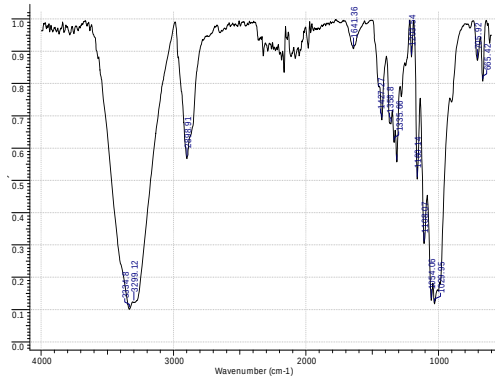


Fig. 1. FT-IR (ATR) Spectrum of untreated reference cotton sample.

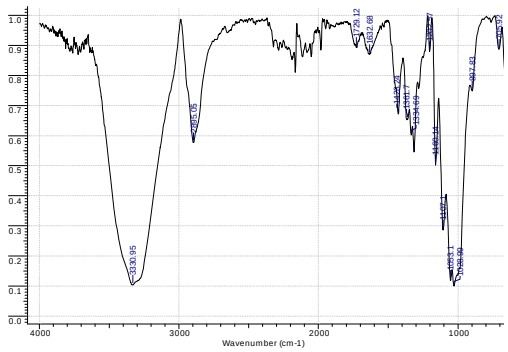


Fig. 2. FT-IR (ATR) of the plasma treated reference cotton sample.

One can remark the appearance of additional absorption bands in the carbonyl region explainable by the formation of aldehyde (-CHO) and carboxyl (-COOH) functional groups at the surface [6-8]. The new resulted aldehyde groups affect the white appearance of the textile material. The absorption at the level of –OH and β-glucosidic groups are not modified; plasma does not affect the macromolecular chain and its degree of polymerization. The changes are not produced in depth but only at the surface at the nanometric scale no more than few macromolecular layers [9].

The FT-IR (ATR) spectra of the untreated and plasma treated paper samples (Fig. 3 and 4) show that plasma has the same effect as in the case of cotton samples.

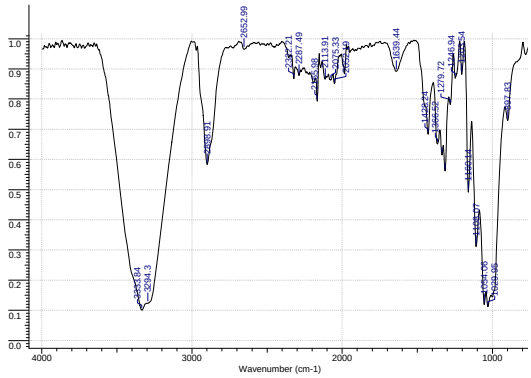


Fig. 3. FT-IR (ATR) spectrum of untreated paper sample.

As to the treated and untreated silk samples the resulted spectra show more important changes than those of the cotton ones. The absorption bands located at 1630 cm^{-1} (amide I) and 1520 cm^{-1} (amide II) become shifted to lower wavenumbers (1630→1620 cm^{-1} and 1520→1514 cm^{-1}) after the treatment, explainable by the partial oxidation of polyamidic chemical bonds. The intensity of the band at 1696 cm^{-1} (amide I, H-bonded possible to be assigned to a crystalline ordered form) evidences a decrease after plasma treated and the intensity of the band at 1170 cm^{-1}, ν(C-O-C), is found to increase. (Fig. 5 and Fig. 6).

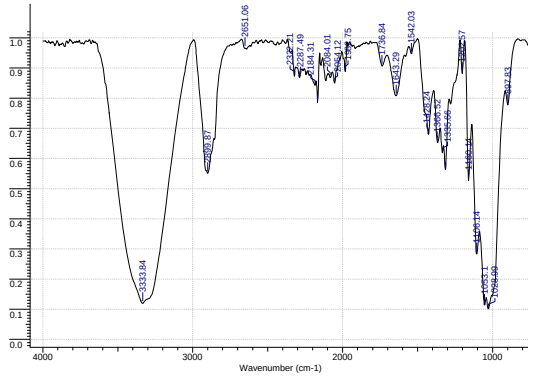


Fig. 4 FT-IR (ATR) of the plasma treated paper sample.

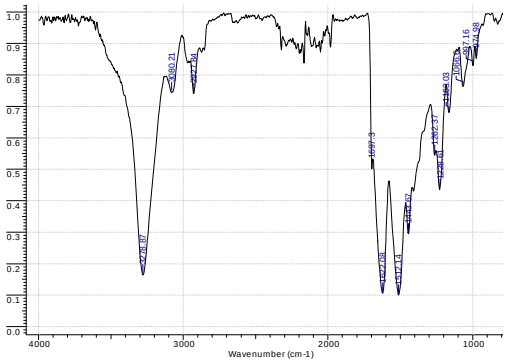


Fig. 5 FT-IR (ATR) spectrum of untreated silk sample.

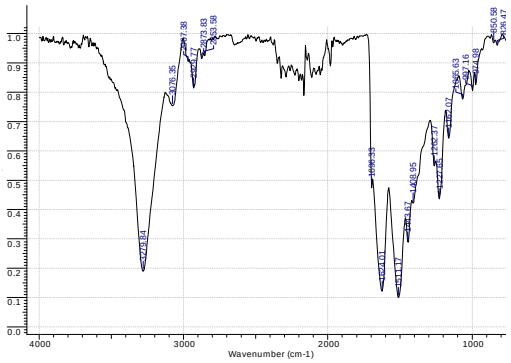


Fig. 6. FT-IR (ATR) spectrum of plasma treated reference silk sample.

This latter result evidences that plasma affects the crystalline order. The conformation of fibroin, the main protein component of the natural silk, suffers a change from a "statistic macromolecular chain" to an ordered β-planar conformation after plasma treatment as a consequence of the involved oxidation processes [10].

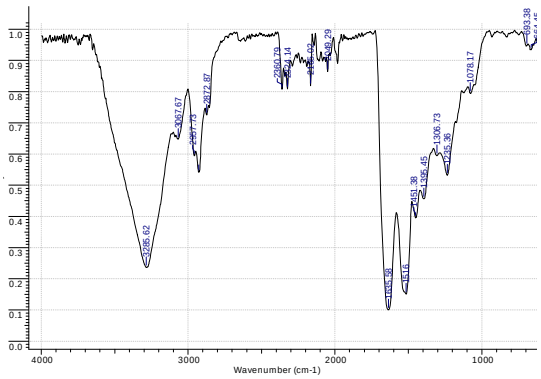


Fig. 7. FT-IR (ATR) spectrum of untreated reference wool sample.

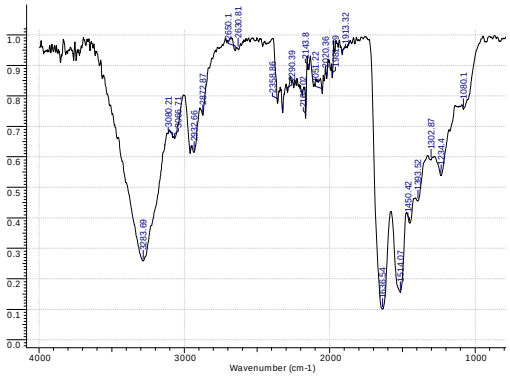


Fig. 8. FT-IR (ATR) spectrum of plasma treated reference wool sample.

Figs. (7 and 8) present the FT-IR (ATR) spectra of the untreated and treated wool samples and in the 2800-3500 cm^{-1} spectral region the following are evidenced:

- the intensities of the absorption bands located at 2925 cm^{-1} (-CH_3) and 2855 cm^{-1}(>CH_2) decreases with increasing treatment time until vanishing as a consequence of oxidation processes and conformational changes;

- no micro structural changes are observed in the 1700-1450 cm^{-1} region (amide I, amide II) this means that amide groups are not affected;

- in the 3650-3150 cm^{-1} (-OH and –NH-) region no changes are observed and this means that the oxidation processes do not involve these functional groups [11].

The action of plasma treatment is involved only at the superficial level being considered non-destructive.

In Figs. 9 and Figure 10, the FT-IR (ATR) spectra of the untreated and treated leather the same modifications as in the case of wool sample can be remarked and this means that plasma affects the protein component similarly. The modifications observed at the level of aliphatic groups are not so important as in the case of wool due to its compactness.

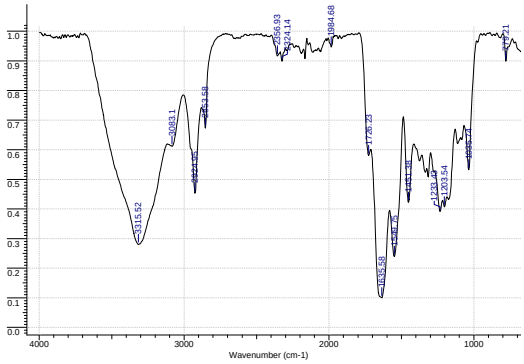


Fig. 9. FT-IR (ATR) spectrum of untreated reference leather sample.

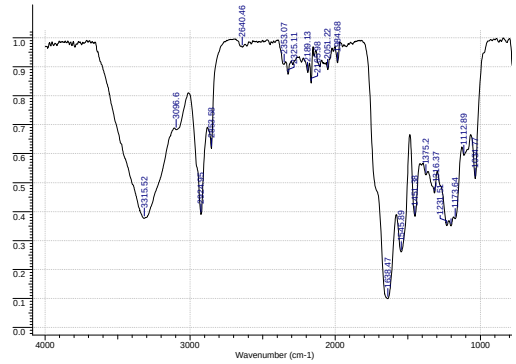


Fig. 10. FT-IR (ATR) spectrum of plasma treated reference leather sample.

XPS analysis

The method ESCA (XPS) allows only the detecting of those photoemitted electrons under vacuum environment from the investigated material surface within a depth of 10 nanometers. Photoelectrons resulted from the depth of the material generated as a consequence of penetration of X-rays up to 5 μm are recaptured and fixed in different excitations states in the material. ESCA represent a non-destructive technique very important in evaluation of the chemical surface structure.

In Table 1 are presented the percentage areas corresponding to the peak signals C1 s for cotton reference sample before and after the plasma treatment.

Table 1. Percentage areas of the component signals C 1s for cotton samples.

Signal	Area, % Reference cotton	Area, % Plasma treated reference cotton sample
- C-OH	56.30	42.90
-C-O-	29.90	30.40
-C-C-	5.40	5.30
-COOH	8.40	15.30
-CHO	-	6.10

Due to the same cellulose nature, for paper are found the same conclusions regarding the XPS results.

The XPS spectroscopic elemental analysis data related to the untreated and plasma treated for all the studied samples are summarized in Table 2. The data reveal minor oxidation processes, which take place due to plasma treatment under remanent air. A decrease in the carbon content and an increase in oxygen content is obtained due to oxidation processes.

Table 2. ESCA (XPS) Elemental analyses for the untreated and plasma treated samples.

Sample	C (%)	H(%) x)	N (%)	S (%)	O (%)
Cotton	45	6	-	-	49
Plasma treated cotton	40	5	-	-	55
Silk	47	5	17	1	30
Plasma treated silk	45	5	16	1	33
Wool	50	8	13	3	26
Plasma treated Wool	47	7	13	3	30
Paper	43	6	-	-	51
Plasma treated paper	38	4	-	-	58

x)–by diference up to 100%

Elemental analyses

Elemental analyses have been performed also providing bulk quantitative results for C, H, N, S and O (Table 3).

If we compare the results presented in these two tables it can be seen that the elemental analyses bulk data for the untreated samples disregarding the nature of the material are close to those of the treated ones whereas the elemental analyses surface data provided by ESCA (XPS) confirm the action of plasma only at the surface at nanometer level.

X-ray diffraction analyses

X-ray diffraction method represent a powerful method used in investigation of museum objects [12-15]. By this technique solid crystalline materials can be investigated. A microfibrillar structure characterizes the cellulose and/or protein materials supports. X-ray method proved to be a non-destructive analysis method of the material constituent of cultural heritage objects [16,17].

Table 3. Elemental analyses for the untreated and plasma treated samples.

Sample	C (%)	H(%)	N (%)	S (%)	O (%) x)
Cotton	44.3	6.3	-	-	49.4
Plasma treated cotton	44.4	6.4	-	-	49.2
Silk	45.7	6.5	17.2	0.7	29.9
Plasma treated silk	46.1	6.4	17.4	0.7	29.4
Wool	48.5	8.3	14.2	2.9	26.1
Plasma treated wool	48.7	8.2	14.3	2.8	26.0
Leather	50.5	8.0	13.3	3.1	25.1
Plasma treated Leather	50.4	8.0	13.2	3.1	25.3
Paper	45.0	6.5	-	-	48.5
Plasma treated paper	45.1	6.4			48.5

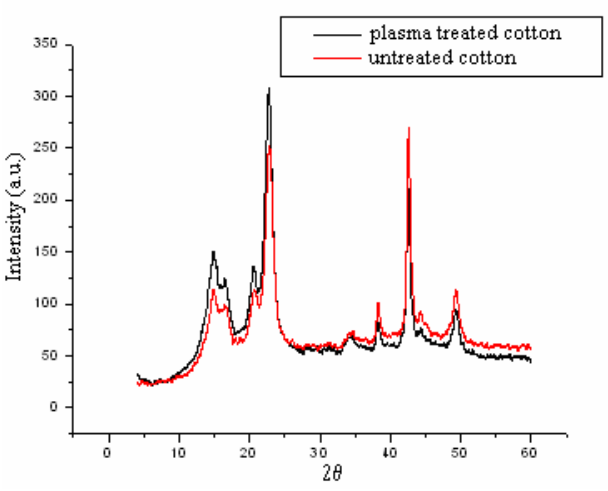
x) – by diference up to 100%

In Fig. 11 a, are depicted the X-ray difractograms of the untreated and treated cotton samples. It can be observed that at $2\theta < 30^o$ (higher d spacings) the diffraction peak intensity is higher for the plasma treated cotton sample than the untreated one, whereas diffraction angles $2\theta > 30^o$ (lower d spacings) the peak intensity decreases through plasma treatment. The differences are not significant; the crystallinity is not affected by the oxidation and cross-linking processes as a consequence of the action of plasma active species; the degree of crystallinity is little affected.

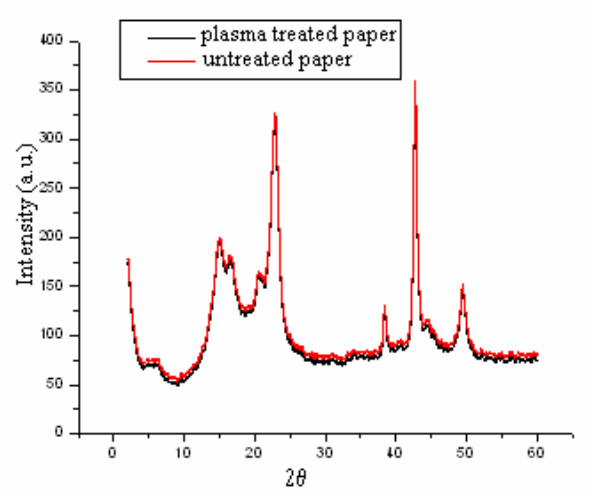
In Fig. 11 b, are presented X-ray diffractograms for the paper samples. It appears that in this case plasma did not affect any structural change nor degree of crystallinity, practically they are superposed.

For the silk samples it can be observed (Figure 11 c) that for $2\theta > 30^o$ (lower d spacings) appear differences between the two X-ray diffractograms and this certifies that the crystalline arrangement of the protein is affected.

For the wool samples the X-ray diffractograms (Figure 11 d) show changes at $2\theta < 20^o$ (higher d spacings) concluding that plasma affects the degree of crystallinity of the wool. Plasma treatment causes modifications of epicuticular layer of the wool fibers, along with the change of the polar character of the fibers altering in this way the electrostatic properties of the fibers. The cross-linking density given by disulfide bridges might be affected causing the change of the crystallinity degree [18, 19].



a



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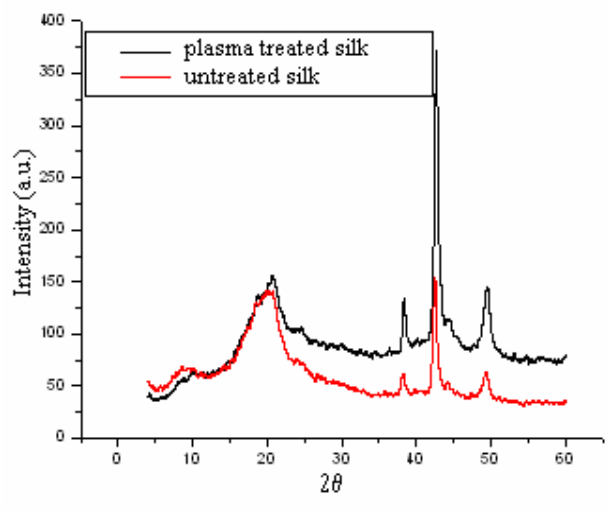
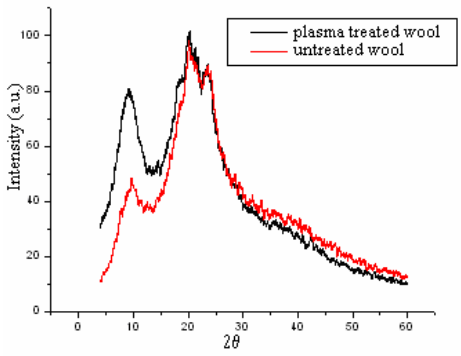
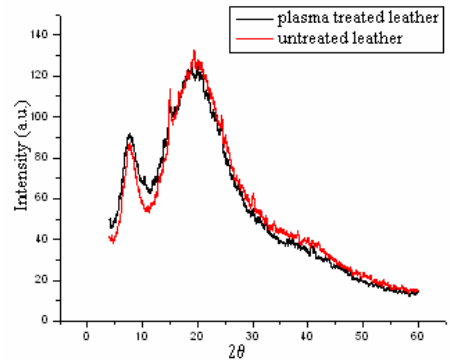


c



d



E

Fig. 11. X-ray diffractograms of the untreated and plasma treated samples.

In Fig. 11 e, are presented the X-ray diffractograms of the leather samples. Unsignificant modifications of the crystallinity degree at $2\theta \cong 10^{o}$ are remarked.

X-ray diffraction data of the studied samples are presented in Table 4.: d (Å), spacing values have been determined by using Bragg relation :

$$2\,d\sin\theta = n\lambda$$

where:

d – planar spacing;

θ - diffraction angle;

λ - wave length;

n – diffraction order.

Crystallinity degree, χ (%), has been determined by using the following relation:

$$\chi = \frac{I_{cr}}{I_{cr} + I_{am}} = \frac{S_{cr}}{S_{cr} + S_{am}}$$

where:

I_{cr}, I_{am} -intensity of the diffracted radiation by the crystalline phase, and amorphous phase, respectively;

S_{cr}, S_{am} - corresponding areas of the crystalline phase, and amorphous phase, respectively.

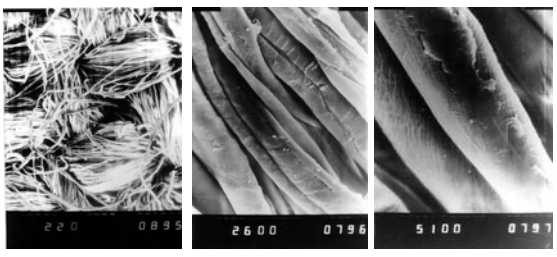
The obtained results show little changes of the crystallinity degree: < 1 % for cotton, silk and leather; < 2 % for wool. An exception is the paper sample which is not affected by plasma treatment.

Table 4. X-ray diffraction data of the studied samples.

Sample	2 θ, (°)	Spacing, d (Å)	χ (%)
Plasma treated cotton	14.8; 16.2; 20.6; 22.7; 34.4; 38.2; 42.5; 44.3; 49.4	5.9; 5.4; 4.3; 3.9; 2.6; 2.3; 2.1; 2.04; 1.8.	48.01
Cotton	14.8; 16.7; 20.7; 22.8; 34.5; 38.3; 42.5; 44.3; 49.3	5.9; 5.3; 4.2; 3.9; 2.6; 2.3; 2.1; 2.04; 1.8.	47.31
Plasma treated paper	15.1; 16.5; 20.7; 22.7; 38.4; 42.8; 44.5;49.5	5.9; 5.4; 4.3; 3.9; 2.3; 2.1; 2.03; 1.8.	64.57
Paper	15.1; 16.6; 20.6; 22.7; 38.4; 42.8; 44.4;49.5	5.9; 5.3; 4.3; 3.9; 2.3; 2.1; 2.03; 1.8.	64.57
Silk	20.6; 38.3; 42.8; 44.4; 49.4	4.3; 2.3; 2.1; 2.03; 1.8.	72.25
Plasma treated wool	9.1; 18.7; 20.1; 23.4.	9.7; 4.7; 4.4; 3.8.	49.38
Wool	9.6; 20.1; 23.5.	9.1; 4.4; 3.8.	50.96
Plasma treated leather	7.7;4.9; 19.5; 24.4.	11.5; 5.9; 4.6; 3.7.	59.44
Leather	7.7; 15.1; 19.4; 24.3.	11.5; 5.9; 4.6; 3.7.	60.25

SEM analyses

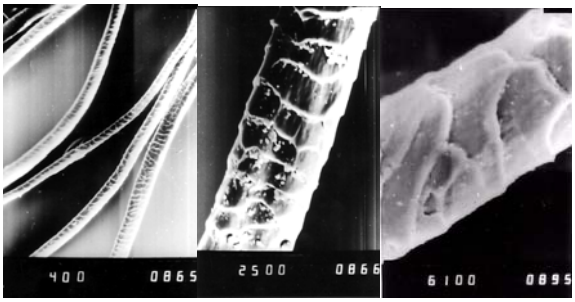
Plasma acts in modifying chemically and topographically the surface of the fiber without affecting it in its interior. Scanning electron microscopy constitutes one of the most important method used for investigation of the surfaces. Plasma treatment of the cultural heritage objects used to prevent the degradative action of microorganisms implicitly demand the preservation of the integrity of the investigated object.



a b c

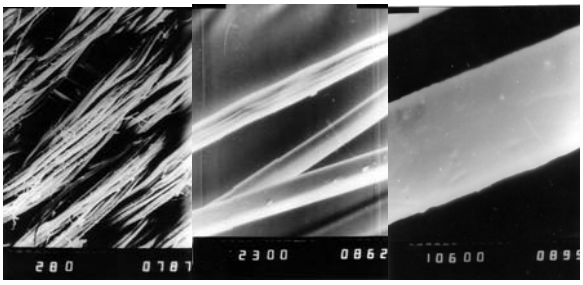
Fig. 12. SEM images of cotton fibers: a-lower magnification; b, c -details at higher magnification.

Topography of the natural fibers is complex and differentiated. Thus, the cotton fiber presents various shapes and cross-section sizes (thinness) along a fiber or different fibers. Wool fiber has circular section of different diameters with a scaly outer layer. The size and distribution mode of the scales differs from fiber to fiber. By comparison the shape and the size of the same silk filament and the surface rugousity are uniform at the microscopic level. These morphological aspects are evidenced in Figs .12, 13 and 14.



a b c

Fig. 13 SEM images of wool fibers: a-lower magnification; b, c - details at higher magnification.



a b c

Fig. 14. SEM images of silk fibers: a-lower magnification; b, c -details at higher magnification.

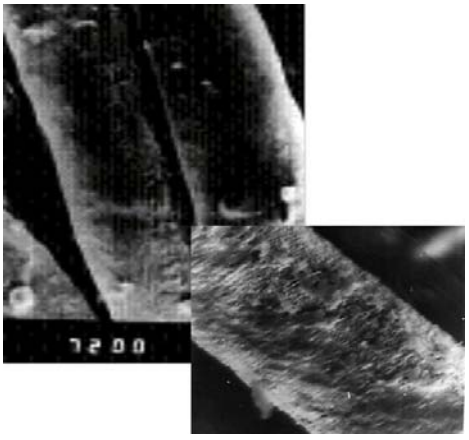


Fig. 15. SEM images of plasma treated cotton strand.

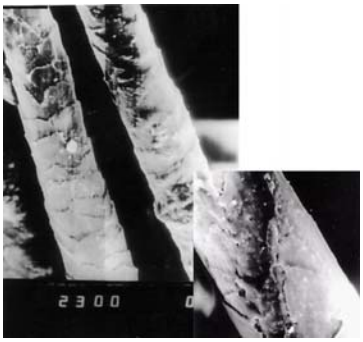


Fig. 16. SEM images of plasma treated wool strand.

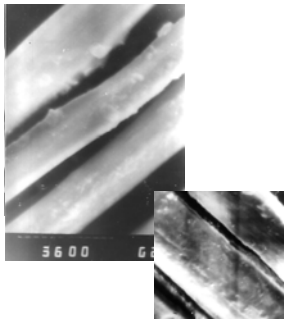


Fig. 17. SEM images of plasma treated silk strand.

Cotton strands from reference sample plasma treated for 1 h do not evidence surface topographical changes of the fiber (Fig. 15).

Plasma treated silk fibers reveal smooth surfaces. Slightly rugousity changes are seen. An aleatory disposition of the formed microcavities caused by plasma etching. All these do not represent an alteration of the silk structure (Fig. 17).

4. Conclusions

Both bulk and surface investigation methods have been employed and the resulted data show that plasma acts only at the surface level within a depth of few nanometers.

The action of HF cold plasma recommends that this method to be used for decontamination of the cultural heritage objects based on natural cellulosic and proteic materials. Plasma does not imply a degradative effect and the integrity of the cultural heritage object is preserved.

Aknowledgements

The authors aknowledge the financial support granted by CEEX 54 / 2006.

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