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HIGH FREQUENCY COLD PLASMA POSSIBILITY OF APPLICATION IN THE STATIONER CULTURAL HERITAGE FIELD

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Abstract

Applying low temperature, high frequency gas plasma treatments for conservation of cultural heritage objects is no longer a novelty, the methods being currently practiced for metallic artifacts. Nevertheless, the literature also indicates attempts to use plasma – process based technologies for materials like paper from historical books and documents.

In recent years, mixed teams of researchers are studying the possibilities of applying a dry treatment in order to allow the decontamination along with cleaning of documents, gathered into a one step method that would reduce the risks of repeated manipulation. In this direction, this paper focuses on characterization by the specific analysis (SEM, FT-IR, DSC, white degree, GMP) of the changes induced by air plasma active species on the cellulosic substrate).

Therefore it is concluded that short-term treatment - within 30 minutes, with strict parameters does not produce additional destruction of the biopolymer used as support (affected by natural aging), but may contribute to the removal of surface impurities which alter the stationer support. These treatments have also a bactericidal and/or fungicide effect.)

Keywords: high frequency cold plasma, cultural heritage, decontamination, paper

1. Introduction

Development of the human species and its progressive evolution could be reconstructed from unwritten and written sources. If graphics were first engraved on clay tablets or litter on the walls of monumental buildings, starting with the evolution of human society more diverse materials have appeared. Papyrus, probably created 5000 years ago, was used in Egypt and surrounding areas for writing; these documents being known today as papyrus scrolls.

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Parchment - obtained by special processing of kid, calf, and sheep leather, is another prevalent support used since antiquity. First appeared in China in the year 75 AD, paper proved to be extremely useful, gradually replacing other supports.

Old paper, originally produced from silk cloth, then from hemp and cotton, was better than the modern one which uses wood cellulose.

Regardless of the raw material used for paper obtaining - cellulose - the main component of paper is a sensitive polymer to environmental factors variation and microorganisms attack. Thus, cultural objects made on stationer support tend to change their shape, colour, chemical composition and physico-mechanical resistance decreases. If the preventive measures are not taken in time, the degradation may continue up to it's decomposing in the initial elements, such as carbon dioxide and water.

The well known established treatments used to stop the evolutionary processes involving the use of some substances with biocidal character in case of microorganisms, or some organic solvents for treatments to remove further deposits which, besides altered aesthetics may accelerate degradation processes. The use of such substances is however a great disadvantage - their high toxicity has negative aspects, in time, both to the object and the environment. This is why, in the last decade, more and more voices are arguing for studying and using less aggressive methods for decontamination and cleansing treatments.

High frequency cold plasma, a phenomenon known since the early twentieth century, with a wide variety of applications, came in the attention of restoration, preservation professionals since 1979, when researchers Daniel and Pascoe [1] studied it for the cleaning metal artifacts. In 1996 Manfred Anders, from the University of Stuttgart published an article in Restauro journal [2] presenting the initial results of plasma treatment of paper, studying especially the effect on the stains and mold spores. In 2001 U. Vohrer and collaborators [3] conclude, that would be possible a 20% increase in paper stability under the action of high frequency cold plasma.

This field of the HF plasma using is insufficient exploited, for which it was tried, by the undertaken studies to supplement existing data. Therefore, this paper focuses on characterization by the specific analysis (SEM, FT-IR, DSC, white degree, GMP) of the changes induced by air plasma active species on the cellulosic substrate.

2. Experimental

2.1. Materials

The study was done on three samples taken from the paper volumes of historical books from the private collections, with the consent of owners. Abbreviations used in this text are in accordance with Table 1.

Table 1. Chemical composition of the investigated brass samples.

Notations	Description and origin
H_1	Page with advertisements inserted in the book ‚Les Miserables', dated: 1920, private collection
H_2	Page 243 from the volume ‚Notre Dame de Paris', dated: 1919, private collection
H_3	The title page from the volume ‚Doine'; dated: 1853, private collection

2.2. Plasma setup

The studies were performed using our own laboratory plasma setup [4], which consists of a bell-shaped reactor, from Pyrex glass, fitted on a steel support. The reactor is capacitive coupled through external electrodes to a high frequency generator with a frequency of 13.5 MHz, which initiate and maintain high frequency electrical discharge. The reactor is connected to a vacuum pump and the carrier gas is accepted into the system through a needle valve.

To achieve plasma treatment, each book page has been suspended through Teflon clips in the positive column formed between two electrodes, when discharge is striking. The samples were treated separately and maintained in plasmogen medium for 30 and 60 minutes.

The photographic image of this installation is present in Figure 1.

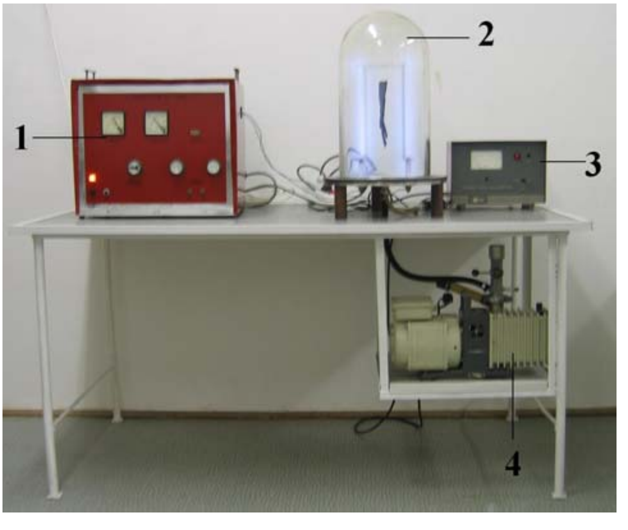


Figure1. Installation for high frequency cold plasma treatments: (1) - high frequency generator, (2) -Pyrex glass, (3) - vacuum pump, (4) - vacuum meter.

2.3. Investigation methods

For morphological characterization of cellulose, the basic constituent of the stationer substrate, before and after air plasma treatment, scanning electron microscopy (SEM) was used. This method provides important data of the topographic effects induced by HF plasma treatment. After a pre-treatment of the samples (which consist in fixing the samples on conducting media and coverage of these with a conductive layer of gold), these were examined with a scanning electron microscope TESLA BS 301, at an accelerating voltage of 10 kV.

FT-IR method (ATR) led to the specific functional groups characterization and highlighting the changes which appear as a result of stationer support exposure to a air atmosphere discharge lamp. The samples were analysed by a VERTEX 7 spectrometer, using ATR technique.

Thermal behaviour of cellulose was evidenced by dynamic differential calorimetry (DSC), which is mainly used to study physical transitions but also the reactions of polymerization, crosslinking, degradation or oxidation. At heating natural polymers, e.g. cellulose, can lose hygroscopic water, and also can appear distortions, defragmentation of macromolecular chain and finally thermal decomposition. Thermogravimetric analysis was done by means of a Q 1500 D MOM analyzer.

The white degree before and after HF plasma treatment of the studied paper samples was determined using the relation (CIE Whiteness) on a DATACOLOR Spetrofklash SF 300 spectrophotometer.

Since in most cases, cellulose fibres degradation is closely related to the macromolecular chain scission and to decrease of polymerization degree, the determination of this parameter before and after plasma treatment was required.

The average degree of polymerization (GMP) determination was done by viscosimetric method, based on the law established by Staudinger: specific viscosity of a dilute solutions from a material with high degree of polymerization is proportional to the concentration of the solution and to the average degree of polymerization of the dissolved polymer [5-7].

3. Results and discussion

3.1. SEM analysis

Micrographic images made before and after HF plasma treatment revealed in all three cases, the presence of cotton fibres. This suggests a good quality of the paper forming the body of the books; pulp fibre being obtained from cotton rags. Overall appearance of the studied surfaces is identical on the untreated and HF plasma treated samples, even after 60 minutes treatment. Detailed examination of the fibre from the surface at high magnifications did not reveal changes in their topography. Due to identical behaviours of the studied paper samples to the plasma treatment in Figure 2 are given only the SEM images of the H sample (before, after 30 minutes and after 60 minutes of treatment).

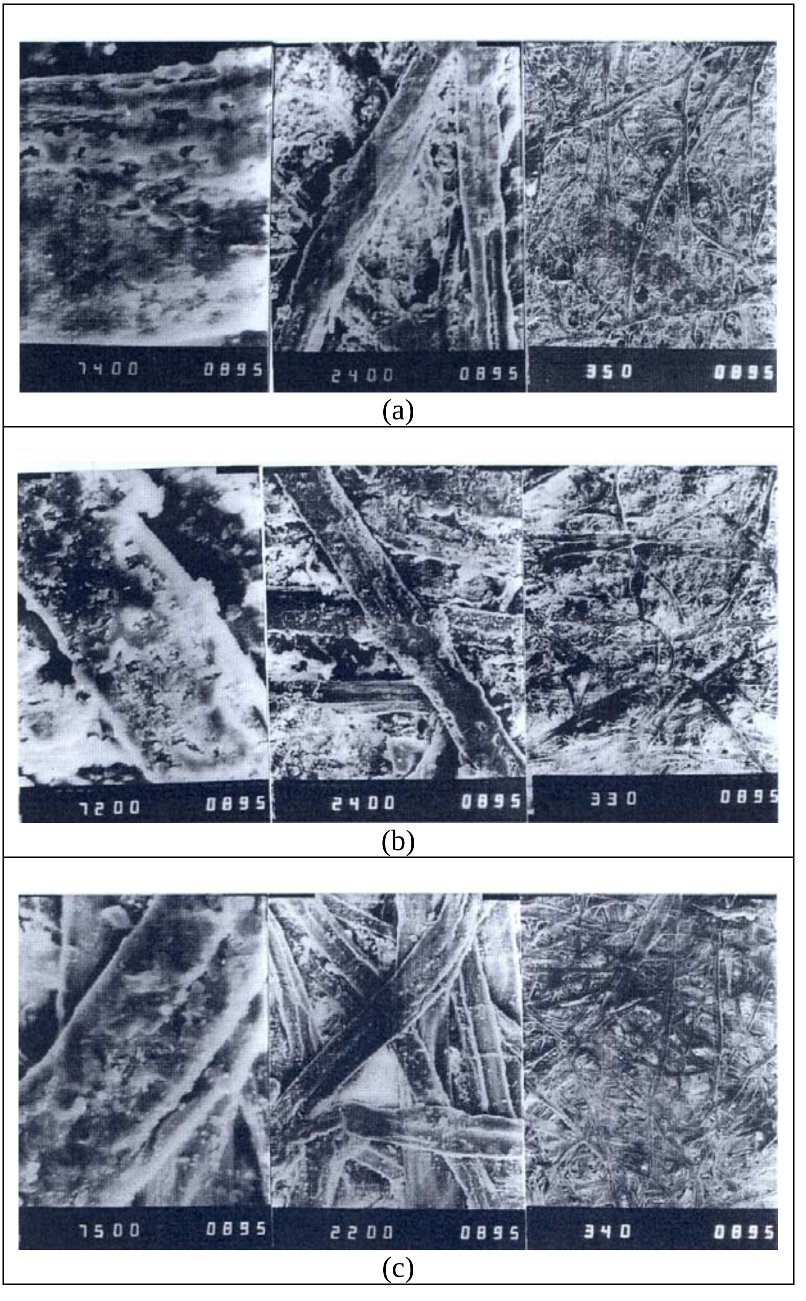
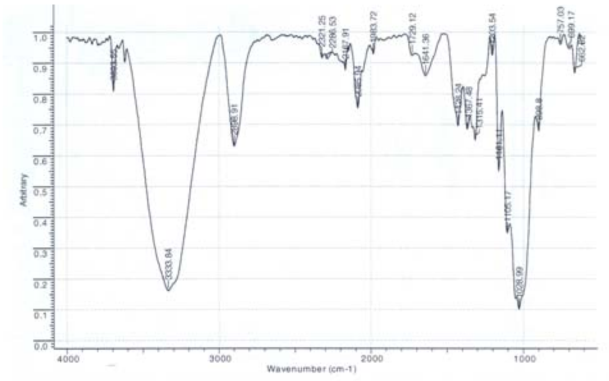
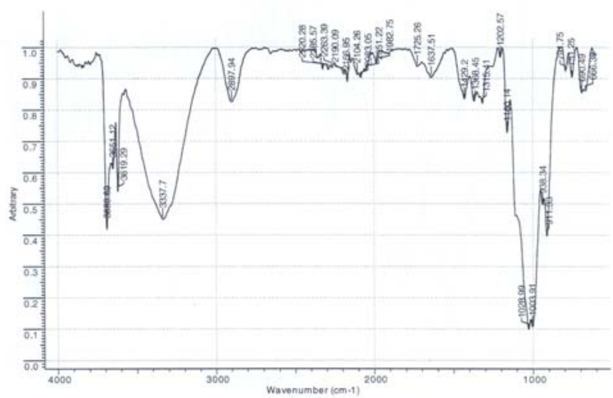


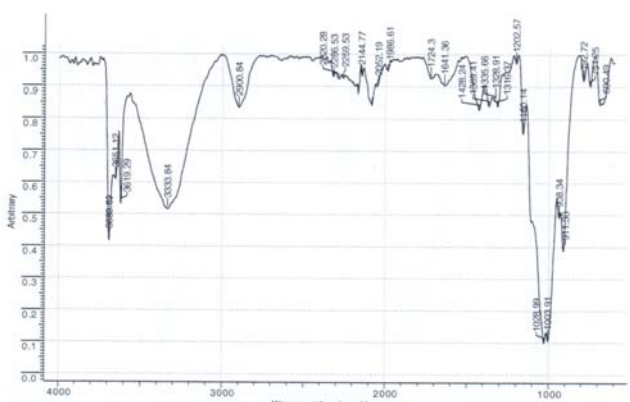
Figure 2. SEM images of the H3 historical paper: (a) before treatment, (b) after 30 minutes plasma treatment and (c) after 60 minutes plasma treatment.



(a)



(b)



(c)

Figure 3. ATR FT-IR spectra of the H_3 sample: (a) before treatment, (b) after 30 minutes of plasma treatment, (c) after 60 minutes of plasma treatment.

3.2. ATR FT-IR spectroscopy

ATR FT-IR spectra recorded before plasma treatment (Figure 3a) show specific absorption bands for the cellulose.

After plasma treatment a new band in the 1730 cm^{-1} region was observed (Figure 3b and c). This band is due to the oxidation reaction, followed by the formation of the carbonyl groups (aldehyde and acid groups) in the cellulose structure. These groups may induce a slightly yellowing surface. Because the spectra of the H_1, H_2, H_3 samples are similar, in Figure 3 are shown only the spectra of the H_3 sample. It should be stressed however that the basic macromolecules are not affected; therefore the physico-mechanical properties of the cellulose are totally preserved.

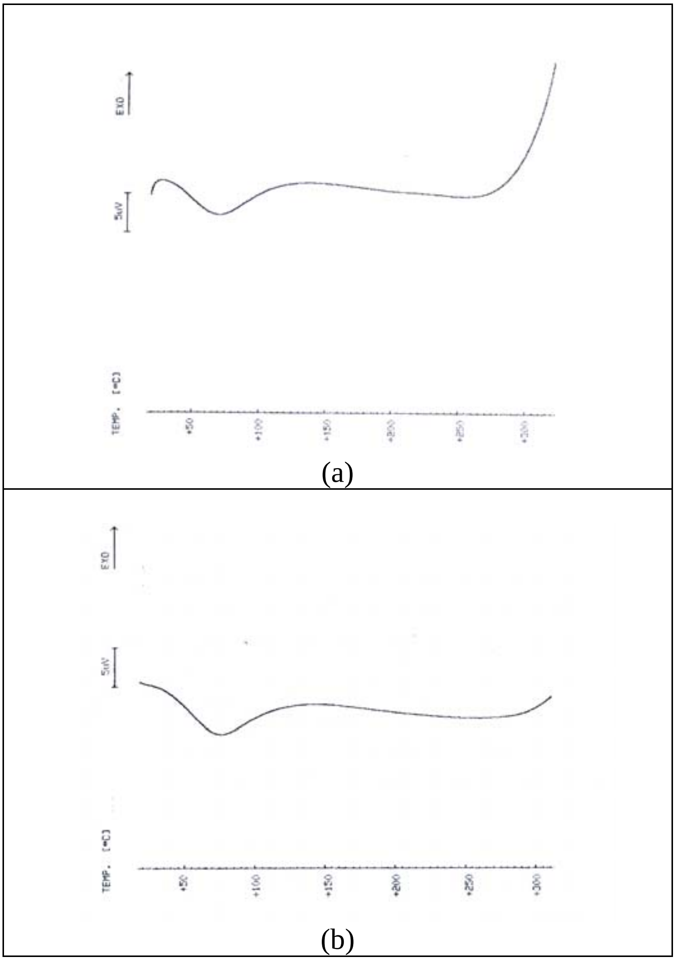


Figure 4. DSC curves for H_3 sample: (a) before treatment and (b) after 60 minutes of plasma treatment.

3.3. DSC analyzes

In Figure 4 are shown the DSC curves of the H_3 paper sample, before and after air plasma treatment. The same observations concerning the thermal behaviours are made in the case of the H_1 and H_2 samples.

Thus, in the case of the untreated samples (Figure 4a) was observed a first endothermic peak in 40-130°C range, assigned to the desorption of water from the hygroscopic structures of the cellulose. Around 270°C cellulose macromolecules start to decompose. DSC curves made on plasma treated samples show small differences, thus under plasma action were not registered important transformations on macromolecular level in the cellulose.

3.4. Chromatic changes

Colour changes induced by high frequency plasma treatment were assessed by the degree of white; the obtained values (white level and brightness) are shown in Table 2.

From Table 2, the decreasing of the degree of white after plasma treatment for all three paper samples can be observed. This is due to the formation of the aldehyde groups observed also from FT-IR spectra. In the same time an increasing of the brightness is observed. This is probably due to removal of some superficial deposits accumulated as result of the functional wear.

Table 2. White and brightness level values recorded for the studied samples

Sample	Time of HF plasma treatment (min.)	Degree of white (%)	Brightness (%)
H_1	0	69.7	49.6
	30	67,5	51.0
	60	62.7	52.1
H_2	0	72.3	45.3
	30	70.1	45.9
	60	69.8	46.8
H_3	0	73.6	55.8
	30	72.8	57.5
	60	71.7	58.2

3.5. Determination of average polymerization degree (APD)

In Figure 5 is shown the average polymerization degree changes depending on the time of treatment for the H_3 sample, which is most representative.

It is noted a decrease in the average polymerization degree of 7.35% after 30 minutes of treatment and of 19.35% after 60 minutes of treatment. As a result, the paper proves to be a sensitive material to the action of active species in air plasma, but a short-term exposure - within 30 minutes, does not produce drastic modification of the cellulose macromolecules.

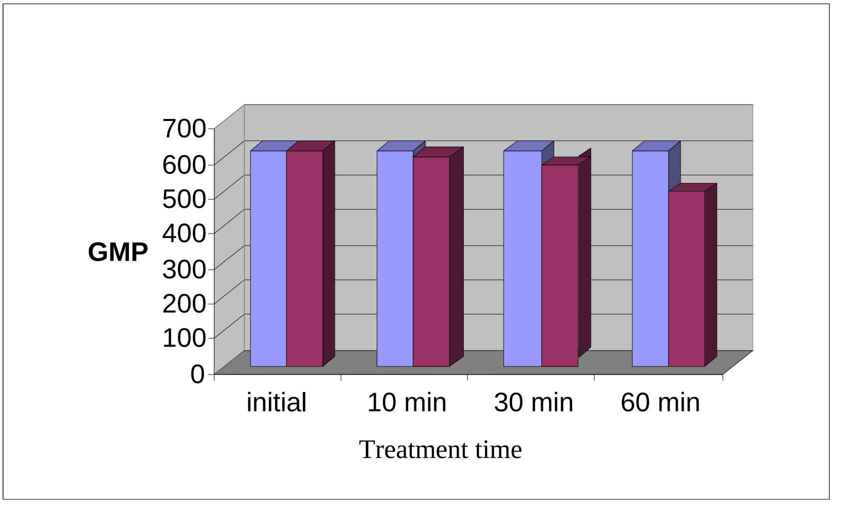


Figure 5. Changes in average polymerization degree for the H_3 sample.

4. Conclusions

The electron-microscopic images obtained by SEM, before and after HF plasma treatment, indicated no changes in cellulose, even after an interval of 60 minutes of plasma action.

The appearance of a new absorption band, in the 1730 cm^{-1} region prove a slight oxidation of cellulose, translated by yellowing of the surface and by reducing the degree of white, due to the formation of carbonyl groups. This phenomenon occurs only to the surface of the biopolymer support, at a few nanometers.

DSC curves recorded after plasma treatment are not significantly modified; therefore the action of plasma did not induce significant changes at the macromolecular level in structure of cellulose.

Progressive decreasing of the average polymerization degree, with increasing the time of HF plasma action, suggest that long-term treatment is harmful to the stationer support, but if it is constantly monitored and the parameters are strictly respected, the degradation is insignificant.

Therefore it is concluded that short-term treatment - within 30 minutes, with strict parameters does not produce additional destruction of the biopolymer used as support (affected by natural aging), but may contribute to the removal of surface impurities which alter the stationer support. These treatments have also a bactericidal and/or fungicide effect.

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