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Plasma treatment — an increasing technology for paper restoration?

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Abstract

An important part of our cultural heritage consists of paper materials, which are stored in archives and libraries. Deterioration of written cultural relics is attributed to several causes, such as microbial contamination, oxidation, acidification, and others. It is therefore desirable to focus research activities on conservation and restoration techniques to develop appropriate treatments. A new technology in the field of restoration could be plasma treatment, which is a well-established technique in a number of other processes, such as plasma cleaning, etching and coating. The main aim of this project is the removal of microbial contamination combined with an increase in paper strength using a plasma-based treatment. Therefore, a special after-glow plasma reactor was constructed to enable careful paper treatment. Current experiments work with oxidising and reducing process-gases to treat naturally aged groundwood paper. A positive effect on the paper stability was achieved by varying treatment parameters, such as flow, pressure, power and time. An overall increase in paper stability of up to 20% was possible. Parallel investigations using plasma treatment for microbial cleaning were carried out. Certain amounts of different fungi and bacteria were spread on naturally aged paper. After plasma treatment, the reduction in microorganisms was measured. This proved the fungicidal and bactericidal action of the after-glow plasma treatment. Nevertheless, optimisation with regard to different microorganisms and kinds of papers must be considered.

Keywords: Plasma treatment; Paper; Cellulose; Microbial contamination; Restoration

1. Introduction

The protection and preservation of cultural heritage, available for example in books, records, and paintings, is an important responsibility for libraries, archives, and museums, which are the guardians of our history and of the evolution of philosophical and scientific thinking. It is estimated that approximately 2.5 million km of paper materials are stored in libraries and archives. Most of these are invaluable pieces of art. The cause of paper deterioration is attributed to internal and external, or environmental, factors. For example, one internal factor is the use of acid aluminium sulfate for paper sizing, which releases sulfuric acid. The acid decomposes the cellulose fibres by catalysing a hydrolysis reaction [1]. One external or environmental factor is, among others, the effect of moisture in paper, leading to the subsequent growth of fungi and bacteria. The growth of fungi will destroy the paper sizing and cause stains, and can be responsible for the loss of paper strength [2,3]. In addition, microbial contamination can cause diseases in the staff of archives or restoration workshops.

It is therefore desirable to focus research activities on conservation, restoration and protection techniques to develop appropriate and long-term resistance treatments. A new technology in the field of protection and conservation of paper documents could be plasma treatment. The main advantage of plasma in paper

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treatment is the inherently dry nature of the process and the possibility of combining different effects, such as cleaning/sterilisation with an increase in paper strength and the deposition of polymer films to prevent the paper from environmental influences.

The application of low-pressure plasma in the field of conservation of cultural objects has been described recently [4,5]. Examples are the restoration of daguerreotypes [6–8], tarnished silver [9,10], and corroded iron artefacts [11] by reductive plasmas.

Further investigations deal with the surface modification of cellulose via plasma, with various goals. Investigations on the etching properties of plasma were mostly carried out with the purpose of studying their internal morphology [12,13]. Others deal with the reduction and oxidation properties [14], water vapour barriers [15,16], and the improvement of wettability, water sorption or adhesion [17–19]. However, little is known about the possibilities of plasma treatment for conservation tasks, e.g. for the removal of microbial contamination from historical polymeric objects in particular.

2. Experimental

2.1. Plasma processing

All plasma treatments of paper substrates were conducted in a specially designed after-glow plasma treatment chamber, which is depicted in a schematic diagram in Fig. 1. The experimental set-up consists of two treatment chambers. The upper chamber is designed as capacitively coupled parallel-plate reactor and the upper electrode is connected to a 13.56-MHz RF transmitter (ENI OEM 25) and a gas inlet system. Here, the paper can be treated directly in the plasma zone. Due to the gas flow system, the paper is treated in after-glow conditions in the lower chamber. This equipment allows a comparison of both kinds of treatment. The size of the chamber is 30×40 cm^2, so paper up to DIN A3 size can be treated, although the best size is DIN A4, because the larger paper can negatively influence the gas flow conditions. The parameters of power, pressure, treatment time, and gas flow were varied.

2.2. Materials

Naturally aged groundwood paper (Bund-es-haus-halts-plan 1955 and 1960) was mainly used for the experiments. The removal of microbial contamination was also carried out on several documents with mould and mildew marks on the surface. Oxygen and hydrogen were mainly used as the process gas.

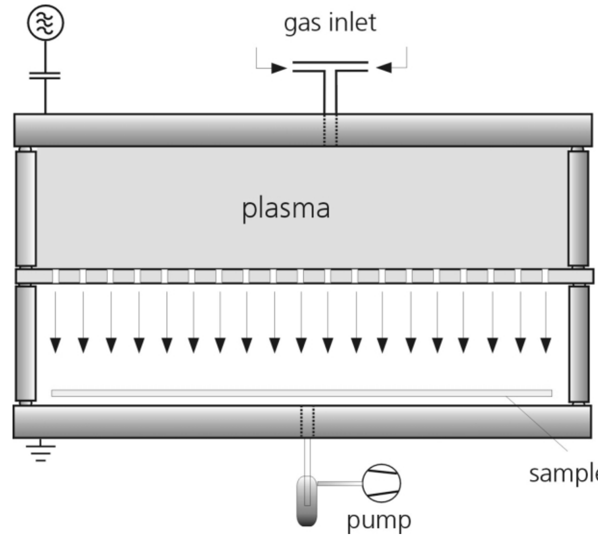

Fig. 1. Schematic view of the specially designed after-glow plasma treatment chamber.

2.3. Microbial work

The inactivation of bacteria and fungal spores on cellulose surfaces was examined with different types of plasma. The inactivation was evaluated with bio-indicators (e.g. *Bacillus subtilis* var. *niger, Aspergillus niger, Micrococcus luteus* and *Trichoderma longibrachiatum*). The bacteria used were cultivated on standard nutrient substrates, consisting of 5.0 g of peptone, 3.0 g of meat extract, and 15.0 g of agar in 1000 ml of water at pH 7.0. For the sporulation of *Bacillus* 10.0 mg/l $MnSO_4 \cdot 7H_2O$ was added. The fungi were cultivated on potato–glucose agar (Merck 10130.0500), consisting of 200 g of potato, 4 g/l D(+)-glucose, and 15 g/l Agar (Fa. Merck, Darmstadt).

The bio-indicators were spread onto the cellulose substrate (8 cm in diameter) at concentrations of 10^1–10^6 and stored under sterile conditions until the plasma treatment was carried out. After the plasma treatment, recultivation of the micro-organisms was carried out. Quantification of the effect of treatment was carried out via the reduction factor $R_f = (\log N_{t,0} - \log N_{t,\text{inakt.}})$. Depending on the type of operation, reduction factors of 4–6 have been achieved.

2.4. Tensile energy adsorption

The tensile strength of the plasma-treated papers was determined after storage of the papers under climatic conditions (15% relative humidity and 20°C). Using this method, the tensile index, the strain at break and the tensile-energy adsorption index (TEA) were obtained. A tensile tester supplied by Zwick was used and papers were tested with and without a fold. The aim was to increase the paper strength, even after folding.

3. Results and discussion

The main focus of our research was the removal of microbial contamination, combined with a strengthening of the treated paper documents. To reach this goal, separate parallel investigations of both topics were performed as a first step to determine appropriate plasma parameters for each. It is conceivable that plasma conditions, which lead to complete inactivation of even radiation-resistant micro-organisms, might also negatively influence the paper strength. Nevertheless, it is important to know the parameter set for complete inactivation of micro-organisms.

3.1. Mechanical properties

It is known from earlier investigations [20,21] that a direct oxygen-plasma treatment is able to inactivate a great variety of micro-organisms on polymer substrates. On the other hand, it is well known that an oxygen plasma leads to etching of the polymer substrate, especially for cellulose [12,13]. Moreover, not only the surface of the cellulose can alter during the plasma treatment, but the bulk properties, such as tensile strength, can also be negatively influenced by the UV radiation under plasma conditions. Considering this, naturally aged groundwood paper was treated with oxygen and hydrogen plasma directly in the plasma zone, as well as under after-glow conditions. Hydrogen was chosen with respect to its reductive potential, because part of the natural alteration of cellulose is due to oxidation. Fig. 2 shows the maximum work of untreated and plasma-treated groundwood paper analysed with/without folding in the tensile strength measurement. The results clearly indicate that the tensile strength decreases drastically after a direct oxygen-plasma treatment. Using water as plasma gas, only a small alteration could be observed, and hydrogen plasma treatment lead to the smallest degradation. Using hydrogen plasma under after-glow conditions in the specially designed plasma treatment chamber, an increase in the mechanical properties could even be obtained. For these experiments, treatment times of up to 60 min and power of 100–500 W under direct plasma conditions, and 300–1000 W for the after-glow treatment, were investigated. A further observation is that high-power oxygen plasma over a long time could lead to not only an extended etching of the paper, especially at the margin of the documents, but bleaching of the ink could also

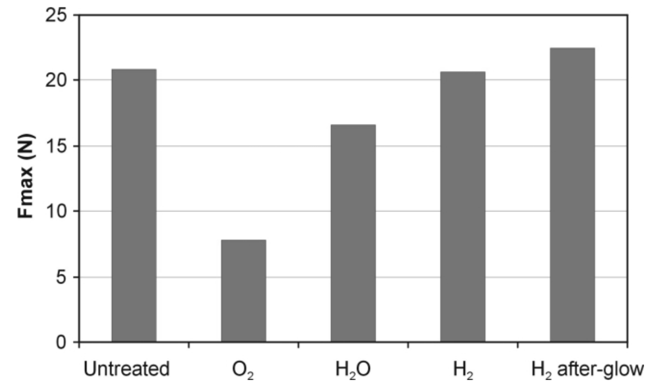

Fig. 2. Results of the tensile strength measurement before and after plasma treatment on naturally aged groundwood paper: (a) untreated; (b) O_2 plasma; (c) H_2O plasma; (d) H_2 plasma; and (e) H_2 after-glow plasma.

occur. With hydrogen plasma, no comparable effect was observed.

Under after-glow conditions, even an oxygen plasma does not lead to a visible degradation of the paper. The mechanical properties decrease slightly. However, subsequent treatment with a hydrogen plasma restores the original tensile strength. This is an important fact, because the effectiveness of an oxygen plasma in the inactivation of microbial contamination is higher than for a hydrogen plasma, as discussed below.

Variations in the power, pressure, gas flow, kind of gas and gas mixtures, and process time, as well as preconditioning of the paper (storage under different humidity) and a treatment on both sides, were investigated. From these results, it could be concluded that power goes through a maximum, with 700 W giving the best results. The influence of pressure was checked in the range 0.17–0.89 mbar. No great influence of the pressure was evident from the tensile energy adsorption measurements carried out on the treated samples.

3.2. Inactivation of micro-organisms

For biological checks on the effectiveness of plasma treatments for the inactivation of microbial contamination, three bio-indicators were chosen. The spores of *Bacillus subtilis* and *Aspergillus niger* are well known as being especially resistant and ubiquitous. *Trichoderma longibrachiatum* decomposes cellulose and is also found in contaminated books, as is *Aspergillus niger*. Certain amounts (10^1–10^6) of these fungi and bacteria were spread on naturally aged paper with a size of 60 cm^2 using a specially developed spraying facility. Fig. 3 shows a scanning electron microscope picture of *Micrococcus luteus* cells on groundwood paper. A homogenous spread of the micro-organisms was obtained. Prepared with this method, samples were produced with the selected micro-organisms and stored and

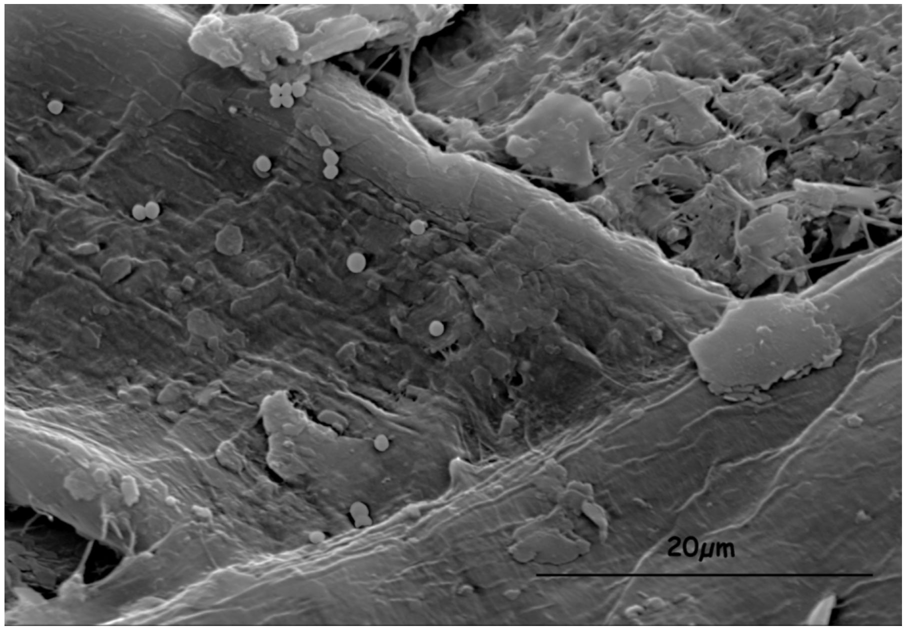

Fig. 3. SEM picture of *Micrococcus luteus* cells on groundwood paper after the spray application. A homogeneous spread of the microorganisms is clearly obtained.

transported under sterile conditions until the plasma experiment started. The effectiveness of the plasma treatment was checked after recultivation of bio-indicators and calculation of the reduction factor ($R_f = (\log N_{t,0} - \log N_{t,\text{inakt.}})$. Fig. 4 shows the results obtained with *Bacillus subtilis* and *Aspergillus niger* in relation to the plasma power used. An after-glow hydrogen plasma was applied for 20 min. From the diagram, two results can be concluded. First, the effectiveness of inactivation increases with increasing power and second, there are differences between the micro-organisms used. In Fig. 5, two further important results are depicted. A comparison of hydrogen and oxygen after-glow plasma treatments and homogeneity of the treatment in the chamber are shown. For each experiment, six samples were placed in different areas of the treatment chamber to prove the homogeneity over the whole area. It is obvious that inactivation of the micro-organisms is independent of the position of the samples in the reactor.

After recultivation of the micro-organisms, a R_f value of 4–5 was achieved with oxygen plasma, whereas treatment with hydrogen plasma resulted in R_f values of 3–4. As expected, the oxygen plasma is more effective than the hydrogen plasma. Nevertheless, a distinct decrease in the number of micro-organisms could be obtained, even under reductive conditions. These conditions are necessary in order to avoid alteration of the

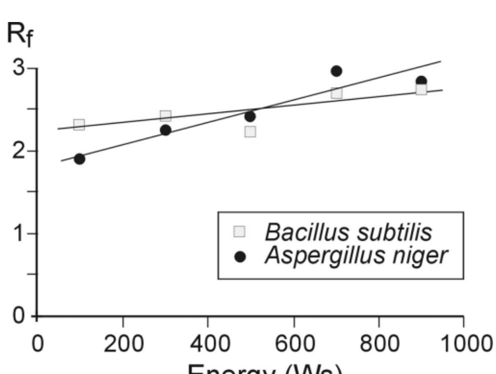

Fig. 4. Reduction factor vs. plasma power for *Bacillus subtilis* and *Aspergillus niger* spores.

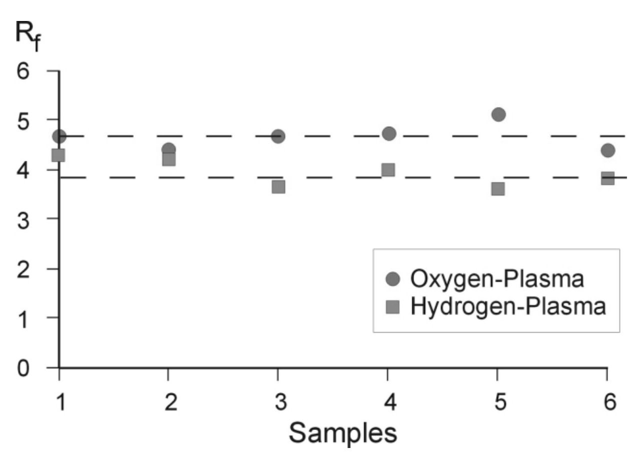

Fig. 5. Comparison of the effectiveness of inactivation of oxygen and hydrogen after-glow plasma treatment (900 W, 20 min) on *Bacillus subtilis*-contaminated groundwood paper. At each experiment, six samples were placed in different areas of the treatment chamber to prove the homogeneity over the whole area.

paper, or even to achieve an increase in strength, as discussed above.

4. Conclusion

An overall increase in paper stability of up to 20% for groundwood paper is possible using hydrogen after-glow plasma. On the other hand, inactivation of microbial contamination combined with cleaning of the paper could be achieved, even with hydrogen plasma; however, an oxygen plasma is more effective. The combination of microbial cleaning and stabilisation of the paper using an after-glow plasma treatment could lead to a new and innovative technique for paper restoration. Nevertheless, further investigations need to be carried out concerning extension to different fungi and bacteria, as well as to different kinds of paper, especially from different production techniques, but also of different age or deterioration state. Another topic will be to investigate the influence of the plasma treatment on different inks used in the past.

Apart from the benefits of plasma treatment for paper conservation, other tasks in restoration could also be eventually solved using this technique. Some possible fields of application are discussed in [22].

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