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Innovative Plasma Processes for Consolidation of Biodeteriorated Ancient Papers

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Summary: Deterioration of paper materials is mainly due to the degradation of cellulose caused by a lot of factors such as chemical attack due to acidic hydrolysis, oxidative agent, light, air pollution and biological attack due to presence of microorganisms like bacteria and fungi. Various technologies exist to limit the degradation of the paper materials but in a few cases are unsuited or produce no good results. Plasma technology is an innovative process which can be an alternative to the conventional methods. The plasma treatment produces a synergetic result of sterilization and coating of the paper. This technology is environmentally friendly and can be used for industrial applications. The aim of this project is the increasing of the paper tensile strength and paper conservation by means of several different plasma treatments.

Keywords: biodeterioration; microbial reduction; paper conservation; paper-based materials; plasma treatment; tensile strength

Introduction

The protection from decay of the paper artefacts poses a serious worldwide problem for numerous libraries, archives and museums. An advanced knowledge of the degradation processes of the paper artefacts was reached in the last few years. It is well-known that the paper undergoes very slow deterioration processes. The overall process of degradation may be seen as a combination of acidic hydrolysis which deteriorates the mechanical properties (shortening the cellulose chains),[1] oxidation which produces mechanical weakening and discoloration [2] and microbial degradation which causes different kinds of damage according to the species of organism responsible for the attack. Some filamentous fungi frequently associated with paper damage can dissolve cellulose fibres by means of the action of cellulolytic enzymes, or produce pigments or organic acids which discolour paper and cause damage to materials of cultural and historical importance made from paper. The microbial degradation produces foxing, word used to identify stains of reddish-brown, brown or yellowish colour, which are generally of small dimensions and show sharp or irregular borders.[3] Foxing formation mechanisms have been studied intensively in the last two decades and some formation models, based on biological [4] or chemical mechanisms [5] have been proposed. External factors such as air pollution, unfavorable climate and lighting conditions are other causes of deterioration. In general, the conventional restoration methods act on the degradation factors, for instance paper deacidification or microbial inactivation, but do not protect the paper from a further future degradation. Furthermore, growing concerns over the use of biocides [6] or chemical agent resulted in the search for alternative methods. As regards the microbial abatment, in a previous articles,[7] showed that the plasma treatment is a new effective technology. The process is safe for the operator of the equipment and the environment. In addition, no harmful residues remain in the treated material. With regard to paper, the main advantages of plasma treatment are the dry nature of the process and the possibility of combining different effects, such as the

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biological agent eradication, the strengthening of deteriorated materials and the conservation through the deposition of superficial layers.

Experimental

Plasma Generation

The apparatus consists of a parallel-plate, capacitive-coupled Plasma Enhanced Chemical Vapour Deposition (PECVD) system, made up of a cylindrical stainless steel vacuum chamber of 35 cm inside diameter and 32 cm height with an asymmetric electrode configuration (Fig. 1). The powered electrode is connected to a 13.56 MHz power supply, associated to an automatic impedance matching unit, while the other electrode is grounded and works as support for the samples. High purity gases (99.9997%) and liquid hexamethyldisiloxane (HMDSO) with 99.9% purity grade have been used. The monomer was heated to a temperature of about 80 °C and injected into the vessel in vapour phase. The temperature inside the chamber during the process is around 300 K. All the deposition of superficial layers were realized on Silicum (100), on Whatman and naturally aged paper.

A residual pressure (measured by a Penning vacuum gauge) in the vacuum chamber of the order of 10^{-4} mbar is obtained by a turbomolecular pump backed with a rotary mechanical pump system. The injection of appropriate gas mixtures is automatically controlled in order to fix the pressure in the vessel.

Characterisation Methods

The identification of chemical groups have been carried out in transmission mode by a Perkin-Elmer Spectrum One FT-IR spectrometer in the range of 4000–400 cm^{-1}. The deposition rate has been deduced from the measurement of the film thickness by an Alpha-Step IQ surface profiler (KLA Tencor). The morphological properties of the deposited films have been investigated by Atomic Force Microscopy (AFM) by a Nano-R^{TM} AFM System (Pacific Nanotechnology, Santa Clara, CA, USA) operating in close-contact mode. Silicon conical tips of 10 nm radius mounted on silicon cantilevers of 125 μm length, 42 N/m force constant and 320 KHz resonance frequency were used. The mechanical tests

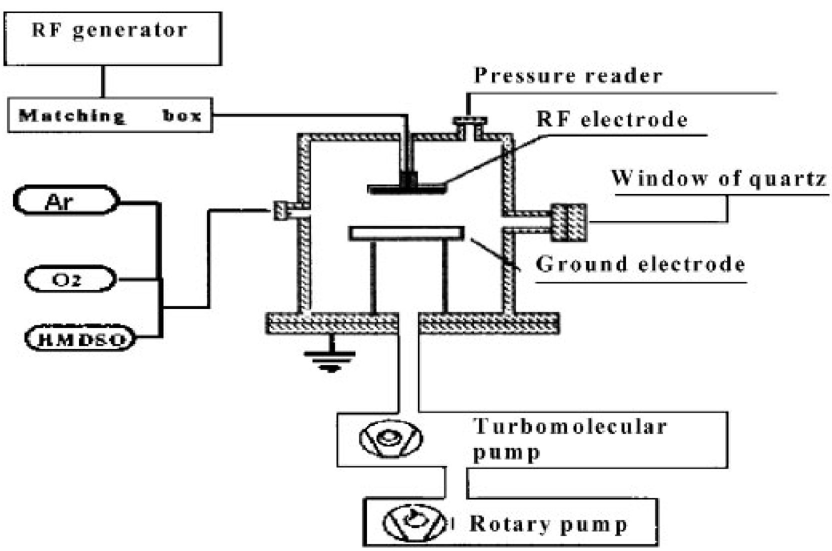

Figure 1.
Schematic representation of the apparatus for the plasma treatments.

have been investigated with ADAMEL-LHOMARGY DY30 dynamometer. The microscopy analysis has been performed by Scanning Electronic Microscopy (SEM) instrument of the Stereoscan 440 Leica-Cambridge microscope.

Results and Discussion

1.0 Enhancement of Mechanical Properties of the Ancient Paper after Plasma Treatments

After plasma treatments the mechanical properties of ancient and Whatman paper were determined by tensile strength measurements.[8] Whatman paper was utilized as a reference substrate.

The tensile strength was evaluated by the stress-strain curves obtained for both paper, in which the maximum strength of the paper correspond to the point where the paper fibres break.

1.1 Ar/H_2 or O_2/H_2 Plasma Treatments

Ar/H_2 or O_2/H_2 mixtures were used. Variation of the tensile strength measurement for ancient and Whatman paper after plasma treatments is showed in Figure 2. Treatments were carried out at 30 sccm total flow, 40 Pa of total pressure, 0,01 W/cm^2 of power density for a time of 2 min. The results clearly indicate that the tensile strength increases after plasma treatment for both samples. An increase in the mechanical properties was obtained.

As reported in same works,[8,9] the tensile strength of the paper depends on the molecular properties of the cellulose, in fact it increases when the degree of polymerisation increases too, evidently the plasma treatment induces an increase of the degree of polymerisation due to formation of inter and intra-molecular ether bonds. Fig. 2 shows that the O_2/H_2 mixture in plasma treatment causes a significant increase of the tensile strength of the paper fibres in respect to Ar/H_2 mixture. Under the same conditions of pressure, power and total flow, using the Ar/H_2 mixture the UV emission intensity is higher than in the O_2/H_2 mixture (Fig. 3). These results show that UV radiation could be responsible for the lower increase of the mechanical properties of the paper fibres when Ar/H_2 mixtures are used. As reported in previous paper,[7] no significant difference can be observed between the spectra of treated and untreated plasma samples. Also

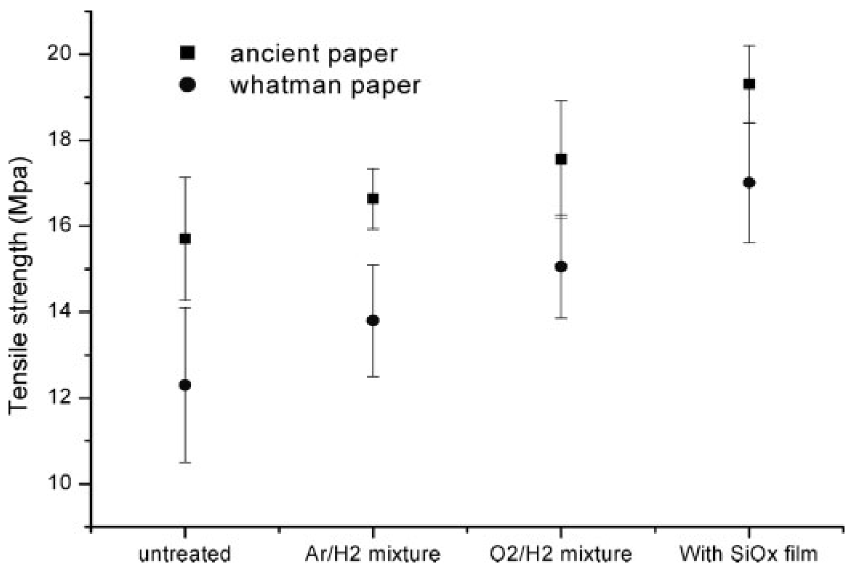

Figure 2.
Variation of the tensile strength as a function of the mixture.

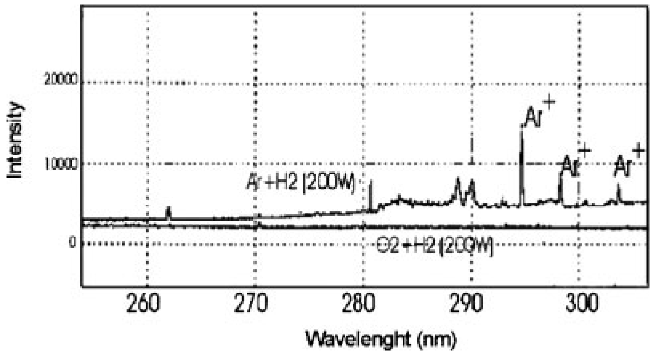

Figure 3.
OES spectra of Ar/H_2 and O_2/H_2 mixture.

the SEM analysis did not show damage to the paper fibres.

1.2 High Purity Gases and Hexamethyldisiloxane Plasma Treatments

Argon and oxygen gases and vaporized hexamethyldisiloxane have been used. Variation of the tensile strength measurement for ancient and Whatman paper after plasma treatments is showed in Figure 2. The deposition was performed at 0,15 W/cm^2 of power density for a time of 3 minutes at a total constant flow rate between 17 and 32 sccm and at a total pressure of about 5 Pa.

The deposited superficial layer on the paper is transparent [20] with a thickness of about 50 nm, evaluated by means of an Alpha-Step IQ surface profiler. As expected the results indicate that the tensile strength increases after plasma treatment for both samples. A further increasing in the mechanical properties was obtained due to the grafting of new chemical groups on the surface of the paper. These chemical groups, identified by means of the FT-IR analyses, are showed in Figure 5. The spectra show the typical Si–O–Si bending mode [10–17] around 820 cm^{-1} and stretching mode in the range 1050–1070 cm^{-1}; the

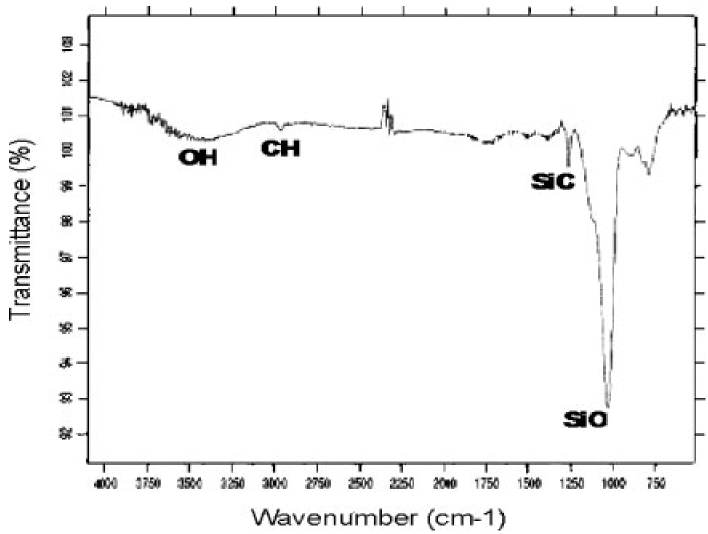

Figure 4.
Typical spectra of $SiO_xC_yH_z$ film.

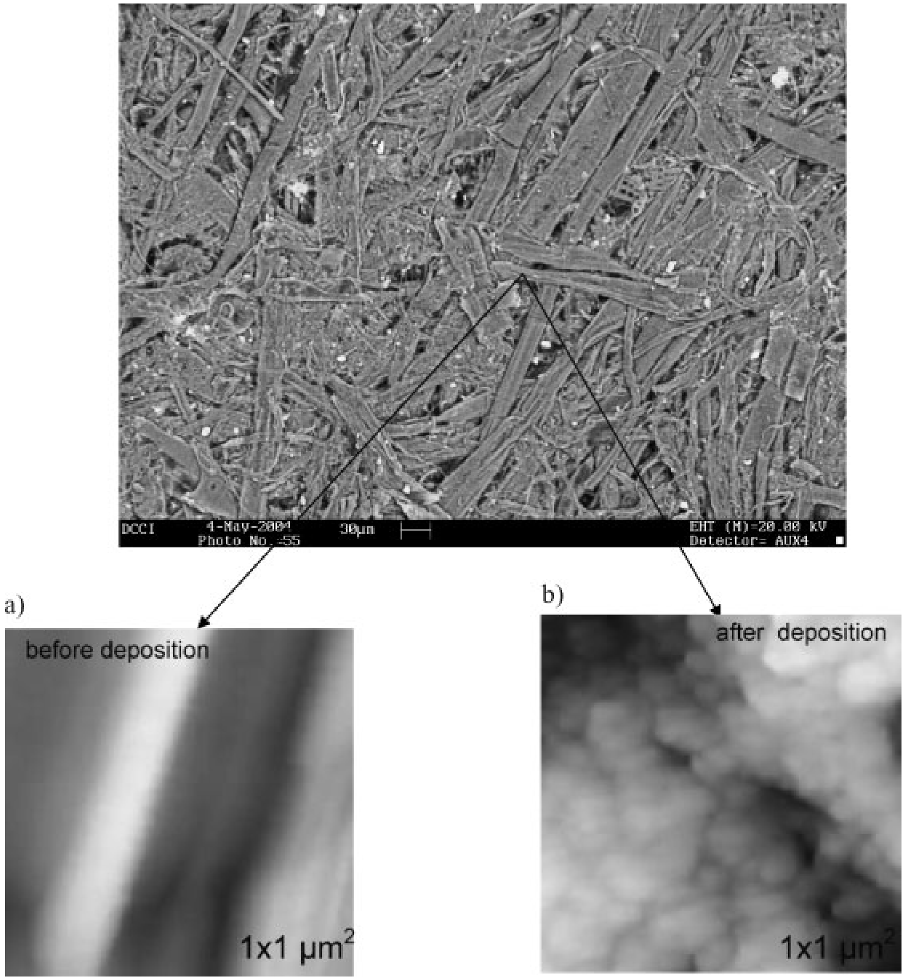

Figure 5.
SEM analysis. a. AFM analysis. b. AFM analysis.

spectrum also shows the absorption bands at 2970 cm^{-1} and 1260 cm^{-1} related to the stretching of CH_x and the bending modes of methyl groups in $Si(CH_3)_x$. Stretching bands of $Si(CH_3)_x$ at 840–885 cm^{-1} as well, mark the presence of organic components in the film. Another important feature is the absorption of the bands characteristic of Si–OH bonds, OH stretching in H-bonded silanol around 3500 cm^{-1} and the bending mode at 930 cm^{-1}.

2.0 Paper Conservation by Means of Plasma Treatments

The restoration process does not preserve the paper for the future; in fact it will be subject still to the various degradation factors (chemical, physical and microbiological). Moreover by means of an opportune PECVD treatment is possible to produce on the paper surface an optically transparent layer of few nanometres of thickness. This layer was produced using the hexamethyldisiloxane as monomer source. The deposited layer confers to the paper surface a high chemical stability,[18] a low permeability to the aeriforms [19] and water repellent property.[20] The Figure 5 shows the scanning electron microscopy analysis of the paper that is not able to see the deposited film. So that the atomic force microscopy has been used. The Figures 5a and 5b show the morphological structure of a paper fibres before and after plasma treatment. It results that the fibres treated with the plasma are completely covered by a silicon-like film constituted by chemical groups identified with FT-IR analyses (Fig. 4). The visible morphology in Figure 5b is characteristic of an amorphous films with an irregular growth of deposit islands.

Conclusions

The increasing of the paper tensile strength and paper conservation could be achieved using plasma treatments. The diagnostics analysis did not show damage to the paper fibres. The deposition (few nanometres) of an optically transparent layer on the paper surface confers new functional properties, in particular, a high chemical stability and a low permeability to the aeriforms in order to preserve the paper for the future. In conclusion, plasma treatment is a new and innovative technique for paper restoration and consolidation. These good results attracted industries and a pilot plant is in progress.

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[1] R.L. Feller, S.B. Lee, J. Bogaard, in: H.L. Needles, S.H. Zeronian (Eds.), Historic Textile and Paper Materials: Conservation and Characterization, Advances in Chemistry Series 212, American Chemical Society, Washington, DC, 1986, p. 329.
[2] J. Aspler, in: TAPPI (Ed.), TAPPI Journal, Norcross, GA,USA, vol. *72*, 1989, p. 192.
[3] P. Choisy, A. de la Chapelle, D. Thomas, M.D. Leroy, in: K.G. Saur (Ed.), Restaurator, vol. *18*, Verlag GmbH, Munich, Germany, 1997, p. 131.
[4] F. Gallo, G. Pasquariello, Boll. Ist. Centr. Patol. Libro,vol. 43, Istituto Centrale per la Patologia del Libro, Rome, Italy, 1989, p. 136.
[5] I. Forsskahl, C. Olkkonen, H. Tylli, Appl. Spectrosc. 49(1995) 92.
[6] L. Tomaselli, G. Lamenti, P. Tiano, Chlorophyll fluorescence for evaluating biocide treatments against phototrophic biodeteriogens, VOLUME 52 (2002), Annals of Microbiology, 197–206.
[7] L. Laguardia, E. Vassallo, F. Cappitelli, E. Mesto, A. Cremona, C. Sorlini, G. Bonizzoni, Applied Surface Science, Vol 252/4 (2005) 1159–1166.
[8] D. J. T. Hill, T. T. Le, M. Darveniza eT. Saha, Polymer Degradation and Stability 49, (1995) 429–435.
[9] J. Kolar, M. Strlic, S. Pentzien, W. Kautek, Appl. Phys. A 71 (2000) 87.
[10] N. Selamoglu, J. A. Mucha, D. A. Ibbotson, D. L. Flamm, J. Vac. Sci. Technol. B 7, 1345 (1989).
[11] C. Bourreau, Y. Catherine, and P. Garcia, Plasma Chem. Plasma Process. 10, 247, (1990).
[12] A. Goullet, C. Vallè, A. Granier, and G. Turban, Plama Sources Sci. Technol. A 18, 2452 (2000).
[13] K. Aumaille, C. Valleè, A. Granier, A. Goullet, F. Gaboriau, and G. Turban, Thin Solid Films 359, 188 (2000).
[14] C. Valleè, A. Granir, A. Goullet, K. Aumaille, C. Carinau, N. Coulon, and G. Turban, Appl. Surf. Sci. 57, 138–139, (1999).
[15] L. Agres, Y. Segui, R. Delsol, and P. Raynaud, J. Appl. Polym. Sci. 61, 2015, (1998).
[16] W. A. Pliskin, J. Vac. Sci. Technol. 14, 1064 (1977).
[17] C. Valleè, A. Goullet, A. Granire, A. van der Lee, J. Durand, and C. Marniere, J. Non-Cryst. Solids 272 (2000) 163–169.
[18] Thomas R. Gengenbach, H. J. Griesser, Polymer, 40 (1999) 5079–5094.
[19] A. Bieder, A. Gruniger, Ph. Rudolf von Rohr, Surf. Coat. Technol. 200 (2005) 928–931.
[20] Osamu Takai, A. Hozumi, N. Sugimoto, J. Non-Cryst. Solids 218 (1997) 280–285.

