

Investigation of the laser cleaning effect on historical wood-pulp paper documents

A. Kaminska, M. Sawczak¹, G. Sliwinski¹

National Museum in Gdansk, Torunska 1, 80-822 Gdansk, Poland, e-mail: alkamin@plusnet.pl

¹ Polish Academy of Sciences, Institute of Fluid-Flow Machinery, Fiszerza 14, 80-231 Gdansk, Poland

ABSTRACT

The pulsed laser cleaning of wood-pulp paper samples systematically investigated for renovation of historical documents indicates on negative effects of the irradiation at 266 and 355 nm on the mechanical and chemical paper properties whenever application of the 532 nm laser and fluence below 0,6 J/cm² reveal satisfactory performance.

Keywords: laser cleaning of historical documents

1. INTRODUCTION

Investigations of the laser cleaning techniques for the paper conservation purpose are carried out since about two decades ^{1,2}. Recently, the experimental results regarding mainly the rag paper or modern cotton cellulose samples are discussed ^{3,4}. The use of lasers for the surface cleaning and renovation of historical paper documents requires a careful selection of interaction parameters according to the chemical composition of the paper material and the surface contamination as well. For diagnostic of the laser cleaning process the spectroscopic techniques such as LIPS and LIF are successfully applied ⁵. The influence of laser treatment on the cellulose based materials is tested by using the chemical and mechanical methods, too ^{3,6,7}.

This work reports results of investigation of the laser radiation influence on the mechanical and chemical characteristics of the paper. The surface cleaning by laser ablation is considered for the case of the model wood-pulp paper. The samples are produced using a traditional technique of the XIX c. and also the chemical composition of the paper is selected in conformance with the historical material. This assures the reproducibility of results and their correlation with the original ones. Experimental data on the ablative laser cleaning of the surface contaminants are concluded from surface analysis and testing of the mechanical and chemical properties. Also the response to the artificial ageing of the paper substrates is discussed.

2. EXPERIMENT

The investigation was performed on the model paper samples of the composition close to that of historical paper produced at the end of the XIX c. The model papers were composed of the cotton cellulose and the wood-pulp mass and were made according to the old technologies of paper production. The mass was sized with 3 % resin glue (Sacosel 309, Krems-Chemie) by weight. The pH value of the model samples was between 4 and 5. The selection of model paper for systematic study assured better reproducibility of the experimental results than in the case of historical paper which is characterized by the structure inhomogeneity and non-identified surface contaminants.

For sample irradiation the Q-switched Nd:YAG laser (Quantel BW) of 6 ns pulsewidth (FWHM), 20 Hz, operating at wavelengths of 1064, 355, 532, and 266 nm was used. The laser fluence was selected from the range 0.3-1.3 J/cm² was applied. In the case of measurements of the dependences of mechanical and chemical properties of the paper samples on the laser irradiation the fixed fluence of 0.6 J/cm² was used. After irradiation, an artificial ageing was applied to the samples. The process was carried out in the conditioning chamber (SAPARTIN 14670) during the period of 10 days (temperature of 80 °C and the relative humidity of 65 %) which corresponded to 50 years of ageing under natural environmental conditions.

After laser irradiation and ageing the samples were subject to the mechanical and chemical resistance measurements such as tearing resistance, fibre elongation and viscosity of the paper solution, respectively. The tearing strength was measured by means of the Elmendorf instrument and the tearing and tensile tests were performed according to standards PN-50131/93 and PN-EN ISO 1924-2, respectively.

In order to define the degree of polymerisation of the cellulose mass the viscosity of the cellulose solution was measured using the capillary-type viscosity meter⁸. The applied solvating agent was the amino-copper hydroxide, the so called Sweizer's reagent. The dependence between viscosity and the polymerisation degree is defined according to relation (1)

$$P^m = K_L h; \quad h = \lim_{c \rightarrow 0} \left[\frac{1}{c} \left(\frac{h_r}{h_0} - 1 \right) \right] \quad (1)$$

where: P – polymerisation degree, η – boundary viscosity [m³/kg], m, K_L – constants η_r – kinematic viscosity of the solution [m²/s], η_0 – solvent kinematic viscosity [m²/s], c – the solution concentration [g/cm³].

The change in length of fibres due to laser irradiation and ageing was measured by means of the microscope (magnification 40 x), by scanning the sample surface with the electron sensor constructed at the Technical University of Lodz. The tests were carried out in the Institute of Cellulose and Paper Research in Lodz.

3. RESULTS

For samples irradiated in the UV range at 266 and 355 nm the optical inspection revealed local damages of the cellulose fibres accompanied by a decrease of the mechanical strength of the paper. The effect was more pronounced after artificial aging of the samples and was confirmed by a length decrease of cellulose fibres. The best cleaning results of the artificially soiled paper were obtained for samples irradiated at 532 nm and at laser fluence just below the damage threshold of 0.6 J/cm², which is in agreement with literature^{3,9}.

Changes of tearing resistance of the laser-irradiated paper at 266, 355, 532 and 1064 nm are shown in Fig. 1. Values measured for the reference samples are equal to 550 mN and 610 mN for the non-sized and glue-sized one, respectively. The sample irradiated at 266 nm laser shows the largest resistance decrease and the effect is even greater by 14 % in case of the paper sized with the resin glue. This is most probably due to fracture of the cellulose chain bonds and formation of shorter chains. The effect can be ascribed to interaction of the UV radiation with the paper fibres and is discussed in literature³.

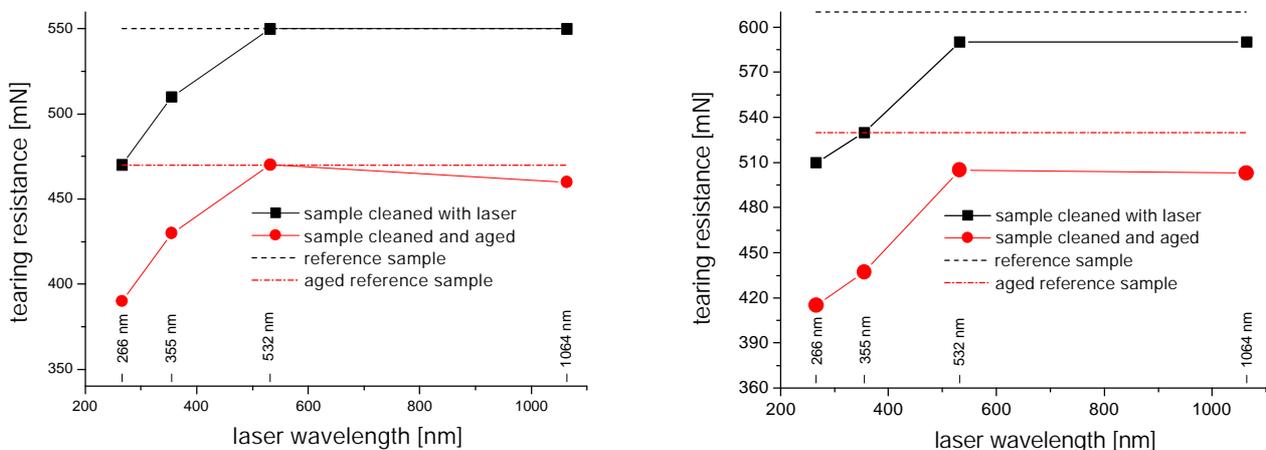


Fig. 1. The tearing strength dependence on irradiation wavelength for the paper samples made of cotton cellulose and leaf-type wood-pulp, with no glue (a) and sized with a resin glue (b), after pulsed laser irradiation at 266, 355, 532 and 1064 nm, and after aging

The effect of laser irradiation on the paper tearing strength decreases with increasing laser wavelength. The relative loss of mechanical resistance measured after irradiation at 355, and 532 and 1064 nm is equal to 7%, and 4%, respectively. After aging the effect becomes even more pronounced for all samples. This is due to the destructive factors such as

high temperature and humidity which cause breaking of hydroxide bridges of the cellulose chains. It results in creation of carbonyls and carboxyls which lead to chains of lower polymerisation degree.

The measured tensile strength (elongation resistance) of the reference sample with no glue and of that seized with the resin glue is equal to 33,5 N, and 42,5 N, respectively – see Fig. 2. Similarly as in case of the tearing resistance, the largest decrease of strength is observed for samples irradiated by the UV lasers at 266 nm and 355 nm. For the non-seized sample irradiated at 266 nm the tensile strength decreases by 12 %. After ageing, this value drops insignificantly by another 4.5 %. Irradiation of the glue seized samples causes a larger drop of the measured resistance than in case of non-seized papers, except for the sample irradiated by the 1064 nm laser. This results from the seizing process of the paper by means of the resin glue which takes place in an acid environment, that has an impact on the mechanical properties of the paper¹⁰. The resistance of the sample irradiated by the 266, 355, and 532 nm laser decreases in relation to the reference sample by 59 %, 53 %, and 23 %, respectively. According to expectation after ageing the elongation resistance of all samples drops insignificantly.

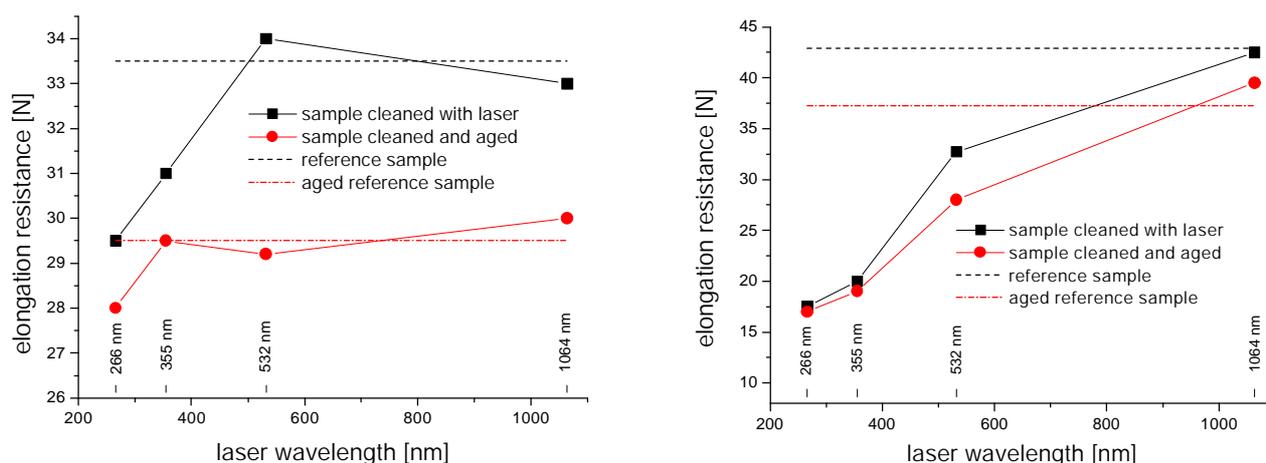


Fig. 2. The dependence of the elongation resistance on irradiation wavelength for the paper samples produced of cotton cellulose and wood –paper mass, with no glue (a) and seized with a resin glue (b) after pulsed laser irradiation at 266, 355, 532, and 1064 nm, and after aging

Results of measurements of the cellulose solution viscosity are shown in Fig. 3. The experimental data on viscosity are given for the non-seized samples only, because the glue admixture has an influence on the solution viscosity and can lead to erroneous results. In case of the reference sample, the measured value of viscosity is equal to 715 dm³/kg. The largest decrease of the cellulose solution viscosity is caused by the laser cleaning of paper in the UV region, i.e. by 25 % and 13 % for irradiation at 266 and 355 nm, respectively. This effect indicates on the decrease of the polymerisation degree of the paper fibres which allows to conclude on fibre degradation. The ageing process results in a further drop of the viscosity by ca. 30 % in case of all samples. The observed negative effect of the UV laser radiation on the cellulose solution viscosity is in agreement with the results obtained from the mechanical resistance tests.

A considerable decrease of the paper fibre length can be observed after sample irradiation by the UV laser compared with the fibre length obtained for reference sample – see Fig. 4. Average values of 0.32 mm (15.6 %) and 0.15 mm (7.3 %) for the beam energy density of 0.6 J/cm² and laser wavelength of 266 and 355 nm, respectively. Enhanced shortage effect of 0.36 mm (17.6 %) accompanies an increase of the radiation energy up to 1.3 J/cm². In case of samples irradiated at 532 nm and 1064 nm, the observed fibre shortage is much smaller, and the corresponding values are 0.07 mm (3.4 %) and 0.11 mm (5.4 %) for irradiation fluence of 0.6 J/cm². The effect is ascribed to the photochemical and photothermal reactions which result in breaking of the bonds between the cellulose particles of the cotton fibres. Measurements of the length change of cellulose fibres support the conclusion on the negative effect of the UV laser radiation on paper in agreement with results obtained from mechanical and viscosity tests.

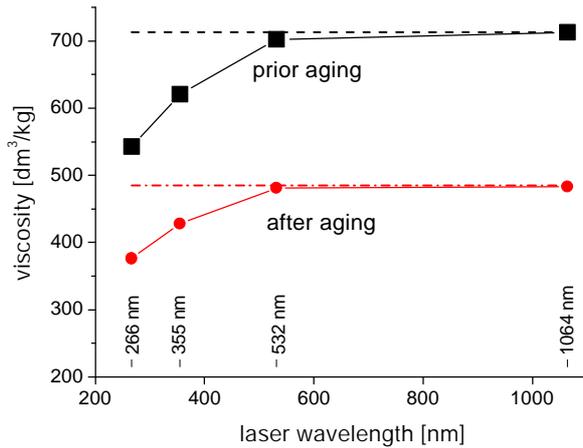


Fig. 3. The dependence of the paper solution viscosity on the laser irradiation wavelength for paper samples produced of the wood-pulp and cotton cellulose, of a surface artificially contaminated.

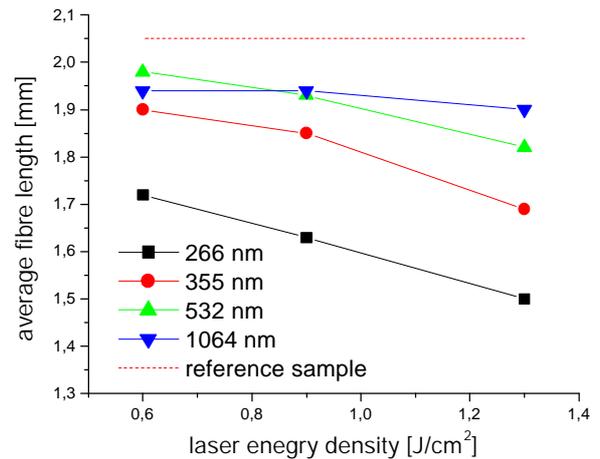


Fig. 4. Dependence of the mean paper fibre length on the laser irradiation wavelength for paper samples produced of the wooden pulp with admixture of the cotton cellulose.

4. SUMMARY

Paper samples produced of cotton cellulose and wooden pulp were irradiated by pulsed laser at 266, 355, 532, and 1064 nm in the energy density range of 0.3 - 0.6 J/cm² below material damage threshold. After irradiation and ageing the mechanical properties such as tearing and tensile strength, paper solution viscosity, and shortage of the paper fibres were measured. It has been concluded from experiment that the laser irradiation at 266 and 355 nm have a negative effect on the mechanical and chemical paper properties. For paper samples irradiated by the 532 nm laser and energy densities below 0.6 J/cm² the satisfactory performance was revealed. The laser operating at 532 nm can be effectively applied for the localized surface cleaning of historical documents.

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