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Characterization of laser-treated paper

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ABSTRACT Paper is one of the most important materials in cultural heritage given its extensive use as the data carrier for religious, artistic and scientific records. For both aesthetic and conservation reasons, cleaning of these materials is often needed. Current paper cleaning methods using conventional means are not always sufficient, e.g. for the local cleaning of paper in the vicinity of sensitive media. In this respect a ns-pulse laser provides a valuable tool for solving difficult cleaning problems. The influence of various laser wavelengths (355 nm, 532 nm, and 1064 nm) and the ageing status of modern paper test systems were studied. Colorimetric measurements, the determination of the average molecular mass of cellulose, and chemiluminescence analysis proved to be useful for the characterization of the laser-treated paper. Treatment with green laser light at $\lambda = 532$ nm below the paper ablation threshold fluence gave the most promising results on pure papers, with no discolouration and no other visible alteration, nor detectable chemical changes.

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1 Introduction

Laser treatment of organic materials for conservation purposes such as paper objects of cultural and historic value has been studied with increasing interest from the conservation community [1–6]. It has to take into account the typically high susceptibility of those materials to thermal and photochemical degradation. Therefore, characterization of paper alterations caused by laser irradiation is relevant, to evaluate laser cleaning as a safe alternative in paper conservation practice. Whereas some of those alterations are clearly perceptible, e.g. discolouration, surface roughening or disruption, invisible chemical changes may as well take place, which will cause the paper to degrade faster.

In this study, optical and chemical alterations of different fresh, pre-aged, and post-aged paper types caused by laser treatment using different parameters (wavelength, energy density, and overlap) are characterized by several analytical methods. As techniques were used the spectral reflectance colorimetry, size exclusion chromatography (SEC), and photon counting, respectively, in order to measure paper colour differences (ΔE^*), the weight-average molecular mass (M_w) of cellulose, and chemiluminescence (CL). Further analysis by mechanical tests on laser-treated paper samples will be presented elsewhere [7, 8].

Discolouration of the paper substrate as a result of laser treatment is considered undesirable. Colours of laser-treated and untreated areas can be measured using spectral reflectance colorimetry. Representation of each colour in the CIE-L*a*b* colour space allows the quantification of small differences in colour (ΔE^*) below the minimum level of perception.

The average molecular mass or, inter-convertibly, the average degree of polymerization (DP) of cellulose, the major structural component of paper, is an important analytical criterion to monitor quantitatively the degradation of paper [9, 10]. Cellulose is a linear, syndiotactic homopolysaccharide consisting of D-anhydro-glucopyranose units connected by β-1,4-glycosidic bonds. The depolymerization of cellulose will negatively affect the mechanical properties of paper, leading to a loss of strength and flexibility, and to an increased brittleness [11]. On the other hand, the apparent increase in cellulose DP due to the crosslinking of cellulose molecules, which occurs as a result of e.g. thermal degradation [12], may affect the hydrophilic and mechanical properties of paper. Size exclusion chromatography (SEC) is the preferred method to characterize the molecular mass distribution (MMD) of polymers, including cellulose [13, 14].

Chemiluminescence is the phenomenon of ultra-weak light emission arising from the relaxation of excited states populated in chemical reactions [15]. The self-recombination of secondary peroxy radicals, i.e. the Russel mechanism [16], yielding excited triplet state ketones and singlet oxygen is generally accepted as the most probable reaction mechanism causing chemiluminescence:

$$\mathrm{R{-}CXH{-}OO^{\bullet} + ROO^{\bullet} \rightarrow R{-}C(X){=}O^{*} + ROH + O_2{}^{*}}$$

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The chemiluminescence of cellulose has been recently studied in the course of thermal and thermal oxidative degradation [17]. Three independent light emitting processes have been identified in dynamic CL experiments under inert atmosphere: (1) decomposition of emitting species (presumably oxygen–cellulose charge transfer complexes) formed by sample pre-irradiation with visible light, at 85 °C; (2) decomposition of macromolecular peroxides, at 135 °C; and (3) chain-scissions, at $T > 160$ °C, which are accompanied by a decrease in degree of polymerization. The two first CL processes are of interest to investigate the effects of laser interaction with paper. Whereas direct photolysis of cellulose is not observed at wavelengths greater than 310 nm [18], photosensitized degradation generating macromolecular radicals is expected to take place to some extent in the paper systems treated with UV lasers. For the lasers of longer wavelengths, such a photochemical effect is far less expected. Detection of peroxides or other emitting species eventually formed by laser treatment would offer insight into the early stages of alteration caused by the different lasers on the investigated paper samples.

2 Experimental

2.1 *Paper models*

Three types of paper were used throughout this study:

- P1: bleached sulphite softwood cellulose paper, no fillers, no sizing
- P2: additive-free cotton linters cellulose paper, no fillers, no sizing
- P3: Acid mechanical pulp paper, alum-rosin sized, kaolin coated

The fibre composition of these papers is representative for a broad range of papers to be found in cultural collections. A detailed description is given in [19].

2.2 *Artificial ageing*

Artificial ageing of subsets of papers P1 and P2 was done prior to laser treatment in order to check for a possibly different susceptibility of 'fresh' versus 'pre-aged' papers. Pre-ageing was performed by exposure to air at 90 °C and 50% relative humidity, in the dark, for 12 d. In order to assess the long-term effects of laser treatment subsets of lasered papers P1, P2, and P3 were artificially aged. Post-ageing for the UV laser ($\lambda = 355$ nm) and for the green ($\lambda = 532$ nm) was done, respectively, by exposure to air at 80 °C and 65% relative humidity, and 90 °C and 50% relative humidity, both in the dark for 12 d.

2.3 *Laser treatment*

Three different laser wavelengths were used: in the ultraviolet range $\lambda = 355$ nm, in the visible field $\lambda = 532$ nm, and in the infrared region $\lambda = 1064$ nm. In all cases a Nd : YAG-laser delivered the laser beam. The system (Spectron Laser Systems, SL 852) used with the third harmonic wavelength at $\lambda = 355$ nm had a maximum output energy of 16 mJ with a pulse duration of 13 ns and a repetition rate of 1.25 Hz. The beam was focussed by a quartz cylinder lens (310 mm focal length) to a spot dimension of $[200 \times 2000]\,\mu m^2$ (area 0.04 cm^2). In this set-up the samples were mounted and scanned on a controlled x-y-z stage. Another laser, a computerized prototype laser-cleaning system, based on a high pulse energy diode pumped Q-switched Nd : YAG laser operating with a pulse duration of approximately 10 ns at 1064 nm and 532 nm is specified with output energies of 5 mJ for $\lambda = 1064$ nm and of 2.5 mJ for $\lambda = 532$ nm. The set-up consisted of a scanning optical system (254 mm focal length) which delivered a spot size of approximately 100 μm and energy densities (fluences) in the range of up to $F_{max}(1064) = 21\,J/cm^2$ and $F_{max}(532) = 10\,J/cm^2$. A repetition rate of less than 1 kHz could be controlled freely. The fluences and number of pulses were varied. Lower and upper limits of the fluence ranges to be studied for each wavelength were chosen around prior determined ablation threshold fluences. The criterion for the ablation threshold used in this study is the fluence level for which a visible destruction of the paper matrix with $N = 35$ pulses per area was observable and additionally a treatment on another area with $N = 10$ pulses did not yield damage.

For colour and M_w measurements matrix-patterned samples were prepared on fresh and pre-aged, P1 and P2 papers. A matrix of $[6 \times 4]$ or $[5 \times 4]$ squares (approx. $8 \times 8\,mm^2$) for each wavelength/substrate combination was laser treated with varying fluences and pulse numbers. For the ultraviolet laser at $\lambda = 355$ nm, the fluences were varied between $F = 0.25$–$1.75\,J/cm^2$, for the green laser at $\lambda = 532$ nm between $F = 0.08$–$2.35\,J/cm^2$, and for the infrared laser at $\lambda = 1064$ nm between $F = 1.2$–$6.7\,J/cm^2$. Additionally the pulse numbers ranged from $N = 1, 2, 5$, and 9. For CL measurements fresh papers P1 and P2 were laser treated at $\lambda = 355$ nm with fluence $F = 1.35\,J/cm^2$, and P3 with $F = 0.19\,J/cm^2$, respectively. The laser treatment at $\lambda = 532$ nm used a fluence of $F = 0.83\,J/cm^2$ for P1 and P2, and $F = 0.08\,J/cm^2$ for P3. The pulse number was always set as $N = 3$.

2.4 *Colorimetry*

Colour measurements on laser-treated areas and untreated background were carried out using a Minolta CM-2002 spectrophotometer equipped with a 5 mm aperture sample holder CM-A49. The spectrophotometer is connected to an integrating sphere, illuminated with a UV-filtered pulsed xenon arc lamp. The illumination/viewing condition is (D/0). Monitoring of changes in gloss was considered important. For this reason spectral reflectance was measured with the specular component included (SCI). Data acquisition and colour analysis was performed with Minolta Chromacontrol (S) V 1.17 software. CIE-L*a*b* colour coordinates were calculated for the 10° standard observer and illuminant D65. Background measurements performed on the untreated areas were always repeated three times at different locations to determine the variability within each single paper sample. Measurements on the laser-treated areas were done only once.

2.5 *Size exclusion chromatography*

Size exclusion chromatography (SEC) was used to characterize the molecular mass distribution of cellu-

lose in laser-treated areas and untreated background. The macromolecules are separated according to their hydrodynamic volume in solution by driving the solution through a porous, three-dimensional network in a chromatography column. From the chromatogram average molecular masses, and the corresponding average DP values, can be determined with good precision. In this study weight-average molecular masses (M_w) are reported.

Cellulose is not soluble in organic solvents typically used as mobile phases in SEC. In this study, cellulose was chemically modified prior to analysis by reaction with phenyl isocyanate (PIC). The resulting soluble cellulose tricarbanilate (CTC) derivative shows enhanced UV detection properties. Advantages of this procedure are that full trisubstitution is achieved in one reaction step, the MMD of the parent polysaccharide remains unaffected, and the long-term stability of the CTC [20–22]. The derivatization procedure was adapted to accommodate the use of small samples of ($1 \times 1\,mm^2$). Details of this procedure will be published elsewhere [23]. The use of alternative solvent systems [24, 25] was not considered due to the absence of UV active groups on native cellulose. Due to the screening action of lignin in the derivatization procedure, the use of the method to determine the M_w of cellulose was limited to the lignin-free papers P1 and P2.

For size exclusion chromatography, equipment from Waters Chromatography B.V. (Etten-Leur, NL) was used. The mobile phase tetrahydrofuran (THF HPLC grade) was delivered by an isocratic 515 pump with a flow rate of 0.3 ml/min. Sample injection, usually 10 µl, was performed by a 717 autosampler. The separation of the macromolecules was done with three coupled PLgel Mixed B columns from Polymer Laboratories Ltd. (Shropshire, UK) thermostated at 30 °C. The SEC system was calibrated with PIC-derivatized pullulan standards and with narrow molecular mass polystyrene standards to cover the whole needed mass range. Both standards showed good correlation. Final MMDs were calculated on the basis of cellulose. Detection was performed by a 996 photodiode array detector at a wavelength of 254 nm for the polystyrene standards and at 235 nm for the PIC-derivatized pullulan standards and the CTC samples. The SEC system was controlled by Waters Millennium[32] software, which was also used to perform data acquisition. The data files were exported as ASCII files to a computer using in-house software for subsequent MMD calculation.

2.6 *Chemiluminescence analysis*

Chemiluminescence experiments (CL) were carried out on a Lumipol-2 photon counting instrument manufactured by the Polymer Institute of the Slovak Academy of Sciences (Bratislava). The CL of the paper samples was recorded during dynamic experiments performed in nitrogen by maintaining a gas flow of 3 l/h. Paper discs ($\varnothing = 5$ mm) were placed onto an aluminium pan, conditioned for 10 min at 40 °C, and then heated up to 200 °C at a heating rate of 2.5 °C/min. The CL response of lasered areas of the test papers has been compared to that of untreated areas. The measurements have been carried out a few days after the irradiation of the papers, as well as after artificial ageing of the irradiated samples. This allowed the study of both immediate and long-term effects of laser treatment on the CL of the samples. All measurements of laser-treated areas of the paper were carried out in duplicate, and those of untreated areas in triplicate.

3 Results and discussion

3.1 *Determination of ablation threshold fluences*

The ablation threshold fluences F_{th} as defined above, for all fresh and pre-aged papers with all laser wavelengths were determined. With a focal spot size of approximately 100 µm, the ablation thresholds for the test papers were determined as depicted in Table 1.

The pre-aged papers seem to be more sensitive to laser radiation and therefore, their ablation threshold fluences are lower. Especially for the infrared laser, all papers show in the aged category a decrease of resistance to laser radiation. The difference is of the order of $\sim 30\%$.

3.2 *Colorimetry*

The colorimetric measurements were performed on P1 and P2. In Fig. 1, a comparison of colour measurements on fresh P1 to pre-aged P1 for all three laser wavelengths is shown. The laser fluences and pulse numbers were varied. A laser-treated matrix pattern of $[6 \times 4]$ or $[5 \times 4]$ resulted, respectively.

Differences of $\Delta E^* > 1$ are visible to the naked eye. Maximal differences of $\Delta E^* < 3$ were observed (with an error of approximately ± 0.2); especially after infrared laser interaction the values deviate. Treatments with the green and ultraviolet laser resulted in similar colorimetric changes. These were more pronounced after laser irradiation for pre-aged than for fresh samples (especially for P2). This observation corresponds with the threshold fluence behaviour where normally the threshold of fresh paper F_{th}(fresh) is slightly higher than for the pre-aged samples F_{th}(aged).

3.3 *Size exclusion chromatography*

On the colorimetric samples the M_w of cellulose was also determined. Paper 3 was excluded because of its lignin content. The laser parameters were varied as mentioned in paragraph 2.3. Typical values for M_w are in the order of up to 7×10^5 Da. M_w results for fresh P1 and pre-aged P1 treated with all three laser wavelengths are presented in Fig. 2. The pre-ageing procedure yielded a decrease of approximately 2×10^5 Da. A comparison between the background and the lasered matrix areas showed that the ultraviolet laser radiation

[J/cm^2]	P1		P2		P3	
	fresh	aged	fresh	aged	fresh	aged
$\lambda = 355$ nm	1.6	1.6	1.6	1.6	0.3	0.2
$\lambda = 532$ nm	1.0	0.7	1.0	1.0	0.1	0.1
$\lambda = 1064$ nm	6.7	4.4	7.5	5.9	3.0	2.5

TABLE 1 Survey of the ablation threshold fluences F_{th} of all three fresh and pre-aged papers with laser wavelength $\lambda = 355$; 532; and 1064 nm

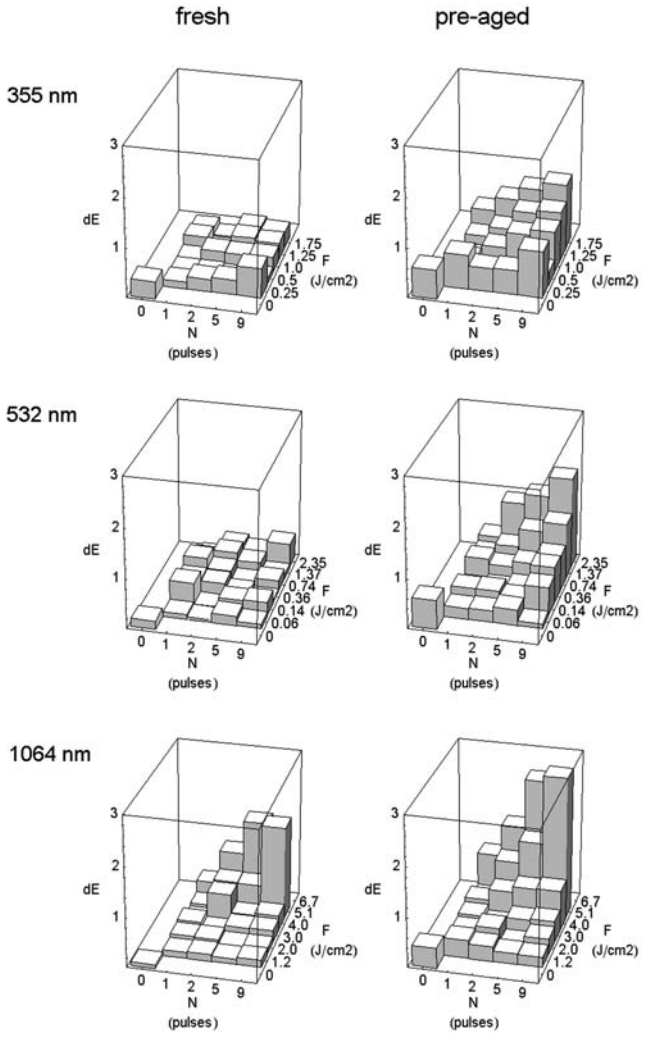


FIGURE 1 Colour measurements; comparison of fresh P1 with pre-aged P1 for all three laser wavelengths. Fluence variation for $\lambda = 355$ nm between $F = 0.25$–$1.75\,\mathrm{J/cm^2}$, for $\lambda = 532$ nm between $F = 0.08$–$2.35\,\mathrm{J/cm^2}$, and for $\lambda = 1064$ nm between $F = 1.2$–$6.7\,\mathrm{J/cm^2}$. Pulse number range $N = 1-9$

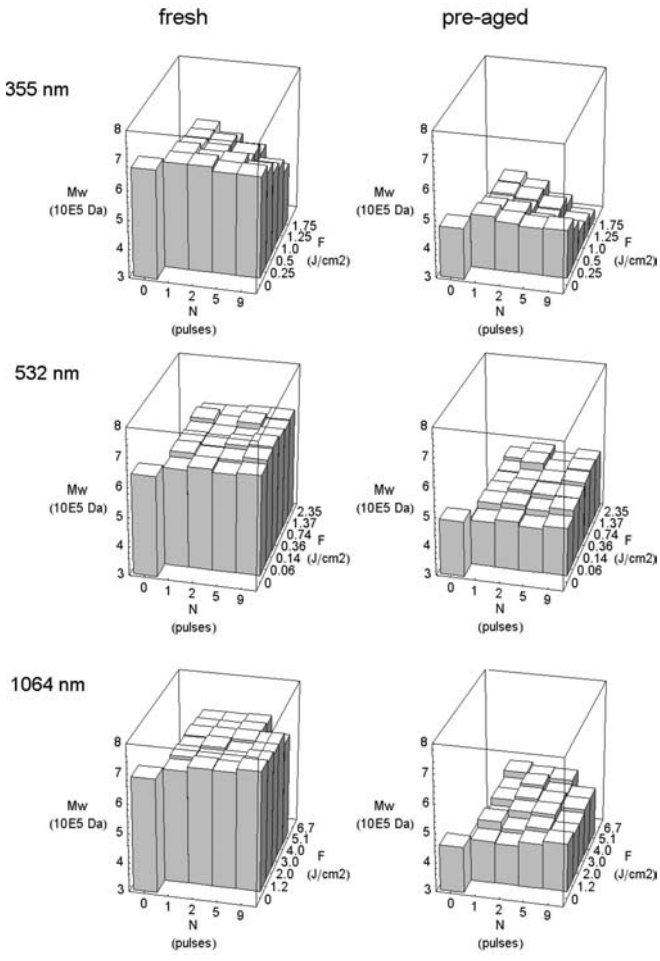


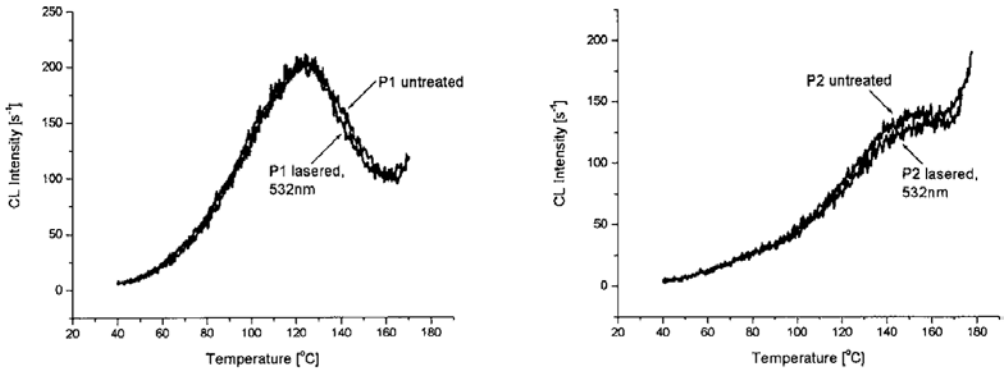
FIGURE 2 Weight-average molecular mass measurements; comparison of fresh P1 with pre-aged P1 for all three laser wavelengths. Fluence variation for $\lambda = 355$ nm between $F = 0.25$–$1.75\,\mathrm{J/cm^2}$, for $\lambda = 532$ nm between $F = 0.08$–$2.35\,\mathrm{J/cm^2}$, and for $\lambda = 1064$ nm between $F = 1.2$–$6.7\,\mathrm{J/cm^2}$. Pulse number range $N = 1-9$

resulted in a significant decrease in the M_w value for higher fluences and higher number of pulses. Whereas the green and the infrared laser light interaction caused no M_w effect related to laser parameters or only a slight decrease towards rougher conditions, respectively. The results for P2 showed similar behaviour.

3.4 *Chemiluminescence analysis*

The chemiluminescence measurements were performed on all three fresh and post-aged paper types. A comparison of fresh P1 and P2 to post-aged samples for the laser treatment with the green wavelength is shown in Fig. 3. No significant differences between the CL responses of treated and untreated areas for the two papers, both fresh and artificially aged, are observed. The bleached sulphite softwood cellulose paper P1 shows the typical CL peroxide decomposition peak centred at 125 °C. Its position and intensity is not altered by laser treatment and/or artificial ageing. For paper P2 a shoulder centred at 150 °C can be seen, which is not affected by laser treatment but the intensity of which is reduced by artificial ageing.

The chemiluminescence of the paper samples P1 and P2 treated with the UV laser is shown in Fig. 4, both before and after artificial ageing. Contrary to the results obtained with the green laser, significant differences between the CL responses of all three papers are observed. UV laser treatment causes the CL intensity of the fresh papers P1 and P2 to increase in the temperature interval of 40–125 °C. A second difference in the CL trace of P2 is the disappearance of the CL shoulder centred at 150 °C in the laser-treated sample. The fresh paper P3 (a rosin-sized mechanical pulp paper, not exhibited here) shows a higher CL emission for the entire temperature interval of the measurement as a result of laser treatment. Artificial ageing reduces considerably the differences between the CL response of lasered and non-lasered areas of all three papers, especially of P2 and P3. These results suggest the generation of emitting species as a result of UV laser treatment, which react further into non-emitting products in the course of artificial ageing. The depletion of the emitting species decomposing between 130 °C and 170 °C in paper P2 by laser treatment seems to be reversed to some extent by artificial ageing.



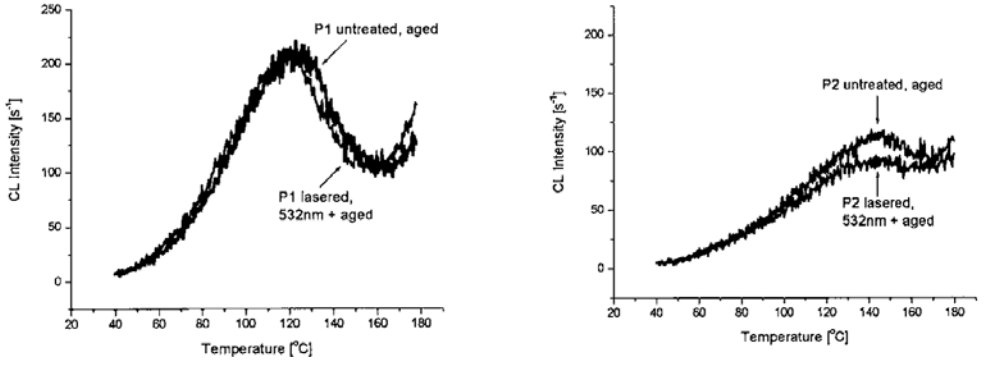
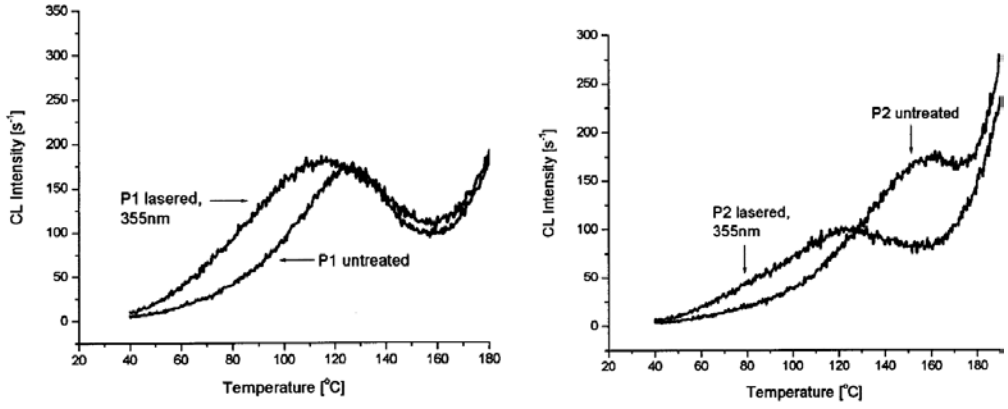


FIGURE 3 Chemiluminescence measurements (dynamic response in N_2); comparison of fresh P1 and P2 with post-aged P1 and P2 for the green laser at $\lambda = 532$ nm. Fluence $F = 0.83\,\mathrm{J/cm^2}$, pulse number $N = 3$. Artificial ageing 12 d at $T = 90\,^{\circ}\mathrm{C}$, 50% rel. humidity



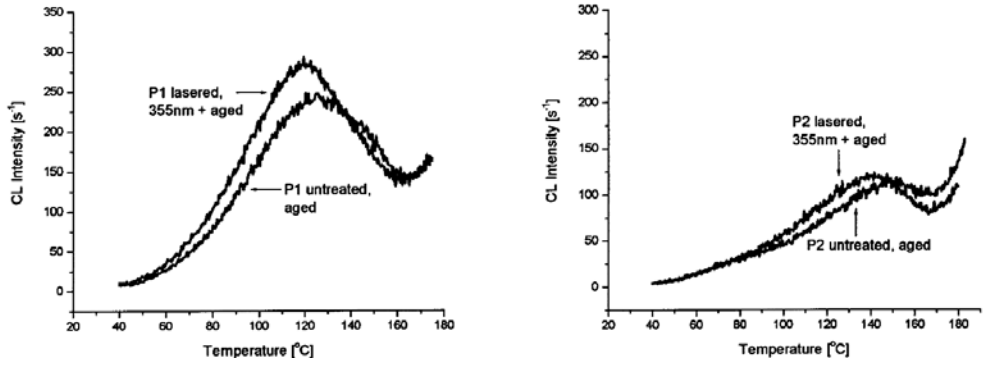


FIGURE 4 Chemiluminescence measurements (dynamic response in N_2); comparison of fresh P1 and P2 with post-aged P1 and P2 for the UV laser at $\lambda = 355$ nm. Fluence $F = 1.35\,\mathrm{J/cm^2}$, pulse number $N = 3$. Artificial ageing 12 d at $T = 80\,^{\circ}\mathrm{C}$, 65% rel. humidity

4 Conclusions

Colour changes after laser irradiation were more pronounced for pre-aged samples than for fresh ones (especially P2). This observation corresponds with the threshold fluence behaviour where normally the threshold of fresh paper F_{th}(fresh) is slightly higher than for the pre-aged samples F_{th}(aged).

The weight-average molecular mass of cellulose significantly decreases towards stronger laser interaction using an ultraviolet wavelength at $\lambda = 355$ nm. The effect is of the same order of magnitude as that of the artificial pre-ageing.

On the contrary, the results of the treatment with the green at $\lambda = 532$ nm and the infrared laser light at $\lambda = 1064$ nm is negligible, and only a slightly decrease of M_w towards higher fluences and pulse numbers is detectable, respectively.

The CL results are consistent with the results of M_w and colour measurements, i.e. no significant immediate or long-term alterations of the paper samples was promoted by laser treatment at $\lambda = 532$ nm below the ablation threshold fluence. On the other hand, immediate chemical alterations of the paper samples occur as a result of UV laser treatment. Cellulose is depolymerized, and new emitting species are formed, probably as a result of photosensitized (radical) degradation reactions induced by the UV radiation. Further reactions of these initial degradation products into coloured compounds may possibly yield significant discoloration of the test papers after artificial post-ageing.

The laser treatment with the second harmonic green light at $\lambda = 532$ nm below the ablation threshold fluence gave the most promising results on pure papers, with no discolouration and no other visible alteration, nor detectable chemical changes.

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