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IR pulsed laser light interaction with soiled cellulose and paper

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ABSTRACT Nd:YAG laser irradiation (1064 nm) of cellulose samples does not lead to immediate nor long-term effects on mechanical properties of paper, which renders the method increasingly interesting for cleaning of historical paper artefacts. However, the technique's usability is so far limited due to discoloration when the treated object's surface contains carbonaceous dirt. By using diffuse-reflectance Fourier-transform infrared spectroscopy, size-exclusion chromatography and viscometry it is demonstrated that the distinct yellowing is accompanied by formation of ether cross-links and dehydration of the cellulose, as well as its depolymerisation. Furthermore, the origin of the discoloration is discussed and it is proposed that yellow chromophores are formed due to carbon-cellulose interactions during laser irradiation.

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1 Introduction

Cleaning of artefacts by laser irradiation offers contactless removal of dirt and stains without the use of an eraser or a solvent. These characteristics make the method particularly appealing for conservation of historic documents.

In our previous work [1], immediate as well as long-term effects of pulsed lasers operating at three different wavelengths (308, 532 and 1064 nm) and fluences below 2.5 J cm^{-2} on cellulose were reported. A strong immediate cellulose-degradation effect after excimer-laser treatment at 308 nm was observed, while Nd:YAG processing at 532 nm resulted in no detectable chemical changes after the treatment, although long-term resistance appeared to be somewhat impaired. Surprisingly, laser irradiation at 1064 nm resulted in a slight increase of the degree of polymerisation (DP) and, during subsequent accelerated ageing, the DP of the irradiated cellulose decreased more slowly than the DP of the untreated control. The effect was ascribed to the formation of inter- and intramolecular ether bonds.

In the present work, the applicability of Nd:YAG processing at 1064 nm for cleaning of cellulose substrates is further examined. In particular, the effect that the laser irradiation

may have on mechanical properties of paper and on paper soiled with carbon particles as a chemically pure model "dirt" are described.

2 Experimental

The paper samples used were purified cotton linters cellulose (Whatman filter paper no. 1; 86.0 g m^{-2} , DP: 2630, relative standard deviation (RSD): 0.74%) and gelatine-sized rag paper from the year 1600 (70.0 g m^{-2} , DP: 891).

Charcoal powder (Riedel de Haen, p.a.) was applied by filtering aqueous suspensions of carbon through pulp sheets.

A Q-switched Nd:YAG laser at 1064 nm with a pulse duration of 6 ns was used for treating the samples. The output beam was of a uniform "top-hat" profile with a spot diameter of 8 mm and a fluence of 1 J cm^{-2} . The peak power at the maximum output energy is estimated to be about 125 MW. The maximum laser repetition rate is 20 Hz; however, for this evaluation the laser was operating in a single-shot regime.

Thermal treatment was performed in a Vötsch VC 0020 climatic chamber at 90°C and 65% relative humidity. Light ageing was performed for 3 h at 50°C in Heraeus Suntest CPS+ equipment, using a xenon light source with energy density 750 W m^{-2} .

Diffuse-reflectance Fourier-transform infrared (FTIR) (DRIFT) spectra were obtained with a Perkin-Elmer Spectrum 1000 spectrometer equipped with a DRIFT cell using KBr as background.

Viscometric determinations of the degree of polymerisation were performed according to the standard procedure [2], using fresh cupriethylenediamine solvent (Carlo Erba, Milano). DP was calculated from the intrinsic viscosity using the equation [3] $\text{DP}^{0.85} = 1.1 \times [\eta]$. Typical RSD was below 1%.

Size-exclusion chromatography was performed on a Hewlett Packard 1100 Series chromatographic system, equipped with a Rheodyne injector (sample volume $200 \mu\text{L}$), a column thermostat (column temperature 80°C) and a refractometric detector. The columns used were a PL Gel Mixed B column and a PL Gel Mixed C column (Polymer Laboratories, Church Stretton, UK). The cellulose samples were dissolved in 1% (w/v) LiCl in N,N-dimethylacetamide (Aldrich, for chromatography), using the usual solvent-exchange procedure. The concentration of the samples was 1 mg/mL in 1% (w/v) LiCl in N,N-dimethylacetamide.

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The columns were calibrated by using pululan standard (Fluka) sample solutions of the same concentration. Two such solutions were used, the first containing pululans with peak molecular weights 5800 g/mol, 24 000 g/mol, 100 000 g/mol, 1 600 000 g/mol and the second containing 728 g/mol, 12 000 g/mol, 48 000 g/mol, 380 000 g/mol. The eluent was 1% (w/v) LiCl in N,N-dimethylacetamide, flow rate 0.5 mL/min.

Colorimetric measurements of solid samples were performed with a Minolta CM-3610d diffuse-reflectance UV-VIS spectrophotometer with the specular component excluded. The reflectance was measured in percent relative to a polymeric Minolta standard. Typical RSD was below 0.7%.

3 Results and discussion

Ideally, the laser light interacts with highly absorbing carbon or dirt particles, while no chemical changes in the less-absorbing substrate occur during the irradiation. Although the treatment of pure cellulose with a Nd:YAG laser at 1064 nm did not result in discoloration of the treated surface, the chemical changes (as determined by viscometry, chromatography and FTIR spectroscopy) suggested that the energy absorbed during the treatment partly leads to the formation of inter- and intramolecular ether bonds [1]. Nevertheless, the extent of chemical alterations associated with the exposure of a non-soiled sample to a high-intensity beam is limited, and it is very likely that the treatment would not impair mechanical properties of the fibres. To verify the hypothesis, two tests of mechanical properties were performed on the treated models.

Formation of cross-links should be most evident in the change in wet tensile strength, as it had been demonstrated that cross-links function as swelling restraints to the network, so that a larger fraction of the pre-existing hydrogen bonds continue to increase the tensile modulus of paper [4]. In addition, a folding-endurance test was used, as the ability to resist repeated folding is considered one of the most important quality criteria for paper [5]. As demonstrated in Table 1, the treatment did not alter any of the mechanical properties of paper to a measurable extent.

As no immediate nor long-term effects of the laser irradiation running at 1064 nm on mechanical properties of cellulose were observed, an attempt was made to evaluate its effect on artificially soiled cellulose sheets and rag paper containing carbon particles. Recent results demonstrated [6] that yellowing may occur upon irradiation of laboratory-dust-soiled

	before ageing		6 days of ageing	
	control	laser treated	control	laser treated
wet tensile strength (ISO 1924)	2.14 ± 0.10	2.05 ± 0.10	–	–
folding endurance (ISO 5626)	1.58 ± 0.65	1.66 ± 0.63	1.11 ± 0.18	1.08 ± 0.39

TABLE 1 Changes in physical properties of laser treated and control samples before and after ageing

paper with a Nd:YAG laser running at 532 nm. Due to the ill-defined composition of the dust, the effect may be ascribed to a variety of sources, such as formation of chromophores on cellulose, redeposition of metals present in the dust or discoloration of its organic impurities. Although, due to their strong absorbing properties, carbon-black particles may be considered a rather severe model for natural dirt, it is used in the present research in order to avoid possible changes of paper colour after irradiation, originating from unknown components found in natural soiling and, on the other hand, to maximise the effect that a light-absorbing particle may exert on cellulose.

To evaluate colour changes, which may result from a laser treatment, the CIELab colour system was used. In this colour space, developed by CIE (Commission Internationale de l'Eclairage) in 1964, colour is expressed in three coordinates. Hue and chroma are defined by the coordinates a^* (red-green) and b^* (yellow-blue), while brightness is expressed by L^* values.

As demonstrated in Fig. 1, addition of carbon lowered the L^* value, while it had no marked effect on b^* values in the $L^*a^*b^*$ colour space. Laser irradiation of unsoiled cellulose did not result in a discoloration of the sample; however, even a minute amount of added carbon particles resulted in a strong increase in b^* , denoting formation of yellow chromophores.

Due to the absence of transition metals and non-cellulosic organic material in purified cellulose and analytical grade carbon, the observed discoloration may be ascribed to degradation of cellulose, brought about by heat transfer from carbon particles to cellulose. Although the formation of chromophores suggests that cellulose degradation takes place, laser treatments result in a minor decrease of DP only (up to 2.3%, Fig. 2).

Additional information is gained by determinations of molecular weight of laser-treated samples with a deposit of carbon using size-exclusion chromatography (Fig. 3). The number of molecules of higher molecular weight increases depending on the density of the carbon deposit on the sample prior to the laser treatment. At the same time the proportion of low-molecular-weight material decreases. This indicates that while degradation into soluble degradation prod-

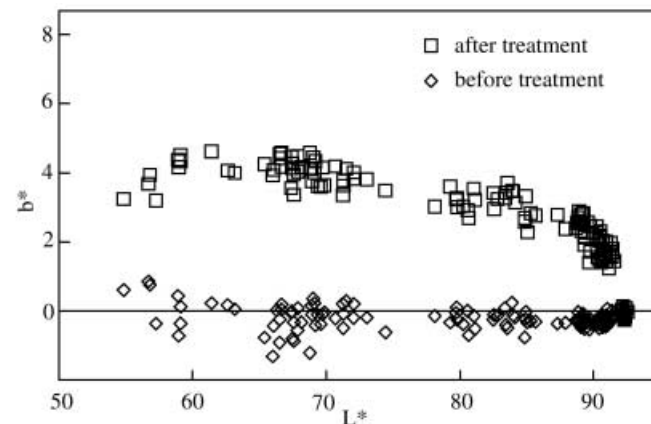


FIGURE 1 Change of b^* between control and carbon-containing paper before and after laser irradiation vs. L^* of control sample with carbon before irradiation

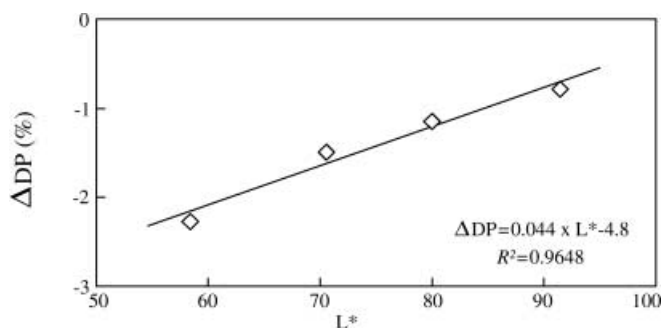


FIGURE 2 Decrease of DP of carbon-soiled samples after laser irradiation vs. L^* before irradiation

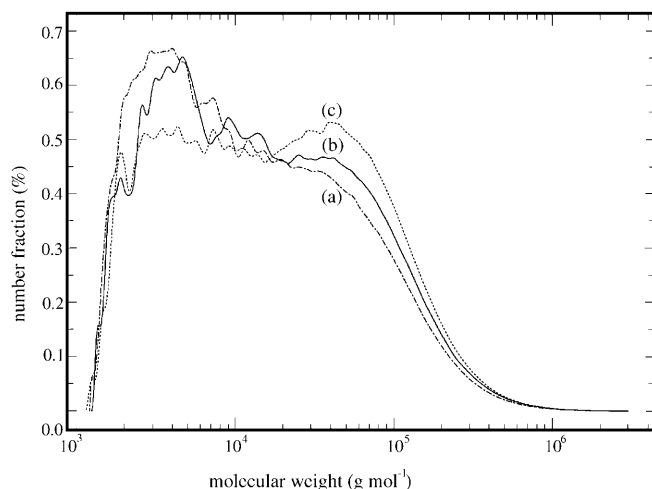


FIGURE 3 Number distributions of molecular weight of three rag-paper samples: (a)–untreated: $L^* = 86$ (M_W 215 000 g/mol, M_N 44 100 g/mol), (b)–treated, light carbon deposit: $L^* = 66$ (M_W 225 000 g/mol, M_N 40 000 g/mol), (c)–treated, heavy carbon deposit: $L^* = 57$ (M_W 225 000 g/mol, M_N 35 500 g/mol)

ucts during laser irradiation may take place, intramolecular covalent bonding also leads to cross linking, resulting in an increased number of molecules of higher molecular weight, which explains the small differences in DP, as determined viscometrically.

This anomalous behaviour may be attributed to the formation of covalent intermolecular bonds, i.e. cross-links. Dehydration reactions, leading to the formation of predominantly ether bonds, have been known to occur during thermal treatment of cellulose [7]. The formation of C–O–C ether bonds as a result of the laser treatments of soiled samples is evident from pronounced absorption bands in diffuse-reflectance FTIR difference spectra (Fig. 4): 986 cm^{-1} (C–O stretching), 1028, 1057 cm^{-1} (C–O stretching), 1109 cm^{-1} (ring asymmetric stretching) and 1157 cm^{-1} (C–O–C asymmetric stretching). The surface also becomes more hydrophobic, as the adsorbed water absorption band (1640 cm^{-1}) is negative relative to the untreated, unsoiled control. The absorption bands are more pronounced if more carbon has been deposited on the samples and if multiple successive laser treatments are applied. However, although the results of the viscometric, size-exclusion chromatography (SEC) and FTIR analysis demonstrate that photothermal decomposition of cellulose takes place during the laser treatment of the soiled paper, the chemical nature of chromophores could not be

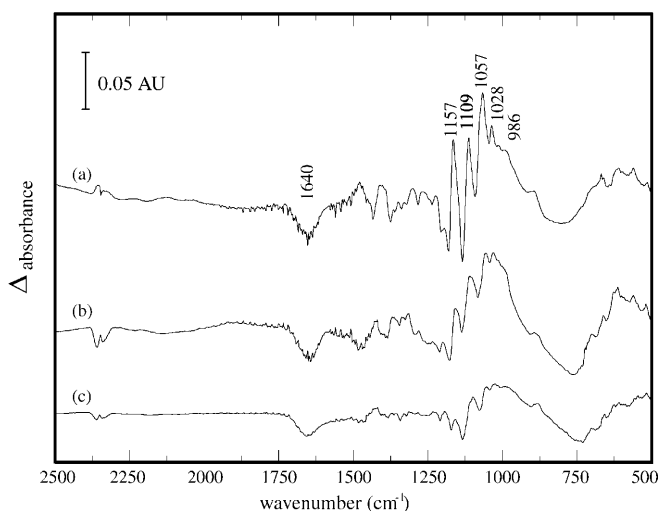


FIGURE 4 Diffuse-reflectance FTIR difference spectra (reference: untreated and unsoiled Whatman filter paper sample) of: (a)–sample with a heavy deposit of carbon ($L^* = 58$); (b)–sample with a medium deposit of carbon ($L^* = 66$); (c)–sample with a light deposit of carbon ($L^* = 91$). Sample (a) treated with laser twice, samples (b) and (c) once

identified. Yellow discoloration of cellulose is typically ascribed to the formation of double bonds, which may be formed as a result of high temperature and the reductive atmosphere accompanying the laser treatment [8]. Unfortunately, the typical IR absorption of carbon–carbon double bonds, if present, is masked by the broad band of bonded water, at 1640 cm^{-1} [9].

In order to identify possible low molecular weight degradation products, the samples were extracted in methanol and analysed using gas chromatography coupled to a mass spectrometer. No peaks could be assigned to coloured cellulose degradation products. It is possible that the chemical species are either non-volatile or non-soluble (macromolecular chromophores) or in a concentration range too low to be detected by the method. However, as the extraction in methanol led to disappearance of the yellow colour, it is also possible that the solvent reacted with double bonds (e.g. addition of alcohols to alkenes).

Double bonds could also be oxidised (and discoloured) into non-coloured products. This proved to be so when the laser-irradiated samples were treated with a concentrated solution of Br_2 in water or with a solution of NaClO_2 (0.1 mol/L in water, pH adjusted to 5 with an addition of 0.1 mol/L HCl solution). After oxidation with NaClO_2 , the reducing carbonyl groups (R–CHO) in cellulose are oxidised into carboxyl groups (R–COONa), which can be detected in the DRIFT spectra at 1600 cm^{-1} . In fact, the more the sample was soiled with carbon, the fewer carbonyl groups were present after the treatment. The evaporation of black carbon particles, heated by the absorption of laser light, could therefore be associated with the formation of a reductive environment.

Chromophores may also be oxidised by singlet oxygen, produced during illumination of samples with daylight or a Xe lamp. As demonstrated in Fig. 5, yellow-colour formation during laser irradiation of soiled samples may be at least partly reversed by the irradiation of the samples with a Xe lamp at 50 °C (Fig. 5).

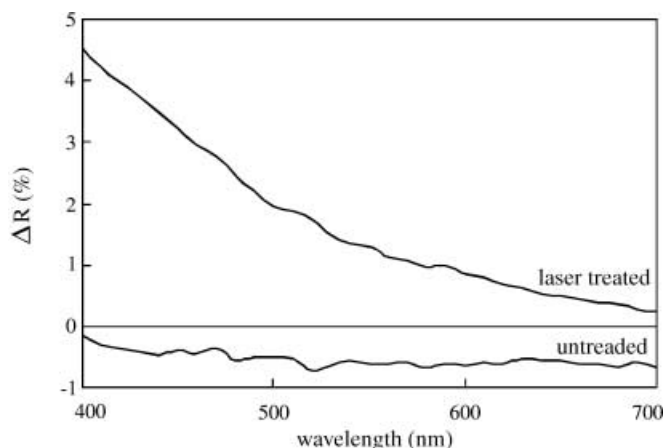


FIGURE 5 Diffuse-reflectance difference spectra after 3 h of light ageing at 750 Wm^{-2} and 50°C for untreated and laser-irradiated soiled samples relative to the spectra prior to light ageing

These results have important implications for the technique of laser cleaning of paper, as they suggest that the immediate discoloration which is brought about by treatment may be minimised, for example by application of another laser which would induce oxidation of the previously cleaned surface.

The absence of oxidised functional groups (which would lead to a positive absorption band at $1710\text{--}1750 \text{ cm}^{-1}$ in the FTIR spectrum) after a treatment with 1064 nm laser light (in contrast with a UV laser treatment [1]), the colour reversion after exposure to a Xe lamp, the formation of cross-links determined by SEC and the already discussed hydrophobic properties of the surface after treatment are indications that support the energy-transfer hypothesis. Such energy transfer is not an unknown phenomenon and is extensively used in matrix-assisted laser desorption mass spectrometry.

4 Conclusions

Measurements of wet tensile strength and folding endurance demonstrate that Nd:YAG laser irradiation of pure cellulose samples does not lead to immediate nor long-term effects on the mechanical properties of paper. Nevertheless, the usability of the method for cleaning historical paper artefacts is so far limited due to discoloration of paper when impurities are present on the treated object's surface. The distinct formation of yellow chromophores is accompanied by photothermal decomposition of cellulose, demonstrated by the formation of ether cross-links and dehydration of the cellulose, as well as scission of glycosidic bonds. Nevertheless, the results of light ageing suggest that the discoloration may be at least partly reversed. The formation of colour chromophores during laser irradiation may be further minimised by modifying the cleaning conditions. This research work is in progress.

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