Laser cleaning of silk: a first evaluation

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Abstract

The effect of laser treatment on undyed, unweighted silk was studied. Three different silk fabrics (new clean, new soiled (carbon dust), and naturally aged) were treated with a computer-controlled Q-switched Nd:YAG laser at 532 nm in 30 combinations of fluence and pulse numbers. Visual evaluation, colourimetry, viscometry and polarized Fourier transform spectroscopy (pol-FTIR) were used to examine changes in surface appearance, light absorption, degree of polymerization and orientation order of the crystals. Although physical changes only occurred above the tested parameters, chemical changes could be detected as low as 0.1 J/cm^2 at one pulse. Yellowing was observed at low, and bleaching at higher, fluence/pulse number combinations. Different chemical processes leading to chain scission and to cross linking seem to occur simultaneously. The results of this study suggest that laser cleaning, even at low fluence and pulse number, might induce radical chain reactions in undyed, unweighted silk.

Keywords

silk, Nd:YAG laser, cleaning, colourimetry, viscometry, pol-FTIR, yellowing

Introduction

Removing surface soiling from textiles remains a difficult task in textile conservation. Conventional methods include the use of vacuum cleaning, various erasing materials as well as water or solvent based cleaning techniques. The result often remains unsatisfying, as the soil, owing to its small particle size, is strongly bound to the textile surface. The cleaning methods used may also cause surface alterations and/or dimensional changes within the textile. Since the 1970s, laser treatment has increasingly been introduced into the field of conservation for surface cleaning. Meanwhile, laser equipment is encountered rather frequently in conservation laboratories. The temptation to 'just try' its effect on different types of object without thorough previous research into the interaction between laser and the specific material is documented by a growing body of case studies. For the present research, silk was chosen as a material because of a specific conservation project for which laser treatment had to be evaluated, and because silk represents one of the most fragile textile materials.

Whereas there is a growing body of research in the field of laser cleaning of inorganic materials and paintings, there is very little for organic materials. Within organic materials, the focus of laser cleaning research lies primarily on cellulose (mainly on paper), and more recently on parchment. As far as silk textiles are concerned, there are only a very few scientific papers published (Strlic et al. 2003, Garside and Wyeth 2002, Kelly et al. 1990), as well as a few case studies (Reichert 1998, Polonovski and Oger 1994). Publications dealing with featherwork (Dignard et al. 2003, Solajic et al. 2002) may be consulted as well.

Yellowing as a result of laser cleaning has been reported by all the above-mentioned authors when using laser at 1064 nm, but only by some for 532 nm. Although laser in the UV region has been reported to cause a decrease of degree of polymerization (DP) (Kolar et al. 2000) caused by direct chain scission within the fibroin chain, and laser in the infrared (IR) at 1064 nm has been reported to cause cross linking in cellulose, increasing the DP (Kolar et al. 2003), some authors found the range of 532 nm very promising even though changes in DP been reported for soiled, but not for unsoiled, samples (Kolar et al. 2003). Therefore the laser wavelength was chosen at 532 nm, and the inclusion of soiled samples seemed important.

Methods

Sample preparation

Three different silk fabrics were chosen for testing: new, undyed, unweighted silk (tabby crepe, 60 × 40 threads per centimetre), the same silk but mechanically soiled with carbon dust, and a naturally aged silk (tabby 55 × 42 threads per centimetre) of unknown provenance, unweighted but slightly yellowed; this fabric appeared to be in good condition. All three silks were treated with a Nd:YAG laser at a wavelegth of 532 nm and with 30 combinations of fluence and pulse rates: 0.025, 0.05, 0.1, 0.2, 0.3, 0.5, 1.0, 1.5 and 4.2 J/cm^2 with 1, 4, 16 and 64 pulses. The laser treatment was performed on 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 9 ns, a repetition rate of 500 Hz, and a maximum energy of 2.5 mJ. The set-up consisted of a scanning optical system (410 mm focal length) which delivered a spot diameter of 240.5 μm and maximum fluences in the range of up to F (532 nm) = 4.5 J/cm^2. An integrated exhaust system served to remove volatile debris. The computerized system allowed for maximal repeatability; the overlap of the gaussian beam distribution was chosen to produce an absolutely even distribution of fluence over the whole sample surface. The wavelength was chosen at 532 nm because the silk fabrics only absorb around 2 per cent at this wavelength.[1]

Visual examination

Visual examination under daylight, ultraviolet (UV) and UV-fluorescence in the integrated observation station of the prototype laser station was as described by Kautek et al. (2003).

Microscopic examination: physical damage threshold

Many publications on laser cleaning of art works refer to a 'safety window' for cleaning, in which a cleaning effect can be achieved without causing (physical) damage. Therefore, the samples were examined by means of binocular, transmitted light and black-field microscopy to detect visible physical damage.

Colourimetry

As yellowing indicates chemical changes in a substrate, colourimetry was performed for each area before and after laser treatment. Using standard daylight D65, the measuring geometry was d8 at an angle of 2°, specular component excluded (SCE). The CIELAB system was used. The mean values and standard deviation for the five measurements taken were calculated for a level of confidence of ±1.96 standard deviations (sd) at 95 per cent. Statistical significance was verified by Student's T-test calculation. The data have been plotted to include error bars, which, however, are too small to show behind the symbols.

Successful and safe removal of black carbon should be measurable as an increase in lightness ΔL^* without simultaneous increase in yellowness Δb^* or of chroma indicated by ΔC^*.[2] An increase of ΔC^* reflects an increase of polar functional groups (for example –OH, $-HN_2$) adjacent to delocalized, conjugated systems, or an increase in possible mesomeric structures of a polymer (Rys and Zollinger 1982). As silk increases in $-NH_2$ and –COOH groups during ageing due to chain scission (Robson 1985, Hersh et al. 1989), the value for ΔC^* could indicate such changes caused by laser treatment. An increase of Δh^* (change of hue angle),[3] on the other hand, is interpreted to indicate increasingly conjugated systems (Rys and Zollinger 1982). Such systems are formed in silk when tyrosin, the most susceptible protein in silk constituting 90 per cent of the amorphous regions of silk fibroin, cross links to form chromophore structures believed to be similar to quinones and to melanin (Robson 1985, Timar-Balaszy and Eastop 1998).

Viscometry

Possible changes in length of polymer chains were therefore studied by viscometry. Silk (50–85 mg) (depending on DP) was dissolved in 8 mL of 10 mol/L^{-1} aqueous solution of LiSCN as suggested by Tse and Dupont (2000). The suspension was stirred for 1 h, then left overnight. To the clear solution, 4 mL of water was added, thus obtaining 12 mL of silk solution, 6.67 mol/L^{-1} LiSCN. The solution was centrifuged for 10 min at 3000 rpm, the clear solution was then used for analysis ('stock solution'). The viscosity of the stock solution was determined, after which 6 ml of it was diluted with 3 mL of 6.67 mol/L^{-1} LiSCN, and a further 3 mL of the stock solution was diluted with 6 mL of 6.67 mol/L^{-1} LiSCN. Viscosities of all these solutions as well as of LiSCN were determined with a Unitex-type (Effe-ci, Italy) viscometer at 25 °C. DP was calculated relative to an area of the same fabric not treated with laser.

FTIR and pol-FTIR

Garside and Wyeth (2002) have demonstrated that silk shows no marked increase of overall crystallinity during ageing, but a change in the degree of orientation of the crystals. As silk fibroin is a highly oriented polymer, most double bonds are oriented perpendicularly to the fibre axes. Upon ageing, the amorphous regions of fibroin are disturbed which causes the crystals to tilt slightly out of their orientation. The degree of orientation is defined as:

$$\textit{degree of orientation}\ \Omega = \frac{X_{90}}{X_0} = \frac{I_{90}\dfrac{1615}{1655}}{I_0\dfrac{1615}{1655}}$$

where X = crystallinity index, I = intensity at the respective peaks, for polarizer position parallel (0°) and 90° to fibre axis.

With pol-FTIR, the polarizer parallel to the fibre axis (0°) will show C=O stretch vibrations in the amorphous regions, the polarizer perpendicular to the fibre axis (90°) will show the combined C=O stretch vibrations of the amorphous and of the aligned crystals in the crystalline regions.

FTIR analysis was performed on a Perkin Elmer Series 2000 FTIR from 4000–580 cm^{-1} with 16 scans, resolution of 4, at an interval of 1 cm^{-1}. The fibres were aligned as well as possible on a diamond cell and flattened with a steel roller. They were placed perpendicularly into the FTIR beam. Five spectra were taken for each of the fibres without polarizer and with the polarizer in each of the directions. The polarizer was placed into the FTIR beam between the fibre and the detection cell. It was equipped with a graded wheel to facilitate precise alignment of the filter. There are two sources of possible inaccuracy: the fibres were slightly crimped as they were removed from a fabric; care was taken to choose straight areas for measurements. The polarizer was fixed only by a clamp system; there was no slot to accommodate a polarizer in the FTIR used. The original data was smoothed (interactive 22) with the program 'Spectrum Lite' by Perkin Elmer. The peak height was measured at 1655 and 1615 cm^{-1} from a baseline drawn between 1725 and 880 cm^{-1}. The mean values and standard deviation for the five measurements were calculated for a level of confidence of ±1.96 sd at 95 per cent and Student's *T*-test was performed for significance. The data were plotted with RtPlot(R) to include error bars.

Results and discussion

Visual examination showed no alteration of the new, unsoiled silk after laser treatment. The two other silks, however, showed visible changes increasing with the amount of energy and the number of pulses used during laser treatment. The naturally aged, slightly yellowed silk exhibited bleaching after laser treatment.

The artificially soiled sample indicated that successful removal of carbon dust is possible above 0.2 J/cm^2; however, there was yellowing at lower and bleaching at higher exposures. These changes occurred throughout the thickness of the silk fabric and were visible on the reverse as well (Figure 1).

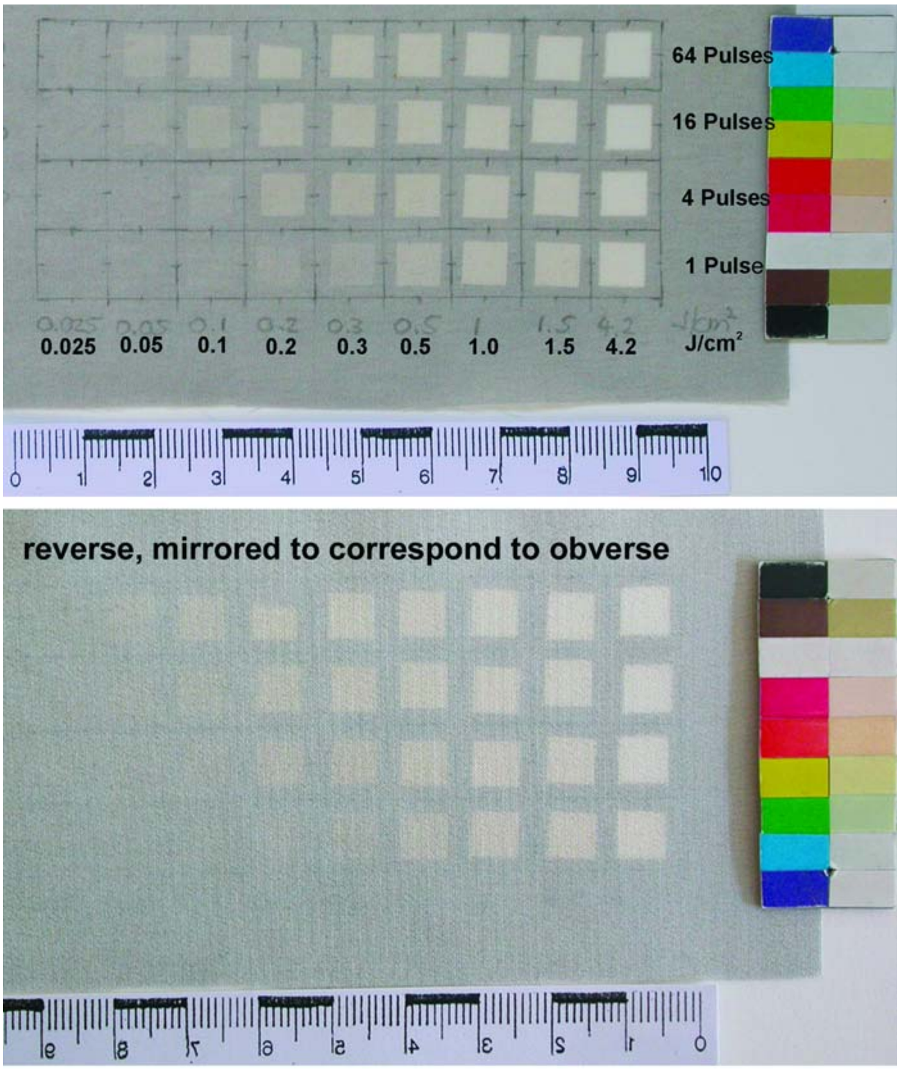

Figure 1. New silk soiled with carbon dust after laser cleaning. Above: obverse; below: reverse (mirrored for easier comparison). Removal of carbon as well as yellowing/bleaching of the silk is visible throughout the fabric thickness and does not only affect a surface layer. (photo: Karin von Lerber)

Microscopic examination showed physical changes such as disruption of parallel fibre orientation, vertical cracks, and bubbles on loose fibrils only for very high fluences (3.2 J/cm^2 and above) and only for very high pulse numbers (100 and above), additional samples prepared in search of the physical threshold limit. It has to be emphasized that the naturally aged silk was the only sample where one of the parameter combinations chosen for this research (4.2 J/cm^2 and 64 pulses) showed melting bubbles and a tiny hole in one out of two test areas. For the other two silks, physical damage could only be observed far beyond the test parameters.

Garside and Wyeth (2002) observed dehydration of fibroin below 100 °C. Above 210 °C slip motion between the β-sheets in the crystalline regions of silk and above 250 °C melting within the crystalline β-pleated sheet structure have been reported (Nagura and Ishikawa 1983).

According to theoretical calculations,[4] the heat absorbed by the carbon and transferred into the silk might be high enough to actually cause severe damage or even melting of the silk even at fluences as low as 0.2 J/cm^2, where slightly below 200 °C seem to be reached at the silk–carbon interface.

Colourimetric measurements show an increase in ΔC^* and Δh^* after laser irradiation even at low fluences, the differences being the most pronounced for soiled silk, the least for new silk (Figures 2 and 3).

Plotting the values for Δ*C** (increase of polar groups) against Δ*h** (increase of conjugated systems), as seen in Figure 4, shows that low fluences seem to produce proportionally more change in Δ*C**, and high fluences more change in Δ*h**. Changes in new silk are minor, and at low fluence levels they are confusing compared with the two other silks. Carbon dust seems to enhance the chemical reaction producing polar groups. Between 0.5 and 1 J/cm^2 there appears to be a peak value for the proportion of Δ*C** compared with Δ*h** for naturally aged and new, artificially soiled silk.

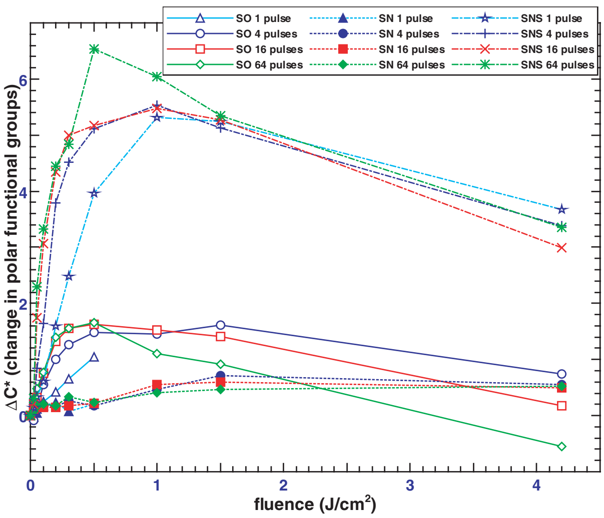

Figure 2. ΔC, indicating change in polar functional groups plotted against fluence of the laser treatment for new silk (SN), new silk soiled with carbon dust (SNS) and old silk (SO) at various laser pulses. A comparison of the plots for new silk (SN) and new soiled silk (SNS) indicates that the carbon dust significantly influences the degree of change induced by laser as of very low fluence. Clean old silk (SO) seems to be more vulnerable than the clean new silk (SN)*

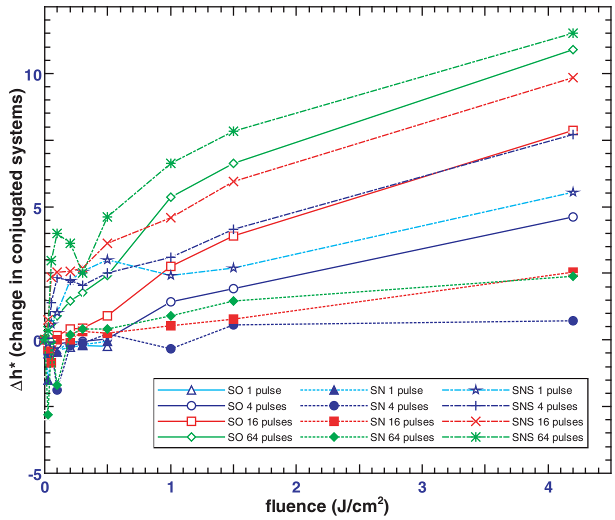

Figure 3. Δh, indicating change in conjugated systems, plotted against fluence of the laser treatment for new silk (SN), new silk soiled with carbon dust (SNS) and old silk (SO) at various laser pulses. Whereas the plots show an irregularity around 0.5 J/cm^2, at a level above this there seems to be an almost linear increase in Δh* with increasing fluence. Again new silk is the least susceptible. Old silk (SO), however, seems to change similar to new soiled silk (SNS), the difference decreasing with increasing pulse numbers*

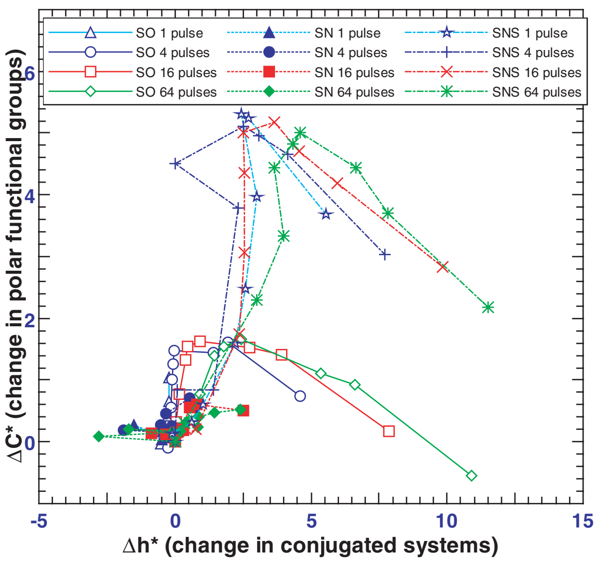

Figure 4. Changes in ΔC plotted against changes in Δh*. Plotted lines connect the different fluences at a respective pulse number. The symbols on the lines stand for fluences of 0.025, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 1.5 and 4.2 J/cm^2 (from left to right). Low fluences cause a large increase in ΔC* compared with Δh* , whereas at increasing fluence, the increase of Δh* surpasses the change in ΔC* significantly. At 0.5 J/cm^2 (fourth symbol from right) there seems to be a turning point in the ratio of ΔC* and Δh**

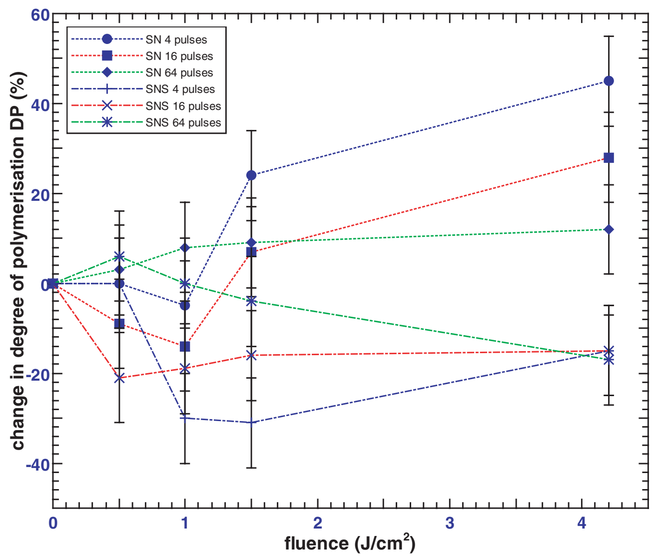

Figure 5. Change in degree of polymerization (DP) plotted against fluence of the laser treatment for new silk (SN) and new silk soiled with carbon dust (SNS) at various laser pulses. Although the standard deviation is rather large, there seems to be the general tendency for new silk to increase in DP and for new soiled silk to decrease in DP with increasing fluence, suggesting a predominance of cross linking for new clean silk (SN) and a predominance of chain scissioning for new soiled silk (SNS)

Table 1. Colourimetry results for naturally aged silk (SO). All values are the mean of five measurements. Where Student's T-test showed no significant Δ values, the plot crosses the axes. Student's T-test values above 2.306 indicate significant differences

Sample	Sample no.	Fluence (J/cm^2)	Pulse no.	L*0	L*t	ΔL*	sd ΔL*	Student T ΔL*	a*0	a* t	Δa*	sd Δa*	Student T Δa*	b* 0	b* t	Δb*	sd Δb*	Student T Δb*	sd ΔC*	Student T ΔC*	Δh*	sd Δh*	Student T Δh*
Silk old (SO)																							
Sa_4	0.025	1	84.47	84.65	0.19	0.02	17.32	1.1	1.3	0.2	0.01	36.83	21.73	21.69	−0.04	0.02	2.64	−0.03	0.02	1.9	−0.52	0.02	41.17
	0.025	4	84.82	84.91	0.08	0.04	3.49	1.21	1.31	0.1	0.01	12.42	21.98	21.89	−0.09	0.04	3.75	−0.09	0.04	3.45	−0.27	0.03	15.6
	0.025	16	84.16	84.47	0.31	0.01	55.81	1.19	1.32	0.13	0.00	50.99	22.18	22.36	0.18	0.02	13.99	0.18	0.02	14.57	−0.3	0.01	44.84
	0.025	64	84.37	84.7	0.32	0.01	43.54	1.17	1.2	0.03	0.00	9.12	21.83	21.93	0.1	0.02	8.74	0.1	0.02	8.89	−0.06	0.01	7.02
	0.05	1	84.55	84.83	0.29	0.01	31.74	1.1	1.25	0.15	0.01	21.07	21.74	21.85	0.11	0.02	7.45	0.12	0.02	7.94	−0.38	0.03	20.76
	0.05	4	84.65	85.08	0.43	0.02	27.78	1.19	1.26	0.07	0.01	7.7	21.76	21.9	0.14	0.01	15.33	0.14	0.01	16.18	−0.16	0.04	6.59
	0.05	16	84.56	85.18	0.63	0.04	26.00	1.17	1.17	0.00	0.03	0.01	21.83	22.15	0.32	0.03	15.61	0.32	0.03	15.05	0.04	0.06	1.14
	0.05	64	84.39	85.46	1.08	0.03	53.83	1.17	0.95	−0.21	0.01	40.98	22	22.5	0.49	0.02	37.92	0.48	0.02	36.86	0.61	0.02	47.34
	0.1	1	84.52	85.04	0.52	0.04	19.06	0.8	0.96	0.16	0.01	33.27	21.65	21.89	0.25	0.05	8.42	0.25	0.05	8.59	−0.39	0.02	38.15
	0.1	4	84.27	85.11	0.84	0.01	89.01	0.93	1.01	0.09	0.00	32.45	21.63	22.17	0.54	0.05	16.74	0.55	0.05	16.85	−0.16	0.01	23.22
	0.1	16	84.3	85.55	0.12	0.01	166.5	0.97	0.93	−0.03	0.01	7.67	21.71	22.48	0.76	0.02	69.36	0.76	0.02	69.53	0.17	0.02	15.21
	0.1	64	84.05	85.64	1.59	0.04	67.23	0.99	0.66	−0.32	0.01	65.69	21.7	22.47	0.78	0.02	56.57	0.77	0.02	55.62	0.91	0.02	71.93
	0.2	1	84.38	85.18	0.81	0.02	59.54	1.07	1.19	0.13	0.01	28.55	21.95	22.38	0.43	0.02	28.02	0.43	0.02	28.62	−0.27	0.02	22.06
	0.2	4	84.22	85.61	1.4	0.02	140.14	1.19	1.28	0.09	0.01	12.21	22.26	23.26	1	0.01	37.14	1	0.04	36.89	−0.09	0.02	5.67
	0.2	16	83.49	58.51	2.02	0.1	32.71	1.28	1.19	−0.09	0.03	4.97	22.2	23.52	1.32	0.06	35.53	1.32	0.06	32.68	0.4	0.06	9.98
	0.2	64	83.67	86.08	2.41	0.03	122.66	1.24	0.71	−0.52	0.02	52.32	22.25	23.66	1.41	0.04	63.37	1.39	0.04	61.3	1.45	0.04	62.76
	0.3	1	84.14	85.16	1.02	0.04	36.03	1.05	1.16	0.11	0.01	22.41	21.73	22.37	0.64	0.03	34.08	0.65	0.03	34.31	−0.21	0.02	15.99
	0.3	4	84.4	85.81	1.42	0.04	56.88	1.13	1.22	0.09	0.00	32.3	21.63	22.89	1.26	0.03	62.5	1.26	0.03	63.04	−0.06	0.01	6.64
	0.3	16	84.1	86.16	2.06	0.01	516.25	1.1	0.99	−0.1	0.00	43.27	21.62	23.17	1.56	0.02	137.89	1.55	0.02	137.7	0.45	0.01	68.19
	0.3	64	83.86	86.44	2.58	0.02	182.12	1.22	0.57	−0.65	0.01	85.94	22.17	23.75	1.58	0.01	183.73	1.55	0.01	180.94	1.78	0.03	96.35
	0.5	1	83.6	84.99	1.39	0.06	34.28	1.24	1.39	0.15	0.01	30.96	22.13	23.16	1.03	0.03	54.95	1.04	0.03	55.01	−0.23	0.02	21.17
	0.5	4	83.5	85.63	2.12	0.04	82.81	1.36	1.44	0.08	0.02	5.61	22.54	24.02	1.48	0.05	51.1	1.48	0.05	50	0.03	0.05	0.98
	0.5	16	83.86	86.42	2.57	0.09	47.71	1.07	0.78	−0.29	0.01	66.37	21.79	23.44	1.65	0.02	131.77	1.63	0.02	131.09	0.91	0.02	79.66
	0.5	64	84.38	87.36	2.98	0.04	114.63	1	0.08	−0.92	0.01	180.25	21.97	23.65	1.68	0.02	158.56	1.66	0.02	157.67	2.42	0.02	183.7
Sa_Bam	1	4	84.36	87.64	3.28	0.04	135.08	0.88	0.39	−0.49	0.02	50.66	20.97	22.44	1.47	0.03	90.37	1.45	0.03	88.62	1.42	0.04	57.67
	1	16	84.29	88.13	3.84	0.05	128.5	0.82	−0.18	−1	0.01	206.88	20.5	22.04	1.54	0.05	45.71	1.52	0.05	45.23	2.75	0.02	217.93
	1	64	84.29	88.68	4.39	0.03	254.9	0.84	−1.17	−2	0.02	199.25	20.75	21.85	1.1	0.02	71.84	1.11	0.02	72.61	5.37	0.04	198.7
	1.5	4	83.88	87.68	3.8	0.01	469.4	1.13	0.43	−0.69	0.01	194.7	21.46	23.09	1.63	0.01	190.86	1.61	0.01	185.07	1.93	0.01	223.82
	1.5	16	83.96	88.16	4.2	0.03	242.29	1.12	−0.35	−1.47	0.01	229.59	21.1	22.53	1.43	0.02	91.94	1.41	0.02	89.1	3.92	0.02	249.08
	1.5	64	83.75	88.7	4.95	0.03	241.53	1.1	−1.4	−2.5	0.01	306.97	21.16	22.06	0.9	0.03	53.28	0.92	0.03	54.26	6.61	0.03	304.4
	4.2	4	84.29	88.84	4.55	0.03	258.33	1	−0.73	−1.72	0.01	190.49	21.06	21.81	0.75	0.04	28.89	0.74	0.04	28.58	4.62	0.04	186.36
	4.2	16	83.8	89.49	5.7	0.02	403.48	1.08	−1.81	−2.89	0.01	407.35	20.93	21.05	0.12	0.05	4.05	0.17	0.05	5.78	7.87	0.03	362.53
	4.2	64	83.65	90.09	6.44	0.03	387.19	1.13	−2.79	−3.92	0.01	915.12	21.06	20.35	−0.71	0.03	39.83	−0.55	0.03	31.22	10.89	0.02	785.43

Table 2. Colourimetry results for new silk (SN). All values are the mean of five measurements. Where Student's T-test showed no significant Δ values, the plot crosses the axes. Student's T-test values above 2.306 indicate significant differences

Sample	Sample no.	Fluence (J/cm^2)	Pulse no.	L*0	L*t	ΔL*	sd ΔL*	Student T ΔL*	a*0	a* t	Δa*	sd Δa*	Student T Δa*	b* 0	b* t	Δb*	sd Δb*	Student T Δb*	sd ΔC*	Student T ΔC*	Δh*	sd Δh*	Student T Δh*
Silk new																							
(SN)Sn_4	0.025	1	93.73	93.28	−0.45	0.02	42.3	−0.3	−0.16	0.13	0.01	33.55	5.38	5.67	0.29	0.01	50.19	0.28	20.01	48.71	−1.52	0.07	36.85
	0.025	4	93.55	93.47	−0.08	0.04	2.96	−0.32	−0.28	0.04	0	23.7	5.5	5.78	0.28	0.01	50.76	0.28	0.01	50.2	−0.53	0.02	33.99
	0.025	16	93.76	93.51	−0.25	0.01	50.36	−0.32	−0.3	0.03	0	11.11	5.56	5.68	0.12	0.01	35.93	0.12	0.01	35.3	−0.33	0.04	14.11
	0.025	64	93.51	93.09	−0.41	0.01	68.31	−0.31	−0.04	0.27	0.01	51.2	5.55	5.64	0.09	0.01	18.63	0.08	0.01	16.86	−2.81	0.09	52.14
	0.05	1	93.57	93.54	−0.03	0.01	4.6	−0.3	−0.26	0.04	0	21.34	5.57	5.61	0.04	0.02	4.22	0.04	0.02	3.98	−0.47	0.03	25.27
	0.05	4	93.57	93.47	−0.1	0.01	20.56	−0.3	−0.29	0.01	0	8.02	5.57	5.75	0.18	0.02	17.6	0.18	0.02	17.47	−0.23	0.03	14.14
	0.05	16	93.65	93.58	−0.07	0.01	11.08	−0.28	−0.2	0.08	0.01	22.32	5.5	5.65	0.15	0.01	38.07	0.14	0.01	37.55	−0.87	0.06	23.88
	0.05	64	93.57	93.75	0.18	0.01	31.15	−0.31	−0.31	0	0	0.04	5.49	5.65	0.16	0	64.25	0.16	0	62.44	−0.09	0.04	3.27
	0.1	1	93.53	93.53	0	0.01	0.06	−0.3	−0.26	0.03	0	11.76	5.35	5.51	0.17	0	63.22	0.17	0	60.18	−0.45	0.05	15.17
	0.1	4	93.61	93.51	−0.1	0.03	5.25	−0.29	−0.12	0.17	0.02	13.6	5.38	5.57	0.2	0	65.14	0.19	0	63.96	−1.89	0.21	14.4
	0.1	16	93.69	93.65	−0.04	0.01	5.81	−0.3	−0.31	−0.01	0	7.04	5.42	5.57	0.15	0.01	25.52	0.15	0.01	25.27	0.03	0.02	2.13
	0.1	64	93.46	93.54	0.08	0.02	7.07	−0.32	−0.16	0.15	0	68.95	5.42	5.63	0.21	0.02	19.23	0.21	0.02	18.58	−1.68	0.04	75.87
	0.2	1	93.46	93.45	−0.01	0.01	2.54	−0.3	−0.32	−0.02	0	5.64	5.32	5.55	0.23	0.01	64.27	0.23	0.01	64.63	0.03	0.05	0.88
	0.2	4	93.69	93.78	0.09	0.01	11.7	−0.32	−0.31	0.01	0	5.64	5.47	5.63	0.16	0.01	28.64	0.16	0.01	28.07	−0.21	0.03	11.38
	0.2	16	93.77	93.47	−0.3	0.01	43.49	−0.32	−0.33	−0.01	0	4.37	5.4	5.55	0.14	0.01	45.22	0.14	0.01	45.22	0.01	0.04	0.46
	0.2	64	93.52	93.64	0.13	0.01	13.74	−0.34	−0.37	−0.03	0.01	9.43	5.35	5.52	0.17	0.01	36.26	0.17	0.01	36.92	0.2	0.05	5.88
	0.3	1	93.8	93.76	−0.04	0.02	4.29	−0.3	−0.29	0.01	0.01	3.59	5.48	5.55	0.08	0.01	18.45	0.08	0.01	17.8	−0.17	0.05	5
	0.3	4	93.61	93.62	0.01	0.02	0.85	−0.33	−0.34	−0.01	0	2.52	5.44	5.69	0.26	0.01	66.34	0.26	0.01	66.15	−0.1	0.03	4.87
	0.3	16	93.62	93.84	0.23	0.01	29.05	−0.32	−36	−0.04	0.01	10.67	5.4	5.58	0.18	0.01	38.5	0.18	0.01	39.42	0.31	0.06	7.71
	0.3	64	93.76	93.65	−0.11	0.01	23.32	−0.34	−0.41	−0.06	0.01	16.72	5.34	5.67	0.33	0.01	70.69	0.33	0.01	70.46	0.42	0.06	11
	0.5	1	93.53	93.45	−0.08	0.01	18.73	−0.34	−0.35	−0.01	0	3.24	5.4	5.61	0.21	1	58.73	0.21	0.01	59.11	−0.04	0.05	1.33
	0.5	4	93.64	93.51	−0.13	0.01	19.16	−0.33	−0.37	−0.03	0	14.38	5.56	5.72	0.17	0.01	30.85	0.17	0.01	30.61	0.24	0.03	11.11
	0.5	16	93.79	93.79	0	0.01	0.13	−0.35	−0.39	−0.04	0	26.75	5.43	5.64	0.22	0.01	52.02	0.22	0.01	52.49	0.27	0.02	17.33
	0.5	64	93.58	93.52	−0.06	0.02	5.4	−0.35	−0.45	−0.1	0.01	27.16	5.41	5.64	0.23	0.01	45.21	0.24	0.01	45.97	0.86	0.06	23.42
Sn_1	1.0	4	93.56	93.71	0.16	0.01	20.68	−0.31	−0.3	0.01	0	2.08	5.26	5.72	0.46	0.02	45.65	0.46	0.02	46.04	−0.32	0.05	9.33
	1.0	16	93.26	93.66	0.4	0.02	33.82	−0.3	−0.39	−0.09	0.01	25.11	5.23	5.78	0.55	0.01	116.71	0.56	0.01	113.82	0.53	0.05	15.91
	1.0	64	93.82	93.97	0.15	0.01	16.34	−0.32	−0.44	−0.11	0	64.75	5.27	5.67	0.41	0.01	55.51	0.41	0.01	56.28	0.9	0.03	50.36
	1.5	4	93.43	93.76	0.33	0.02	20.97	−0.27	−0.37	−0.09	0.01	28.04	5.35	6.05	0.7	0.02	61.83	0.71	0.02	62.54	0.55	0.06	14.37
	1.5	16	93.54	93.91	0.37	0.02	23.9	−0.3	−0.42	−0.12	0	42.39	5.2	5.8	0.59	0.02	40.86	0.6	0.02	41.37	0.79	0.04	28.07
	1.5	64	93.66	93.84	0.19	0.02	16.43	−0.32	−0.49	−0.17	0	58.65	5.24	5.7	0.46	0.01	61.46	0.47	0.01	64.04	1.45	0.05	44.02
	4.2	4	93.39	93.73	0.34	0.02	21.83	−0.28	−0.38	−0.1	0.01	26.56	5.51	6.06	0.55	0.01	106.31	0.55	0.01	103.38	0.72	0.06	20.43
	4.2	16	93.65	93.84	0.19	0.01	22.01	−0.26	−0.54	−0.29	0.01	86.13	5.42	5.9	0.48	0.01	53.02	0.5	0.01	55.25	2.53	0.05	74.3
	4.2	64	93.79	94	0.21	0.01	34.37	−0.32	−0.6	−0.27	0	97.8	5.29	5.79	0.5	0.01	61.69	0.52	0.01	64.17	2.39	0.05	82.31

Table 3. Colourimetry results for new silk soiled with carbon dust (SNS). All values are the mean of five measurements. Where Student's T-test showed no significant Δ values, the plot crosses the axes. Student's T-test values above 2.306 indicate significant differences

Sample	Sample no.	Fluence (J/cm²)	Pulse no.	L*0	L*t	ΔL*	sd ΔL*	Student T ΔL*	a*0	a* t	Δa*	sd Δa*	Student T Δa*	b* 0	b* t	Δb*	sd Δb*	Student T Δb*	sd ΔC*	Student T ΔC*	Δh*	sd Δh*	Student T Δh*
Silk new soiled (SNS) Snv_4	0.025	1	74.88	75.37	0.48	0.05	15.06	0.81	0.84	0.03	0.01	8.8	5.8	5.94	0.14	0.01	18.87	0.14	0.01	19.42	–0.11	0.06	3.07
	0.025	4	76.68	76.97	0.3	0.03	17.02	0.76	0.77	0.01	0	2.95	5.84	5.98	0.14	0.01	33.38	0.14	0.01	35.7	0.08	0.05	2.46
	0.025	16	76.94	77.33	0.39	0.02	40.41	0.74	0.68	–0.06	0.01	16.62	5.91	6.11	0.2	0.01	49.99	0.2	0.01	46.85	0.76	0.05	24.45
	0.025	64	77.82	78.37	0.55	0.01	87.68	0.67	0.67	0	0	0.35	5.87	6.18	0.31	0.01	43.51	0.31	0.01	43.81	0.34	0.04	12.03
	0.05	1	74.92	75.55	0.63	0.02	40.63	0.82	0.8	–0.02	0.01	3.03	5.78	6.12	0.33	0.01	50.93	0.33	0.01	49.01	0.6	0.09	10.63
	0.05	4	75.96	77.07	1.11	0.08	22.59	0.77	0.72	–0.06	0.01	15.18	5.87	6.73	0.86	0.01	194.36	0.84	0.01	203.48	1.41	0.06	39.31
	0.05	16	76.73	79.15	2.42	0.02	165.31	0.72	0.62	–0.11	0	45.02	5.96	7.72	1.76	0.01	319.57	1.74	0.01	316.57	2.36	0.03	120.14
	0.05	64	77.84	82	4.15	0.08	82.54	0.66	0.49	–0.17	0.01	46.96	5.92	8.23	2.32	0.01	291.22	2.29	0.01	294.95	2.99	0.06	83.66
	0.1	1	75.13	76.08	0.95	0.03	51.15	0.78	0.74	–0.04	0	15.8	5.84	6.46	0.62	0.02	64.21	0.61	0.02	63.56	1.04	0.04	44.21
	0.1	4	75.3	77.75	2.46	0.08	46.62	0.79	0.7	–0.09	0.01	27.84	5.96	7.62	1.66	0.01	303.34	1.64	0.01	321.38	2.33	0.05	68.32
	0.1	16	75.85	80.59	4.74	0.02	364.71	0.75	0.73	–0.02	0	9.67	5.97	9.05	3.08	0.01	360.25	3.06	0.01	361.64	2.55	0.03	124.2
	0.1	64	77.23	83.92	6.69	0.03	363.87	0.75	0.5	–0.25	0.01	75.16	6.03	9.39	3.37	0.01	547.02	3.33	0.01	534.16	4.01	0.04	176.22
	0.2	1	74.75	77.37	2.62	0.02	255.98	0.78	0.7	–0.08	0	35.77	5.95	7.57	1.62	0.02	139.96	1.6	0.02	139.46	2.22	0.04	89.73
	0.2	4	75.34	81.17	5.83	0.04	252.26	0.77	0.87	0.1	0.01	21.1	6.04	9.84	3.8	0.01	452.07	3.79	0.01	440.39	2.23	0.05	64.59
	0.2	16	76.22	84.01	7.79	0.05	235.07	0.72	0.77	0.05	0	20..95	6.06	10.42	4.36	0.01	502.51	4.35	0.01	497.14	2.56	0.03	151.48
	0.2	64	77.39	86.15	8.76	0.05	301.95	0.67	0.49	–0.18	0	57.83	6.01	10.48	4.46	0.01	516.37	4.44	0.01	511.14	3.64	0.04	143.47
	0.3	1	73.76	77.94	4.17	0.06	103.31	0.8	0.76	–0.04	0.01	7.01	5.82	"8,32"	2.5	0.01	385.55	2.48	0.01	386.51	2.58	0.07	58.34
	0.3	4	75.21	81.97	6.76	0.04	282.57	0.79	0.99	0.21	0.03	9.45	6	10.51	4.51	0.01	523.5	4.51	0.02	425.53	2.06	0.32	10.29
	0.3	16	76.62	84.74	8.12	0.03	407.18	0.7	0.78	0.08	0.01	20.96	6.11	11.13	5.02	0.02	498.97	5	0.02	490.71	2.52	0.03	128.32
	0.3	64	77.69	87.09	9.4	0.03	468.44	0.71	0.43	–0.28	0.01	43.19	6.16	11.02	4.86	0.02	500.86	4.83	0.02	479.02	4.35	0.08	84.15
	0.5	1	74.37	82.25	7.88	0.05	274.27	0.78	0.77	0	0	1.92	5.92	9.91	3.99	0.01	607.14	3.97	0.01	604.8	3.02	0.03	177.84
	0.5	4	75.14	84.57	9.42	0.02	723.19	0.76	0.92	0.16	0.01	46.98	5.98	11.11	5.12	0.02	51ß2.24	5.11	0.02	507.49	2.52	0.04	107.99
	0.5	16	76.2	86.6	10.4	0.01	1406.26	0.72	0.62	–0.1	0.01	30.85	6.08	11.28	5.2	0.01	567.8	5.17	0.01	565.81	3.64	0.04	140.44
	0.5	64	77.26	88.07	10.81	0.02	919.58	0.69	0.26	–0.33	0	116.47	0.06	11.11	5.05	0.02	403.71	5.01	0.02	404.34	4.61	0.04	185.27
	1.0	1	74.36	85.16	10.8	0.01	1611.16	0.78	0.99	0.21	0	102.02	5.94	11.26	5.32	0.01	719.79	5.31	0.01	712.08	2.43	0.02	158.82
	1.0	4	75.19	86.65	11.47	0.04	436.1	0.76	0.78	0.02	0	7.01	6.06	11.04	4.98	0.02	433.53	4.96	0.02	433.46	3.1	0.04	132.75
	1.0	16	76.45	88.26	11.81	0.01	1969.4	0.71	0.39	–0.32	0	103.77	6.09	10.84	4.74	0.01	845.82	4.71	0.01	850.47	4.57	0.04	182.12
	1.0	64	77.18	89.43	12.25	0.03	716.08	0.68	–0.04	–0.72	0.01	206.63	6.06	10.54	4.48	0.01	843.13	4.44	0.01	837.08	6.64	0.04	265.37
	1.5	1	74.53	86.19	11.66	0.03	722.71	0.75	0.89	0.14	0.01	39.49	5.92	11.18	5.26	0.02	481.94	5.25	0.02	477.34	2.69	0.04	96.43
	1.5	4	75.24	87.87	12.63	0.03	590.57	0.74	0.55	–0.19	0	91.39	5.97	10.66	4.69	0.02	493.38	4.66	0.02	487.68	4.14	0.02	308.12
	1.5	16	76.45	89.35	12.91	0.01	1496.3	0.7	0.1	–0.59	0	259.18	6.08	10.3	4.23	0.03	235.57	4.19	0.03	233.16	5.96	0.03	353.03
	1.5	64	77.36	90.55	13.19	0.04	498.73	0.66	–0.31	–0.97	0	459.13	6.21	0.94	3.73	0.02	297.32	3.7	0.02	295.63	7.83	0.03	419.64
	4.2	1	75.02	89.48	14.46	0.04	589.64	0.76	0.26	–0.5	0	162.66	6.13	9.85	3.72	0.02	294.65	3.68	0.02	290.24	5.55	0.04	209.08
	4.2	4	75.57	90.86	15.29	0.03	848.92	0.73	–0.15	–0.88	0	291.86	6.13	9.2	3.07	0.02	309.78	3.03	0.02	310.52	7.71	0.05	242.44
	4.2	16	75.64	91.79	16.14	0.02	1179.05	0.73	–0.5	–1.23	0.01	351.77	6.22	9.08	2.86	0.01	426.29	2.83	0.01	421.56	9.85	0.04	374.46
	4.2	64	77.12	92.5	15.38	0.01	2883.23	0.68	–0.79	–1.47	0	683.57	6.29	8.47	2.18	0.01	250.44	2.18	0.01	247.4	11.5	0.02	887.56

Table 4. Viscometry results for new silk (SN) new silk soiled with carbon (SNS). Standard deviation has been estimated to be around 10 per cent. Changes beyond 10 per cent therefore indicate significant change in the degree of polymerization

Sample	Sample fabric	Fluence (J/cm²)	Pulse no.	[η] (dLg-1)average	ΔDP in %
silk new (SN)	Sn_2	untreated	untreated	0.193	n.a.
		0.5	16	0.175	–9
		0.5	64	0.199	3
		1	4	0.183	–5
		1	16	0.166	–14
		1	64	0.207	8
		1.5	4	0.239	24
		1.5	16	0.206	7
		1.5	64	0.211	9
		4.2	4	0.279	45
		4.2	16	0.246	28
		4.2	64	0.215	12
silk new soiled (SNS)					
	Snv_5	untreated	untreated	0.198	n.a.
		0.5	16	0.156	–21
		0.5	64	0.210	6
		1	4	0.139	–30
		1	16	0.161	–19
		1	64	0.197	0
		1.5	4	0.137	–31
		1.5	16	0.167	–16
		1.5	64	0.190	–4
		4.2	4	0.167	–15
		4.2	16	0.169	–15
		4.2	64	0.165	–17

The naturally aged silk sample proved to be too degraded; viscometry values reached stayed within the error margin, which was estimated to be as big as ±10 per cent. Therefore, viscometry was only performed on the new and the new soiled silk samples. While new silk generally increased in viscosity, the carbon soiling applied to the new silk caused a decrease in viscosity (Figure 5 and Table 4).

A comparative plot of the results for colourimetry and viscometry shows high ΔC^* values to correspond with low viscosities (Figure 6). Especially at low energy/pulse numbers, the loss of DP seems significant, and the high ΔC^* suggests chain scissions causing an increase in polar functional groups. At higher fluences and pulse numbers, ΔC^* decreases and there seems to be slightly less loss of viscosity, in unsoiled silk there is even a gain of viscosity. This is explained by comparing the viscosity to Δh^* (Figure 7). An initial increase of Δh^* seems to be outweighed by the simultaneous increase in ΔC^*, the total effect being a loss of viscosity. However with increasing fluence, cross linking indicated by Δh^* seems to predominate over the simultaneously occurring chain scissions, resulting in an overall increase in viscosity.

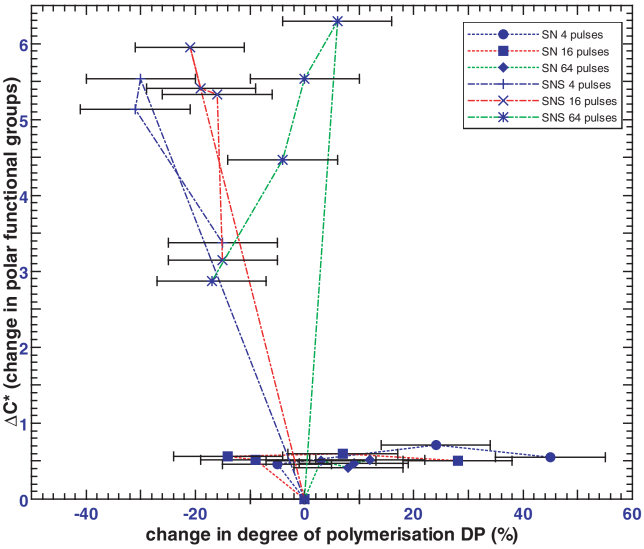

Figure 6. Change in ΔC^* indicating change in polar functional groups plotted against change in degree of polymerization (DP) for new silk (SN) and new silk soiled with carbon dust (SNS). Plotted lines connect the different fluences at a respective pulse number. The symbols on the lines stand for fluences of 0.5, 1, 1.5 and 4.2 J/cm^2 (from left to right). New silk (SN) increases in DP without a change in ΔC^*, new soiled silk (SNS) decreases in DP with simultaneous changes in ΔC^*; the lower the pulse number, the more significant the change in DP seems to be. It is suggested that the change in DP is a cumulative result of two concurring reactions (Figure 7)

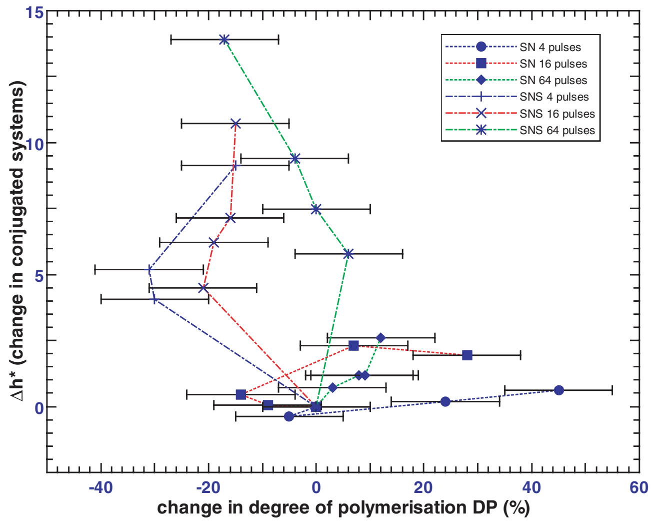

Figure 7. Change in Δh^* indicating change in conjugated systems plotted against change in degree of polymerization (DP) for new silk (SN) and new silk soiled with carbon dust (SNS). Plotted lines connect the different fluences at a respective pulse number. The symbols on the lines stand for fluences of 0.5, 1, 1.5 and 4.2 J/cm^2 (from left to right). An increase in Δh^* seems to suggest an increase in DP; however, it is suggested that the change of DP is a cumulative result of two concurring reactions (Figure 6)

Pol-FTIR indicated a significant decrease in the degree of orientation in new, soiled silk (caused by the mechanical action during preparation of the artificially soiled silk) to a level even lower than the one of naturally aged silk (Figure 8). Standard deviations are large; the results therefore can only be used to show a trend. The most important indication is that new silk loses its degree of orientation upon laser treatment even at low fluences and pulse rates to a degree that is comparable to natural ageing and to mechanical damage.

The FTIR-plots only showed visible differences for the naturally aged silk treated with 64 pulses at high fluences (Figure 9), where the first amide peak (left arrow) slightly decreases in respect to the second amide peak (right arrow) with increasing fluence. This indicates that the amount of C=O stretch vibrations/primary amine scissors in plane/C=C stretch vibration are decreasing, while N–H bending in plane (in the fibroin backbone) and carboxyl groups (which also show around 1500 cm^{-1}) remain more or less unchanged.

The naturally aged silk seems to suffer greater overall change than new silk.

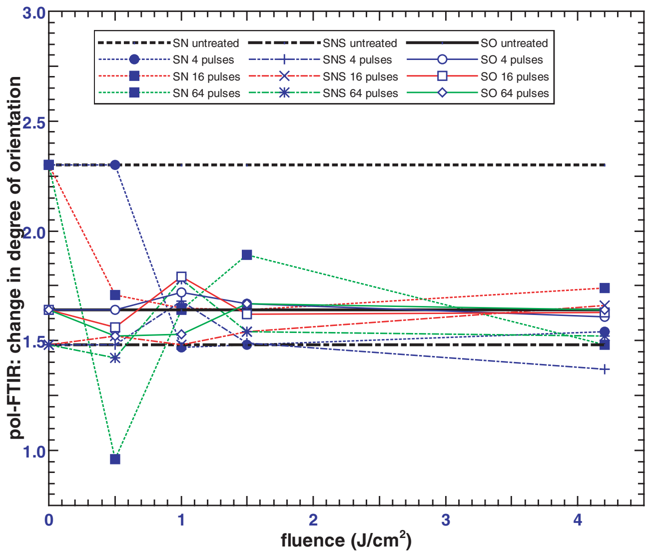

Figure 8. Change in degree of orientation as measured by pol-FTIR plotted against fluence of the laser treatment for new silk (SN), new silk soiled with carbon dust (SNS) and old silk (SO) at various laser pulses. Vertical lines show the untreated samples. New silk loses its degree of orientation of crystalline regions upon laser treatment even at low fluence to a degree similar to naturally aged silk (SO) and mechanically damaged new silk (SNS) (damage inflicted during application of carbon dust). The very large standard deviations have been omitted in the graph for clarity

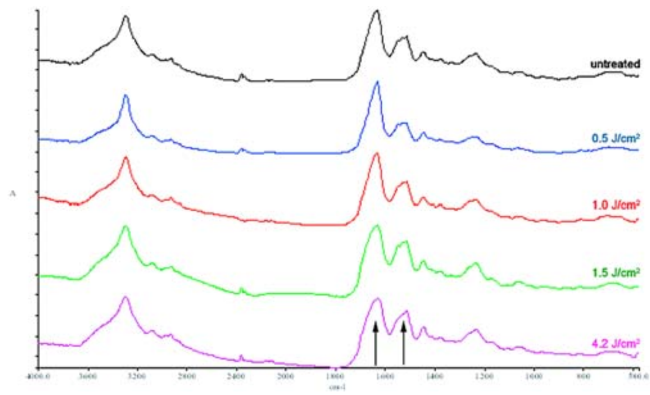

Figure 9. Pol-FTIR spectra (polarizer perpendicular 90° to fibre axis) for old silk (SO), laser treated with 64 pulses. The two arrows mark the first (left) and second (right) amide peak. The ratio of these peaks changes with increasing fluence. Such a visible difference of the spectra has not been observed for the other silk fabrics nor at lower fluences for the old silk

This hypothesis is supported by compiling colourimetrical and viscometrical results in one table (Table 5).

There appear to be two general trends in changes to undyed silk fabrics after laser irradiation. At lower fluence/pulse numbers, an increase in polar functional groups (ΔC^*) coincides with loss of viscosity. This suggests a predominance of chain scission reactions during laser treatment at lower fluences. At higher fluences/pulse numbers, an overall increase in conjugated systems (Δh^*) coincides with an increase in viscosity, suggesting a predominance of cross linking. Carbon dust seems to enhance the process that causes chain scission, either by raising the surface temperature or by catalysing the chemical reaction leading to chain scission. Naturally aged silk, being already so low in viscosity that no measurements could be taken, shows an increase in conjugated systems at much lower fluences than new silk.

Table 5. Schematic compilation of colourimetry and viscometry results

Sample	**No of pulses**	**Fluence J/cm2**			
		0,5	**1,0**	**1,5**	**4,2**
Old silk (SO)	**64**	**h**	**h**	**h**	**h!**
	16	**O**	**h**	**h**	**h**
	4	**-**	**C**	**C**	**h**
New silk (SN)	**64**	**h**	**h**	**h**	**h**
	16	**CC**	**C**	**h**	**h**
	4	**-**	**CC!**	**C**	**O**
New silk soiled (SNS)	**64**	**C**	**C**	**h**	**h**
	16	**C**	**C**	**O**	**h**
	4	**-**	**C**	**C**	**h**

[shaded] = decrease in viscometry; **CC** *= $\Delta C^* >> \Delta h^*$ (much more increase in polar functional groups than in conjugated systems);* **C** *= $\Delta C^* > \Delta h^*$ (more increase in polar functional groups than in conjugated systems);* **h** *= $\Delta h^* > \Delta C^*$ (more increase in conjugated systems than in polar functional groups);* **hh** *= $\Delta h^* >> \Delta C^*$ (much more increase in conjugated systems than polar functional groups);* **h!** = decrease *in* ΔC^**;* **C!** = decrease *in* Δh^*

Conclusions

Visual examination of laser cleaned silk might be deceiving: bleaching at high fluences and pulse rates might be misinterpreted as 'cleaning', and microscopic observations only indicated changes occurring at very high exposures. The observation of yellowing occurring at low fluences and pulse rates suggests chemical alteration caused during laser cleaning. Therefore defining a 'safety window' based on physical observations does not seem appropriate, at least for silk. Laser cleaning appears to cause chemical alterations within the silk fibres at very low fluence. However, no statement can be made at the moment about how significantly the observed changes affect the long-term preservation of the silk fabric. Chain scission in silk is reported to happen at the peptide bond (C–N), which possesses low binding energy (360 kJ/mol) and is affected both during light as well as heat ageing, leading to a radical chain reaction. It can therefore be assumed that even the small, observed changes might have significant impact. This needs to be confirmed by future research.

Acknowledgements

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Notes

1 Mean absorption for naturally aged silk 2.17 per cent (sd 0.02), for new silk 1.798 per cent (sd 0.001), for new silk soiled 1.95 per cent (sd 0.03), measured with a Perkin Elmer Lambda 2 UV/Vis Spectrometer.

2 $\Delta C^* = \sqrt{(a^x)^2 + (b^x)^2} - \sqrt{(a_t^x)^2 + (b_t^x)^2}$.

3 $\Delta h^* = \tan^{-1}(b^x/a^x)$.

4 To be published by Krueger, Pentzien and von Lerber at *Lacona VI*, Vienna, September 2005.

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Materials

Minolta spectrophotometer CM-2002 with matching software

Nd:YAG Laser, prototype manufactured 2001/2002 by IB Laser and Bauer+Mück for the German Institute for Material Testing, Berlin

RtPlot-science®, version 2.1, release 3.4 2002, shareware software by Horst Reichert
Web site: www.rt-science.de

Silk crepe, tabby weave, crepe structured, without any sizing, corresponding to ISO 105-F06 (unsoiled and mechanically soiled with carbon dust, particle size 29.5 nm)
EMPA Testmaterialien AG
Mövenstrasse 12
CH-9015 St Gallen
Switzerland
Web site: www.empa-sg.ch/testmat

Silk naturally aged, tabby structure. Unknown provenance, lining of cope.
Abegg-Stiftung
CH-3132 Riggisberg
Switzerland

Viscometer: Unitex-type
Effe-ci
Italy