A new perspective on plastics cleaning: assessing the impact of laser cleaning on cellulose acetate

Francesca Azolini
UCL Medical Physics and Biomedical Engineering, London WC1E 7JE, UK
francesca.azolini.21@ucl.ac.uk

Katherine Curran
UCL Institute for Sustainable Heritage

Simoní Da Ros
WMG, University of Warwick

Daren Caruana
UCL Department of Chemistry

Adam Gibson
UCL Medical Physics and Biomedical Engineering

ABSTRACT: A 2019 UCL survey at Tate (Lee *et al.* 2023) and the 2008-2012 project POPART (EU 7th Framework Programme project Preservation of Plastic Artefacts in Museum Collections) showed that dust and ingrained dirt are common causes of damage to plastic museum objects. Cleaning strategies for plastics are currently limited and not completely effective (due to sensitivity to aqueous and solvent-based systems, permanence of residues and potential mechanical damage caused by the cleaning process itself). Even though laser technology has been exploited successfully for cleaning heritage objects for more than thirty years, its use on plastics remains relatively unexplored. This study will help understand the impact of Nd:YAG laser radiation at 1064 nm on both clear and artificially soiled plasticised cellulose acetate undergoing accelerated ageing conditions (70°C, 80% relative humidity), as well as no accelerated ageing. The surface appearance, colour and chemical composition (namely plasticiser content and degree of substitution) of the irradiated samples were assessed through optical microscopy, visible spectrophotometry/colourimetry and attenuated total reflectance Fourier-transform infrared spectroscopy. The results showed satisfactory cleaning efficiency and no detectable chemical changes in the polymer due to the laser. This suggests that lasers can play a role in cleaning plastics, especially when traditional methods are unsuitable.

KEYWORDS: Cellulose Acetate, Laser, Cleaning, Artificial Soiling, Artificial Ageing

INTRODUCTION

Plastics have become essential for many aspects of human activity since their invention in the 19th century. Thanks to their highly adjustable properties, versatility, and low cost, plastics have become valuable objects of social life, science and technology, and, by extension, acknowledged objects of heritage value. However, their complexity makes the mitigation, inhibition and reversion of degradation and damage challenging. Consequently, predictions of plastics' lifetime may be less reliable compared to traditional materials (Shashoua 2008).

While preventive conservation practices to inhibit degradation have been widely investigated (Shashoua 2006), interventive treatments have been less developed, probably due to the high sensitivity of most plastics to cleaning solutions, poor abrasion resistance and the irreversibility of some damage phenomena. According to Shashoua *et al*. 2021, methods developed within the EU NANORESTART project (2015-2018) proved to cause minimal damage and effectively clean carbonaceous depositions from some plastics, performing better than methods previously examined in the POPART project.

Cellulose acetate (CA) is a semi-synthetic polymer, derived from the acetylation of cellulose. It is often found in collections and, as it degrades, emits acetic acid, a harmful degradation product that may contaminate other objects nearby (Williams 2002; Curran *et al.* 2014). It is one of the earliest and therefore oldest plastic displayed in museums, and is often unstable due to its poorly stabilised and largely experimental formulations (Shashoua 2008).

POPART surveys estimated that between 15-30 per cent of plastic objects across a selection of European museums are in poor or unacceptable condition for display (Barabant *et al.* 2012). Given that dirt is a primary cause of instability and degradation (Grau-Bové and Strlič 2013)

and alternative highly selective, non-contact, solvent-free cleaning methods for plastics are limited, we choose to investigate use of lasers for cleaning plastics.

Lasers have been used in the heritage field for cleaning purposes (see for example: Cooper 1997; Fotakis *et al.* 2006; Siano *et al.* 2012; Zanini *et al.* 2018). When a focused short-pulse laser beam hits a material's surface, heat is generated (Ahmed *et al*., 2016). Thermal mechanisms can lead to cleaning by ablation but can also damage the object by causing melting or cracking on the substrate. According to Ravi-Kumar *et al.* 2019, the most important parameters when considering laser ablation of polymers are: (i) shorter pulse duration results in more vaporisation and less melting, (ii) the absorption coefficients of given materials differ with wavelengths, (iii) higher molecular weight in polymers can result in lower ablation rates due to the formation of highly viscous molten material, (iv) a higher thermal conductivity of the polymer can lead to a larger heat affected zone, especially with longer pulse durations.

For these reasons, a Q-switched laser in the near-infrared was chosen for the removal of a carbonaceous soiling from CA samples. This wavelength is expected to be preferentially absorbed by the artificial soiling (Strlič *et al.* 2003), where the short pulse duration will reduce the heat penetration in the substrate (Zhu *et al.* 2022).

This study explores the impact of a nanosecond laser radiation on CA in terms of cleaning efficacy and the short-term risk of modifying the surface appearance or chemistry of the underlying CA.

MATERIAL AND METHODS

Synthesis of Diethyl Phthalate Plasticised Cellulose Acetate

CA with an average degree of substitution (DS) of 2.45 ± 0.05 and plasticiser diethyl phthalate (DEP) (99.5%) were supplied by Sigma Aldrich (London, United Kingdom). The plasticisation

of the CA samples was conducted in our lab to ensure reproducibility and accuracy, which cannot be guaranteed with commercially available plastics. Plasticised CA samples were prepared via solvent casting with 20 wt% of DEP, as described elsewhere (Bao *et al.* 2015b; Da Ros *et al.* 2021). The resultant mixture was kept under reflux for 4.5 h at 60-64°C with continuous stirring, allowed to cool for 1 h with stirring and finally poured into a flat glass tray. Slow evaporation was allowed by keeping a glass lid over the sample tray at room temperature. Finally, drying was performed in a vacuum oven (150 mbar) for 96 h at 20°C.

The newly formed CA sheets were cut into square samples (2 × 2 cm × 0.5 mm) with scissors. The samples were stored in individual polyethylene bags at 4 °C when not in use. Two repeats of each sample were made. In this initial study, colourless and transparent CA samples were prepared so as to exclude the influence of pigments. This should minimise absorption of laser light at 1064 nm by the CA samples, giving a best-case scenario with negligible polymer damage.

Model Soiling

Black Crayola® crayons were used to model carbonaceous soiling as suggested in personal communication by Yvonne Shashoua, a leading expert in plastics research. Wax crayons are made from paraffin wax, stearic acid, powder pigment (Reid et al., 2002) - in this case assumed to be carbon black- and sometimes, a mixture of additives including polyethylene to improve softening resistance (Brinkman, 1976). Black crayon can be considered a carbonaceous type of soiling and used as a simplified surrogate for diesel particulate matter (Grau-Bové and Strlič 2013), because it contains a mixture of elemental carbon (black pigment) and organic carbon (hydrocarbons). To support this, we cite the artificial soiling used during the POPART project, a blend of paraffin wax and carbon black (Lavédrine 2012: 237).

A 1.8 × 1.8 cm area was soiled on half of the CA samples (entries 9-16, Table 1) using the black crayon before the samples were left undisturbed for a week at room temperature. Then, unaged samples (entries 5-8 and 13-16, Table 1) were treated by laser and analysed by Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), colour measurements and optical microscopy.

Artificial Ageing

Artificial ageing conditions were used to accelerate decay mechanisms, reflecting the potential conditions to which CA objects may be exposed after years of storage/display, as well as to obtain possibly more embedded soiling.

The choice of ageing parameters (temperature and relative humidity (RH)) and times was based on previous experimental work (Richardson *et al.* 2014). The ageing temperature was fixed at 70°C, safely below the samples' glass transition temperature (T_g) so as to prevent molecular mobility. Bao (2015a) reported a T_g at 93°C for CA (DS of 2.45 and 20% DEP) and del Gaudio *et al.* (2021), calculated a minimum T_g of 78.3°C for CA (DS of 2.45 and 20% DEP). Half of the samples (entries 1-4, 9-12, Table 1) were subjected to a RH of 80% and temperature of 70°C for 33 days, inside an oven (VENTI-Line® Prime, Avantor, UK). The high RH of 80 per cent was chosen in order to initiate decay mechanisms involving high moisture (such as deacetylation and chain scission) and increase the plasticiser loss, which are typical degradation phenomena of historic CA objects (Littlejohn *et al*. 2013).

Soiled (entries 9-12, Table 1) and unsoiled (entries 1-4, Table 1) samples were placed in desiccators within the oven, each of which contained 51.3 g potassium chloride in 100 mL deionised water to keep humidity constant inside the container (Greenspan, 1977). The samples were placed on top of ceramic plates so that they did not come into contact with the saturated solution at the bottom. Humidity and temperature were monitored using TinyTag Ultra2®

sensors (Gemini Data Loggers Ltd, UK). At the end of the artificial ageing, all samples were removed from the oven and allowed to stabilise at room temperature, within their desiccator, for a few hours. Thereafter, aged samples (entries 1-4, 9-12, Table 1) were treated by laser, then analysed with ATR-FTIR, visible spectrophotometer and microscopy.

Laser Irradiation

The laser treatment was performed with a Q-Switched Nd:YAG (Neodymium-doped Yttrium Aluminuim Garnet) 1064 nm laser (Compact Phoenix, Lynton, UK), provided by UCL Culture. The laser delivered 130 mJ per pulse with a spot diameter of 3 mm (giving an energy density per pulse of 1.83 J/cm^2), at 1 Hz repetition rate and a pulse duration of 5 ns. One and five consecutive number of scans (herein referred to as 1s and 5s) were delivered consecutively at a distance of 16 cm from the samples at ambient air and pressure. No damage thresholds were estimated in this study; the threshold was kept below the safety energy density of 2.9 J/cm^2 presented elsewhere (McPhail *et al.* 2015), minimising the risk of damage. All the samples were irradiated. To maximise consistency, the laser was fixed to the table, while the samples were placed on a fixed stage that could be oriented in x and y directions.

Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) Spectroscopy

Infrared spectra in absorbance mode were collected from all the samples using a ATR-FTIR (Alpha-P, Bruker) equipped with a diamond cell, over a wavenumber range of 400-4000 cm^{-1}, using a wavenumber resolution of 4 cm^{-1} and 32 scans. A background spectrum was collected under the same conditions before each analysis.

The spectra were baseline corrected by fixing the average absorbance between 2200 and 2000 cm^{-1} at zero before the extraction of individual band intensities. The analysis was intended to identify changes in DEP content, DS, and the formation of any new bonds due to laser exposure of pristine and soiled CA samples, before and after accelerated ageing. DEP

concentrations were quantified using the ratio between the maximum absorbance intensity around 745 cm^{-1}, corresponding to the CH benzene band (phthalate), and 602 cm^{-1}, representing the C-C-C backbone of the cellulose ring (CA). The 602 cm^{-1} peak was used as an internal standard, as it appears to remain unaffected by the concentration of plasticiser and the hydrolysis process (Richardson *et al.* 2014). The calibration curve used was developed by Da Ros *et al.* 2021 using CA samples with different DEP concentrations, and its coefficients were calculated by linear regression using the least-square objective function.

The quantification of DS by ATR-FTIR was based on the ratio between the maximum absorbance intensity of the C-O ester vibration, observed around 1215 cm^{-1}, and the C-O-C vibration from the CA backbone around 1030 cm^{-1}, also assumed to remain unaffected during this experiment. DS was calculated from IR spectra in accordance with Da Ros *et al.* (2021). Measurements were taken only on the side affected by the laser treatment, guided by a polylactic acid (PLA) 3D-printed mask. Each sample had three spot measurements, each of which was repeated twice to account for variation in the measurement process. The average of these six measurements was taken to assess any variabilities across the sample's surface.

Colour Measurements

Colour measurements were carried out before and after laser treatment. Three repeated measurements were taken using a visible spectrophotometer (Ci62x, X-rite, USA) with illuminant D65, standard observer angles of 2°, specular component included, and then averaged. Colour differences magnitude values (ΔE*) were calculated in accordance with the CIEDE 2000 (ISO/CIE 11664-6:2022(E); Sharma *et al.*2005; Luo *et al*. 2000). ΔE* up to 3 corresponds to a noticeable perception of colour difference (Yang *et al.* 2012).

Particular interest will be given to the L* (lightness) and b* (the more yellow a sample appears, the higher the b* value) scales. In soiled samples, ΔL* will be used to describe the difference in

the density of the dirt deposit before and after laser treatment - an increase in the value of L* describes an efficient removal of dirt (corresponding to a decrease in b* values). Any Δb* value above 0 in unsoiled samples indicates yellowing phenomena as a result of artificial ageing (Strlič *et al.* 2003).

Optical Microscopy

The extent of mechanical damage and the evaluation of soil residues before and after laser treatment were assessed by collecting microphotographs with two different 3D microscopes (VHX 5000 and 7000, Keyence, Japan), lenses 100-1000X, black background, reflected LED vertical illumination 255 full ring with VHX-5000, and transmitted light, coaxial light and polarising filter with VHX-7000, to help reducing the glare and increase overall image contrast. The microphotographs were acquired on a black background, where each CA sample was placed on the top of the white PLA mask, except when observed in transmission. The 3D software of the microscope was used to extrapolate information on the depth of the sample, to provide detection of annealing/softening or circular voids with through cracks, which may occur if the damage threshold is exceeded (Brand *et al.* 2023).

RESULTS AND DISCUSSION

Effects of Laser Cleaning on Non-Aged Cellulose Acetate

Microscopy showed no detectable surface damage to pristine CA samples following laser irradiation (Figure 1.b'-b'') {*insert fig.1*}. Figure 2.a {*insert fig.2*} shows very small ΔL* and Δb* values for these samples (ΔE_{00} 0.7 ± 0.1 for 1s and ΔE_{00} 0.6 ± 0.2 for 5s). Scratches and imperfections in the surface are suspected to be a result of the preparation process, as they appeared both before and after laser irradiation (Figure 1.b).

ATR-FTIR spectra (Figure 3) {*insert fig.3*} of unsoiled and non-aged samples show modest differences before and after the laser irradiation. The calculation performed on the DS values

listed in Table 1 agrees within 0.1%, which is within the margin of error. The difference in DEP between before and after laser treatment lies within the experimental uncertainity. We compared these values with thirty average measurements of pristine CA (unsoiled, unaged, not lasered) samples and concluded that this difference was not a systematic reduction, thus there was no evidence of DEP loss after laser. However, there appears to be a difference on the samples between 1s and 5s irradiation.

Laser cleaning did successfully and equally remove most of the black crayon over 1 and 5 scans. However, the cleaned samples showed an opalescent patina on the surface after the laser treatment (Figure 1, a-a'). This could be due to the wax component of the crayon, that, when heated, releases paraffin (Cho and Folger 1999; Reid *et al.* 2002) creating a halo.

Colour analysis (Figure 2.b) in soiled samples showed an increase of ΔL^* equal to 36.6 ± 5.3, an average decrease in Δb^* of -2 ± 0.4 (ΔE_{00} of 27.5 ± 4.6) for 1s irradiated, and ΔL^* of 48.1 ± 5.1 and Δb^* of -0.4 ± 0.4 (ΔE_{00} of 39.1 ± 5.2) for 5s irradiated. The large standard deviation can be attributed to heterogeneity of density of the crayon across the samples, and the irregular, slightly curved surface. However, the large ΔE_{00} describes a significant colour change, indicating successful removal of black particles.

The quantification of DEP and DS on the soiled samples are not reliable and appear to be compromised due to an overlap between a peak from the black Crayola® crayon and one from the plasticiser (Figure 4) {*insert fig.4*}. Therefore, these results are not presented here (entries 13-16, Table 1).

Effects of Artificial Ageing on the Deterioration of Cellulose Acetate

Discolouration

Discolouration of cellulose has been attributed to the presence of carbonyl (C=O) and carboxyl groups (-COOH) (Area and Cheradame 2011; Batterham and Rai 2008). It is anticipated that similar chemical changes are responsible for discolouration in CA.

Following 33 days of accelerated ageing and laser treatment, the unsoiled CA samples yellowed visibly (Figure 2.c), confirmed by a ΔE_{00} of 2.2 ± 0.1, ΔL^* of -2.1 ± 0.3 and Δb^* of 2.2 ± 0.1 for 1s irradiated, compared to a ΔE_{00} of 3 ± 0.3, ΔL^* of -2.9 ± 0.3 and Δb^* of 2.9 ± 0.5 for 5s irradiated. These changes are much more significant than those observed for the unaged samples, suggesting that these colour changes are due to the ageing rather than the laser treatment. However, it is worth noting that the 5s samples showed a slightly larger colour change than the 1s.

Soiled samples showed what appeared to be a significant colour variation of ΔE_{00} of 19.8 ± 4.1, ΔL^* of 27.1 ± 5.1 and Δb^* of 0.6 ± 0.9 for 1s irradiated, compared to a ΔE_{00} of 25 ± 7.5, ΔL^* of 33.5 ± 8.6 and Δb^* -0.1 ± 1 for 5s irradiated (Figure 2.d). Here, the effective removal of black particles combined with the yellowing due to ageing, made colorimetry difficult to interpret and further work is needed to understand the distinct influence of artificial ageing, dirt and laser irradiation.

Deacetylation and Plasticiser Loss

After artificial ageing, no significant changes in the surface appearance or shape of the aged and unsoiled CA samples were observed by eye or microscopy. No odour of acetic acid, a known sign of deacetylation (Ahmad *et al.* 2020) was detectable; this seems to be confirmed by insignificant peak variations at 1366 (C-H), 1033 (C-O-C pyranose group) and 1214 (C-O-C) cm^{-1} (Figure 5) {*insert fig.5*}. The average decrease in DS in 5s-samples is small but greater than the experimental uncertainty and may justify a further study. Although this did not correlate to perceivable change, it would be worth investigating the quantification of acid further. These results agree with findings from del Gaudio *et al.* (2021).

Interestingly, the band at 745 cm^{-1} significantly decreased in intensity, suggesting a reduction due to ageing (Figure 5). Calculated DEP content on the surface after accelerated ageing in unsoiled samples dropped by half with an average value of 10.9 ± 0.5 (wt%) for 1s and 10.5 ± 0.1 (wt%) for 5s. This is in line with results from Da Ros *et al.* (2022) who observed significant DEP loss after ageing CA samples, where high temperature and RH contribute to plasticiser loss (Rambaldi *et al.* 2014).

Comparing these results with the non-aged samples suggests that the observed reduction in DEP content is more likely due to ageing than to laser irradiation (Figure 6) {*insert fig.6*}. Only the results obtained from the aged and unsoiled samples will be shown here, because the presence of the crayon (overlapping peak around 720 cm^{-1} from the paraffin structure) likely compromised a correct reading of the plasticiser concentration on each soiled sample.

Impact of Laser Cleaning on Aged Samples

Laser irradiation at 1.83 J/cm^2 effectively cleaned the black particles of crayon from aged samples, while leaving the same oily residue on the surface. Artificial ageing did not lead to the soiling becoming more embedded. This was further supported by the fact that, upon wiping the surface, the halo was completely removed. Laser cleaning appeared to be equally effective on aged and non-aged samples, where the 5s irradiation appeared less suitable given the equal effectiveness in cleaning and the greater influence on colour, DS and DEP values compared to 1s.

CONCLUSIONS

This work investigated the stability of CA after a Q-switched Nd:YAG 1064 nm laser treatment, aiming to understand the interconnected mechanisms between laser irradiation, polymer degradation, and cleaning effectiveness. According to these findings, an energy density per pulse of 1.83 J/cm^2 at lower pulse repetition rate (1 Hz) can successfully clean carbonaceous particles from CA but is less effective on the oily component of the soiling. Laser treatment was

found to successfully clean both aged and unaged samples. Minimal plasticiser loss or chemical change to the polymer were observed following laser irradiation, although these results could not be obtained for soiled samples due to interference from the soil.

Colour measurements, DS and DEP quantification pointed to a small but real difference between the two treatments, where 5s exposure appeared to have higher impact at equal cleaning effectiveness, therefore, a 1s exposure is recommended.

This study may pave the way to novel approaches for conservation cleaning of plastics. Moreover, further investigation regarding different types of soiling depositions should be pursued, leading the way to investigate their heat diffusion and absorption coefficients, and to help defining their cleaning thresholds and damage thresholds for the underlying polymer. {*insert Table 1*}.

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AUTHORS' SHORT BIOGRAPHY

Francesca is a second year PhD student at UCL Medical Physics and Biomedical Engineering with an EPSRC funding, researching safe laser cleaning on historical cellulose acetate. She is a postgraduate teaching assistant for the UCL Institute for Sustainable Heritage and the Institute for Materials Discovery, as well as the student representative for ICON UK Heritage Science Group. She graduated in 2017 from a five-year programme in Conservation of Cultural Heritage at the Academy of Fine Arts in Bologna. Her current interests include the conservation of modern heritage materials in collections and understanding polymers degradation paths.

Katherine is an Associate Professor in Sustainable Heritage at the UCL Institute for Sustainable Heritage. Katherine's research interests include the conservation of modern cultural heritage materials, polymer chemistry and degradation, and the analysis of volatile organic compound (VOC) emissions from historic objects. Katherine was the Principal Investigator for the ERC Starting Grant funded project "COMPLEX: The Degradation of Complex Modern Polymeric Objects in Heritage Collections: A System Dynamics Approach" which developed new approaches to understanding and modelling the degradation of modern polymeric materials in collections.

Simoní is a Teaching Fellow in Sustainable Materials and Manufacturing at WMG, University of Warwick, where her teaching lies in the application of sustainability principles in the analysis of materials and processes. Before joining WMG, she worked as a Research Associate in polymer degradation chemistry at the UCL Institute for Sustainable Heritage, as part of the above-mentioned ERC-funded project 'COMPLEX'. Simoní has also worked as a Research Assistant and Post-doctoral Researcher at the Chemical Engineering Programme from the Federal University of Rio de Janeiro, where she obtained her PhD in Chemical Engineering in 2017.

Daren's training is interdisciplinary, having read Biochemistry at the University of Warwick, and then completing a PhD in Electrochemistry at the University of Southampton. Daren held postdoctoral positions at the University of Malta, University of Texas at Austin, and at the Department of Chemistry at UCL. Daren has been at UCL as an academic since 1999 and he is currently Professor of Physical Chemistry and Electroanalysis at the Department of Chemistry.

Adam is Professor of Medical Physics and Heritage Science at UCL. His research in heritage science has mainly involved multispectral, hyperspectral and X-ray fluorescence imaging of heritage objects. In medical physics, his main research area is in developing diffuse optical tomography for functional brain imaging of adults and children. He led the UK's contribution to IPERION HS, a major EU research infrastructure grant which is part of a series of grants that aims to become a European Research Infrastructure Consortium.

TABLES WITH LEGENDS

Table 1. Investigated samples and their characteristics. Average and absolute standard deviation from six measurements of DEP contents (wt%) and DS by ATR-FTIR, before ([b]) and after ([a]) laser irradiation, with or without artificial ageing (70°C, 80% RH).

Entry	Soiling agent	Number of consecutive scans	Condition	Laser (Yes/No)	DEP (wt%) [b]	DEP (wt%) [a]	DS [b]	DS [a]
1	None	1	Aged	Y	20.42 ± 0.39*	9.72 ± 0.24	2.441 ± 0.011	2.445 ± 0.003
2		1		Y	21.68 ± 1.06*	10.58 ± 0.24	2.451 ± 0.004	2.443 ± 0.002
3		5		Y	20.00 ± 0.19*	9.79 ± 0.11	2.451 ± 0.001	2.439 ± 0.002
4		5		Y	20.17 ± 0.25*	9.43 ± 0.19	2.450 ± 0.002	2.435 ± 0.001
5		1	Not aged	Y	20.39 ± 0.38	19.56 ± 0.31	2.450 ± 0.003	2.451 ± 0.001
6		1		Y	21.51 ± 0.60	21.49 ± 0.16	2.451 ± 0.002	2.453 ± 0.001
7		5		Y	20.84 ± 0.27	20.10 ± 0.24	2.452 ± 0.001	2.450 ± 0.002
8		5		Y	21.97 ± 0.29	21.26 ± 0.17	2.453± 0.0004	2.450 ± 0.0004
9	Black Crayola® crayons	1	Aged	Y	+	+	+	+
10		1		Y	+	+	+	+
11		5		Y	+	+	+	+
12		5		Y	+	+	+	+
13		1	Not aged	Y	+	+	+	+
14		1		Y	+	+	+	+
15		5		Y	+	+	+	+
16		5		Y	+	+	+	+

*Values before the ageing. [+] Results not reported due to interference with the spectrum of the soil.

LIST OF FIGURES CAPTIONS

Figure 1. Microphotographs of soiled-CA sample (entry 14, Table 1) before (a) and after (a') laser irradiation, with full-ring illumination 100X (a-a') and polarised-coaxial illumination (a'') and pristine CA (entry 8, Table 1) before (b) and after (b'-b'') laser irradiation, with full-ring illumination 100X (b-b') and polarised-coaxial illumination (b'').

Figure 2. Colorimetry results for laser-irradiated CA samples at 1s and 5s exposure (1.83 J/cm^2), in terms of change in ΔL* and Δb*. (a) Clear not-aged; (b) Soiled not-aged; (c) Clear-aged at 70°C and 80% RH; (d) Soiled-aged at 70°C and 80% RH. Error bars represent absolute standard deviations.

Figure 3. ATR averaged spectra of a non-aged and unsoiled CA sample (entry 5, Table 1), before (black line) and after (grey line) laser irradiation (1.83 J/cm^2). The insert shows a zoom at 745 cm^{-1} with a slight decrease in intensity of the DEP peak.

Figure 4. Three ATR-FTIR marks on soiled-CA surface (entry 15, Table 1) show how the quantification of DS and DEP cannot be reliable due to the interference caused by the presence of surface residues. Also, black Crayola® crayon has a reference peak at 720 cm^{-1} that may overlap with the plasticiser.

Figure 5. ATR averaged spectra of aged and unsoiled CA sample (entry 3, Table 1), before (black line) and after (grey line) 33 days at 70°C and 80% RH, followed by laser irradiation (1.83 J/cm^2). The insert shows a zoom at 745 cm^{-1} with an evident decrease in the DEP peak, whereas -OH and C-O-C peaks have not changed significantly.

Figure 6. Comparison between ATR averaged spectra of unsoiled sample before [1] and after [2] artificial ageing, and unsoiled sample not aged [3] (entry 4-8, Table 1), where [2-3] were laser irradiated (1.83 J/cm^2). Arrows on the dash-line show the increase in C=O groups around 1735 and 1634 cm^{-1}, which caused the yellowing, whereas the arrow on the dot-line shows the decrease in DEP at 745 cm^{-1}. The yellowing and DEP loss only appear in the aged samples, so it can be concluded that they are not due to the laser irradiation.