SURFACE DEGRADATION OF LINEN TEXTILES INDUCED BY LASER TREATMENT: COMPARISON WITH ELECTRON BEAM AND HEAT SOURCE

Franco FERRERO, Franco TESTORE
Dipartimento di Scienza dei Materiali e Ingegneria Chimica,
Politecnico di Torino,
Corso Duca degli Abruzzi, 24
10129 Torino, Italy
E-mail : ferrerof@athena.polito.it

Claudio TONIN, Riccardo INNOCENTI
Consiglio Nazionale delle Ricerche,
ISMAC, Istituto per lo Studio delle Macromolecole, Sez. Biella
Corso G. Pella, 16
13900 Biella, Italy
E-mail : C.Tonin@irl.to.cnr.it

Abstract

Surface degradation of linen fabric induced by laser treatment with the aim of reproducing an image was investigated and compared with the degradation induced by an electron beam and a heat source. The results confirm that the brown shades obtained by the laser beam are mainly due to surface tar formation, and that the degradation pattern is similar to that observed by treatment with an electron beam. Surface thermal treatment, however, showed different fibre behaviour.

Key words

linen fabrics, laser treatment, electron beam, heat, surface degradation

Introduction

Thermal degradation of cellulose has been extensively investigated [1] in order to explain the pyrolysis mechanism occurring in combustion of cellulosic materials. Moreover, the textile, pulp and paper industries have been concerned about ageing and degradation occurring at high temperature in the manufacture or drying of cellulose fibres.

In a previous paper [2], thermal degradation of linen fabrics was investigated and a similar pattern to that for cotton degradation was found. However, the essential influence of textile cleaning on thermal behaviour was clearly demonstrated.

Another work was carried out by Testore [3] in order to contribute to explain the formation of the image visible on the Shroud of Turin, undoubtedly the most studied of the ancient linen fabrics. The latest sampling of the Shroud was performed in 1988 for radiocarbon dating only [4], and further investigations were unauthorised until now. The rigorous scientific studies on the Shroud image carried out by the STURP (Shroud of Turin Research Project) researchers in 1978 [5] concluded that the image appearing on the Shroud could not have been made by painting or printing, and was the result of a chemical surface change of the linen due to dehydrative acid oxidation of the cellulose, without the addition of any kind of extraneous materials. Moreover, since the image was recognised to have a three-dimensional feature, this could not be obtained simply by a hot device (statue or bas-relief) transfer, which generally yields deformed images.

Therefore Heller [6] further considered the ionising radiations as gamma rays, X-rays, UV plus electrons and alpha particles, though he believed that ionising radiations produce alkaline oxidation. He exposed linen to six hours of intense UV radiation and found neither acid oxidation nor a straw-yellow colour. Moreover, the same scientist observed that the radiation coming from an ordinary

source radiates in all directions, whereas it becomes unidirectional and parallel (as the image feature requires) when it comes from a laser.
The aim of Testore's project [3] was thus to reproduce the image of the Shroud of Turin by a laser marking system. Since the image colours are a variation of brown shades, the surface of linen fabric was burned by a laser beam, and the degree of darkening was varied by varying the laser beam power. The main task was to find the best parameters for a high contrast with dark and light shades with no significant material damage. After many trials, a good reproduction of the face of the Shroud was obtained with a three-dimensional feature as the original image. The photograph of this reproduction yields a reversed image, quite similar to that obtainable with the Shroud itself.
In the present paper, the surface degradation of linen resulting by this laser treatment was analysed and compared with the modification induced by an electron beam and a heat source. The results will lead to better knowledge of the interaction between ionising radiations and cellulose fibres, similar to that which was supposed to explain the fascinating problem of the formation of the Shroud's image.

Experimental

Materials

Five types of linen fabric were laser treated:

- type 1: very fine (180 g/m^2) unbleached light brown herring-bone twill, woven on purpose in order to reproduce a fabric very similar to the Shroud;
- type 2: rough unbleached brown raw flax cloth with coarse threads (320 g/m^2);
- type 3: fine (200 g/m^2) bleached light shade cloth;
- type 4: ancient Egyptian linen from 1200 BC;
- type 5: ancient Egyptian burial cloth linen from 2500 BC.

Laser treating

At first, some attempts at laser treating were made at RTM, Vico Canavese, Torino, Italy. Later, several linen treatments were done at the Fraunhofer Institute for Laser Technology (ILT), Aachen, by means of a Laser Graver SE225CV, produced by Laser Machining Inc.. It consists of a CO_2 laser and two CNC-controlled axes, where one axis moves the focusing optic (fast scanning direction), and the lateral movement is made by a slow but precise spindle drive on which the linen fabric is fixed. The laser is a pulsed system with a maximum average power of 30 W, but in the linen treatment the power was set in the range from 7.8 to 14 W according to desired shade (from light to dark) with a frequency from 279 to 327 Hz.
The laser graving machine works like a printer. The image is generated with a design software or imported in any graphic file format. The file with the necessary information for the laser graving machine is generated by a printer driver and sent to the machine via the parallel port. All the specific data (laser power, speed, etc.) can be adjusted in the printer driver menu.
Moreover, many trials on type 3 linen were done at FER.TECNIC, Oleggio, Novara, Italy, with the same machine type with a maximum average power of 18 W, by setting the distance of the linen from the laser source at 42 mm. The resulting darkenings were light brown shades without any apparent fibre weakening.

Electron beam treating

The samples were mounted for the SEM analysis as described later, and were exposed to an electron beam of 30 kV for 5 sec in the vacuum chamber of the electron microscope. SEM analysis only was afterwards performed on these samples.

Heat source treating

Linen samples were darkened with the aid of a soldering-iron by varying the degradation intensity with the contact time, whereas the iron temperature was kept at 150°C or 160°C.

SEM analysis

The samples were mounted in aluminium specimen stubs with double-sided adhesive tape, and coated with a 20-nm-thick gold layer in a rarefied argon atmosphere at 0.1-0.2 mbar, an Emitech K 550 Sputter Coater being used with a deposition current of 20 mA for 180 s. Microscope investigation was performed with a Cambridge S 240 SEM, with an acceleration voltage of 15 kV and a 16-mm working distance.

DSC analysis
DSC analysis was performed with a Mettler TA 3000 apparatus equipped with a DSC 20 cell purged with nitrogen. The temperature program was set in the range from 50 to 450°C, at heating rate of 20°C/min. The data was collected on a computer by using the Mettler Graphware TA72 software.

FTIR-ATR Spectrometry
The linen surface was examined by a FTIR-ATR apparatus, consisting of a Nicolet FTIR spectrophotometer equipped with a diamond single-reflection ATR cell (Golden Gate by Graseby Specac). This device allows analysis of a thin surface layer of the sample (4.4 μm effective path length) with a focused sample aperture of 0.6 mm, under strong and reproducible pressure (up to 3 kbar). Hence, single fibre and particulate micro-sampling analysis is routine.

Results and discussion

At first, two samples of types 1 and 2, laser treated, with dark shades, were analysed. Very fine cloth (type 1) was strongly weakened even at low laser beam power. The SEM analysis showed cellulose degradation as swelling and explosion, yielding a sponge-like structure (Figure 1). The same degradation pattern was shown by the type 2 sample (Figure 2), although the rougher cloth has higher residual strength after the treatment.

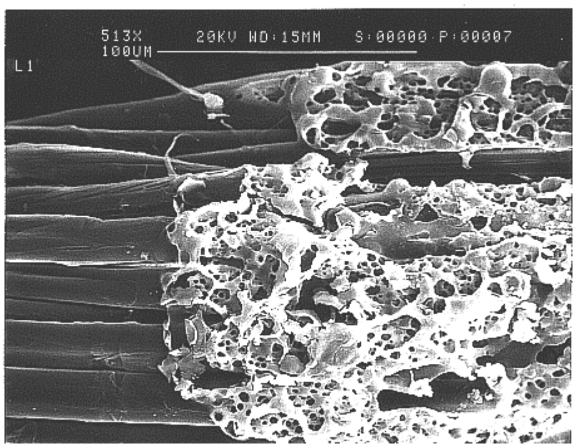

Figure 1. SEM micrograph of linen of type 1 laser treated

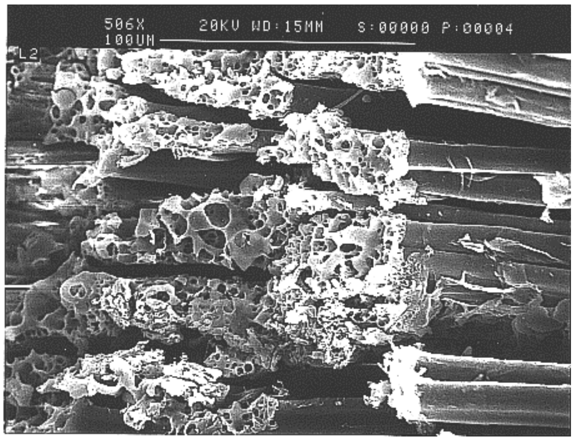

Figure 2. SEM micrograph of linen of type 2 laser treated

The chemical modification induced in these linen fibres by laser treatment was investigated by FTIR-ATR spectrometry. In Figure 3, six spectra are compared in the wave number range from 1900 to 1500 cm^{-1}: type 2 raw cloth, unbleached and bleached, type 2 laser treated, light and darkened, and type 1, light and darkened. Marked differences in spectra arise in the range from 1620 to 1640 cm^{-1} attributable to carbonyl groups. Surprisingly, in FTIR-ATR spectra absorbance decreases with laser treating and darkening, as well as after bleaching. The dehydration hypothesis, however, was confirmed by the SEM analysis, which clearly showed the evolution of gaseous products such as water vapour and/or carbon dioxide. Consequently, the dark shades could be ascribed to surface tar formation rather than conjugated carbonyl chromophores.
On the other hand, DSC analysis of the above samples showed no significant difference between treated and untreated samples, due to the fact that DSC differs from FTIR-ATR spectroscopy because it is a bulk, not surface, analysis; and the degradation induced by the laser beam, although locally deep, was strictly limited to the dark shades as confirmed by the SEM micrographs.

The linen of type 3, bleached and hence cleaner than the others, allowed milder conditions of laser treatment to obtain a wide contrast range. Thus, treated samples appear to be practically unweakened by the laser. The SEM analysis, however, confirms a degradation pattern very similar to the other samples, as can be seen in Figure 4, although the sponge-like effect is limited to a surface layer of fibres. FTIR-ATR analysis showed a marked absorbance decrease in the spectra of the sample laser treated at 3250 cm^{-1} only (peak due to OH groups), in comparison with the spectra of the untreated sample (Figure 5), and this result reconfirms the dehydration hypothesis.

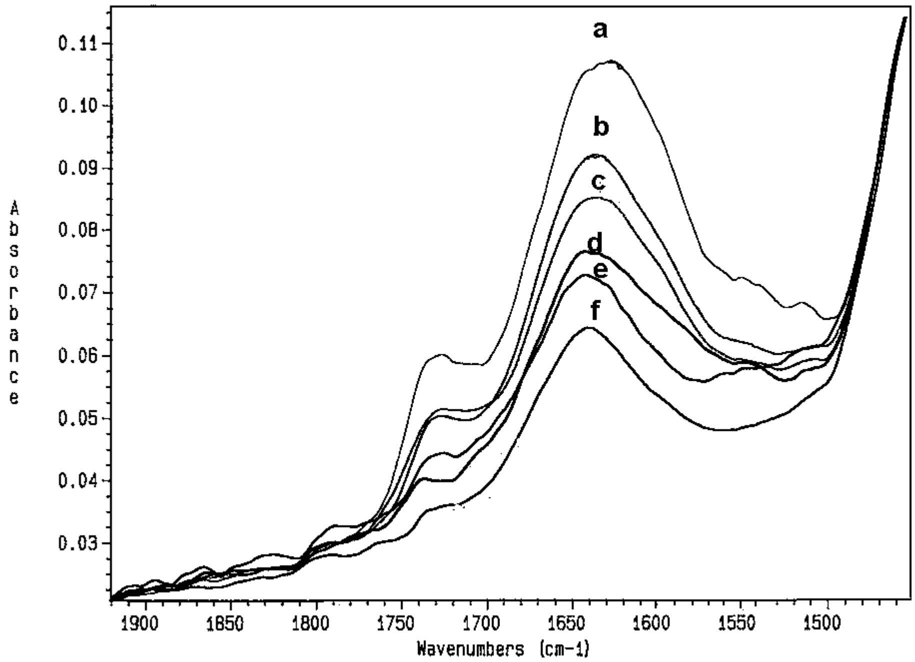

Figure 3. FTIR-ATR spectra of six linen samples: a) raw linen of type 2, b) linen of type 2 laser treated light, c) linen of type 2 laser treated darkened, d) linen of type 2 bleached, e) linen of type 1 laser treated light, f) linen of type 1 laser treated darkened

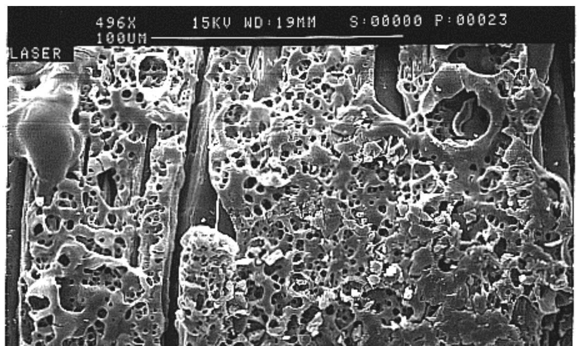

Figure 4. SEM micrograph of linen of type 3 laser treated

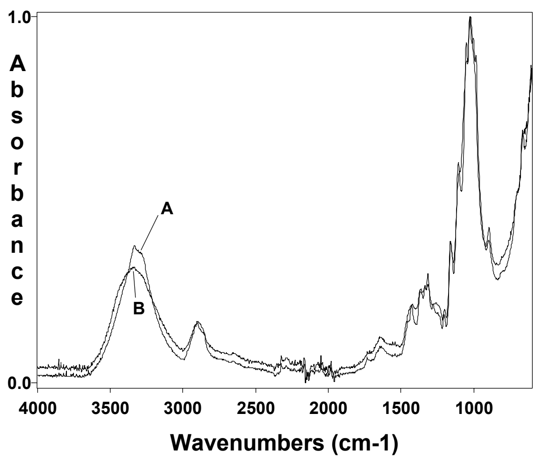

Figure 5. FTIR-ATR spectra of linen of type 3: A) untreated, B) laser treated

The ancient linen of types 4 and 5 after laser treatment showed the same surface modification (Figures 6 and 7) practically unaffected by the age and impurities of the samples.

A sample of linen of type 3 was then treated with the electron beam source, and the surface degradation was found very similar to the laser induced one. However, the fibres were not linked in a sponge-like structure, probably because the treatment in this case was carried out under vacuum where the evolution of gaseous products is favoured without swelling of the material (Figure 8).

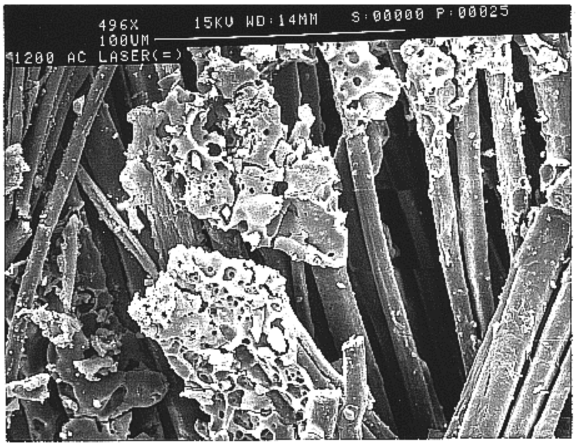

Figure 6. SEM micrograph of linen of type 4 laser treated

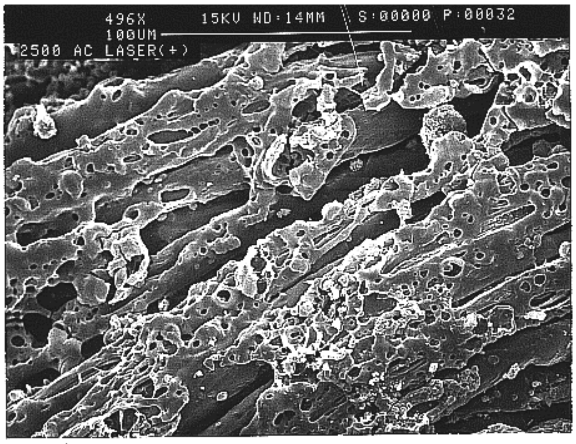

Figure7. Figure 7. SEM micrograph of linen of type 5 treated

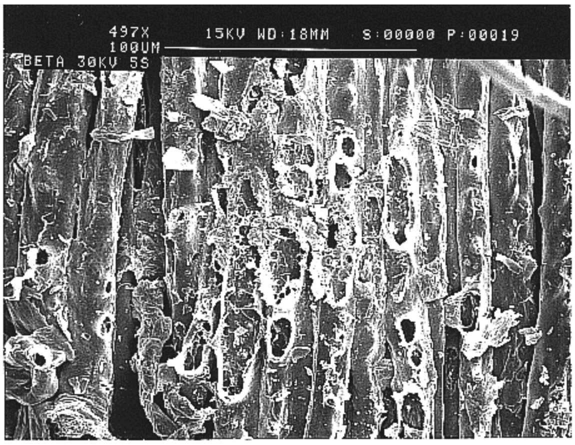

Figure 8. SEM micrograph of linen of type 3 after electron beam treatment

Finally, many tests were carried out with the heating source described above. The micrographs of two linen samples of type 3 treated at 150°C and 160°C respectively for 10 min are shown in Figures 9 and 10.

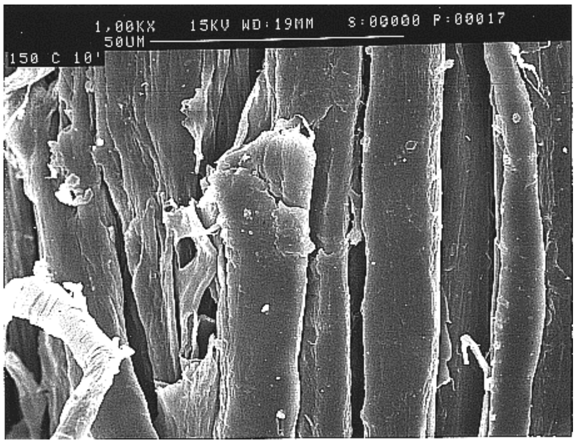

Figure 9. SEM micrograph of linen of type 3 after heat treatment at 150°C for 10 min

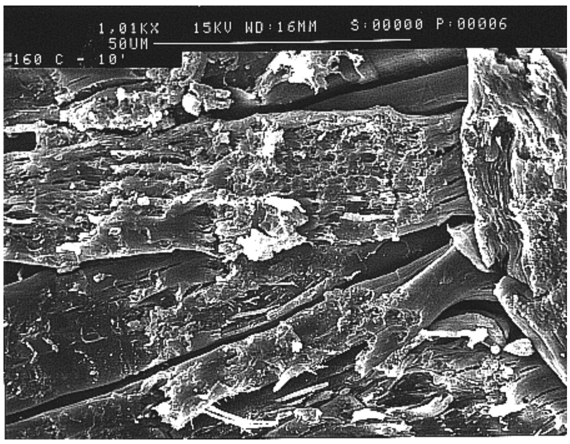

Figure 10. SEM micrograph of linen of type 3 after heat treatment at 160°C for 10 min

The degradation clearly increased together with the increase in temperature, but the pattern was quite different to that found with the ionising radiations. In fact the fibres seem to be morphologically unaffected at 150°C showing only some breaking points, whereas at 160°C a surface erosion of the fibres becomes evident.
A progressive darkening effect was however observed by reflection microscopy; this was stronger on the external threads which came into contact with the soldering iron. On the other hand, the FTIR-ATR spectra of these samples showed slight differences only in the content of OH groups, and the carbonyl group peak was practically unaffected by the thermal treatment.

Conclusions

The results of the present work confirm that the brown shades made on linen fabric by means of a laser beam in order to reproduce an image are due to a surface dehydration which results in surface tar formation. FTIR-ATR analysis did not prove the formation of conjugated carbonyl chromophores, whereas the SEM analysis has shown a localised surface degradation with a sponge-like structure, presumably due to the swelling and evolution of gaseous products. The degradation was deeper as the laser power was increased, and was substantially unaffected by ageing and cleaning of the linen sample.
The laser degradation was found to be quite similar to that induced by an electron beam, although in this case the fibres were not linked in a sponge-like structure. However, thermal treatment by heat source showed a different fibre behaviour with breaking and surface erosion, but a limited dehydration was found by FTIR-ATR analysis.
Moreover, the examination of some threads of the Shroud of Turin collected from the image area, according to the principles discussed in this work, could explain whether the darkening is due to a physical phenomenon such as ionising radiation or heat treatment.

Acknowledgements

The authors are very grateful to RTM, Vico Canavese, Torino, to Ing. Dieter Hellrung of the Fraunhofer Institute for Laser Technology (ILT), Aachen, and FER.TECNIC, Oleggio, Novara, for the many laser treating trials. This work was partially supported by the Fondazione Cassa di Risparmio di Torino.

References

1. *Shafizadeh F., "Thermal degradation of cellulose", Cellulose Chemistry and its applications (edited by T.P. Nevell and S. H. Zeronian), Ellis Horwood, Chichester, West Sussex, England (1985), pp. 266-289.*

2. *Ferrero F., Testore F., Malucelli G., and Tonin C., "Thermal Degradation of Linen Textiles: The Effects of Ageing and Cleaning", J. Text. Inst., Vol 89, Part 1 (1998), pp. 562-569.*

3. *Testore F., The Turin Shroud, past, present and future (edited by S. Scannerini and P. Savarino), Effatà, Cantalupa, Torino, Italy (2000), pp. 531-532.*

4. *Damon P.E., Donahue D.J., Gore B.H., Hatheway A.L., Jull A.J.T., Linick T.W., Sercel P.J., Toolin L.J., Bronk C.R., Hall E.T., Hedges R.E.M., Housley R., Law I.A., Perry C., Bonani G., Trumbore S., Woelfli W., Ambers J.C., Bowman S.G.E., Leese M.N., and Tite M.S., "Radiocarbon Dating of the Shroud of Turin", Nature, Vol 337 (1989), pp. 611-615.*

5. *Heller J.H., and Adler A.D., "A Chemical Investigation of the Shroud of Turin", Can. Soc. of Forensic Sciences J., Vol 14 (1981), pp. 81-103.*

6. *Heller J.H., "Science and the Image", Report on the Shroud of Turin, Houghton Mifflin Co., Boston, USA,(1984), pp. 206-218.*