Material characterization of historical parchment using terahertz time-domain spectroscopy

Tiphaine Bardon¹, Robert K. May², Philip F. Taday² and Matija Strlic¹
¹Centre for Sustainable Heritage, Bartlett School of Graduate Studies, University College London, 14 Upper Woburn Place, London WC1H 0NN, UK
²TeraView Ltd, Platinum Building, St John’s Innovation Park, Cambridge CB4 0DS, UK

Abstract—In this study we discuss the influence of the state of degradation, the three-dimensional fibrous structure and the presence of calcium compounds on terahertz absorption properties of historic parchment in the interval 45 – 85 cm⁻¹, based on the analysis of 32 archival parchment samples, with terahertz time-domain spectroscopy in transmission mode, optical microscopy and Fourier-transform infrared spectroscopy in attenuated total reflectance mode.

I. INTRODUCTION

PARCHMENT is prepared from wet de-haired skin of mainly calf, goat and sheep. It is constituted of collagen fibres and the three dimensional fibre structure depends on the animal species, degradation as well as the skin layer (grain or flesh) [1]. Collagen fibres are composed of fibrils of transverse collagen molecules held together by inter-molecular bonds, with each collagen molecule consisting of a triple-helical structure held by hydrogen bonds and water molecules. During degradation, the inter-molecular bonds between collagen molecules can break, causing the fibrous structure to collapse [1]. Many degradation processes, chemical as well as structural, can lead to denaturation of the collagen structure, and ultimately to the conversion of the ordered collagen fibres into a disordered gelatin-like material [2].

The state of degradation of parchment is most commonly determined using microscopic assessment of the shrinkage temperature of its fibres [3], with lower shrinkage temperature being indicative of more degraded material. This method requires sampling and is therefore micro-destructive. Since terahertz light is sensitive to water and inter-molecular vibrations [4], we investigated whether information such as the state of degradation can be non-invasively assessed based on the terahertz absorption properties of a parchment.

II. RESULTS

Thirty two parchment sheets of approximately 2 cm x 2 cm were sampled from documents dating from the mid-17th to the early 20th century, with known thickness and shrinkage temperature [2], and were analyzed with terahertz time-domain spectroscopy using a TPS spectra 3000 (TeraView Ltd, Cambridge) in transmission mode within the range 5 – 85 cm⁻¹ (0.15 – 2.55 THz). 1800 scans were collected at 1.2 cm⁻¹ spectral resolution. The sample compartment was purged with nitrogen to minimize terahertz absorption by atmospheric water vapour. Each parchment sample was analyzed in triplicate while changing the orientation of the sample between each measurement to account for any scattering effect. Their absorption coefficient in the spectral region with the lowest standard deviation is shown in Figure 1. Spectral features in the low frequency region (5 – 45 cm⁻¹) arise from the Fourier-transformation of the partially overlapping pulses reflected from the front and back surfaces of the parchment sheet and are therefore largely influenced by the thickness of the sheet. The slope of the linear absorption in the region 45 – 85 cm⁻¹ (extracted from the linear fit of the curves) appears however to be influenced by several other parameters, as shown in Figure 2.

Both flesh and grain sides of the 32 parchment samples were also analyzed with attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, using the Alpha-P Bruker at 4 cm⁻¹ resolution. The presence of calcium compounds on either sides of the sheet was certified by the spectral features at ~ 710, 875 and 1410 cm⁻¹ for calcium carbonate and ~ 670, 1110 and 1620 cm⁻¹ for calcium sulfate [5]. These salts probably originate from the lime (Ca(OH)₂) solution in which the skin is originally soaked, or from powdered chalk (CaCO₃), gypsum (CaSO₄) and quicklime (CaO) applied on the surface of the de-haired skin to remove the excess of grease and moisture, improve the adhesion of ink on the fatty and porous parchment skin and prevent it from running [6].

The surface on both flesh and grain sides was also observed with an optical microscope in reflection mode (SP-400, Brunel Microscope), and it either showed a clear network of parchment fibres, or a very dense and uniform structure in which barely any fibre could be distinguished even at the highest magnitude (x 400).

Principal Component Analysis (PCA) was performed using Origin Pro 8.6 software on a dataset containing, for each of the 32 samples (i.e. observations), the value of the slope of its linear absorption coefficient in the spectral region 45 – 85 cm⁻¹ (Slope), its thickness (d), the shrinkage temperature of fibres sampled from its surface (ST), the absence (0) or presence (1) of calcium salts on either of its surfaces (Ca) and the absence.
(0) or presence (1) of a clear and loose fibre network on either of its surfaces (FS, for Fibrous Structure). The correlation matrix of the set of data was calculated and used to extract the principal components. We present the results in Figure 2 as biplots, i.e. 2D scatter plots with the first two principal components as x and y axis and the 32 samples as points, with superimposed loading vectors for each variable (Slope, Ca, d, ST, FS) indicating their associated direction of variance separation. The percentage of variance associated with the first two principal components cumulatively is 62.45%.

The state of degradation, i.e. the shrinkage temperature (Figure 2a), does not seem to contribute to the absorption properties of parchment, as the angle between ST and Slope vectors is close to 90 degrees.

However, it appears that the presence of calcium salts is strongly positively correlated with the slope. There is therefore a very good separation of the samples according to their calcium content (Figure 2b) along the first principal component axis, which is the factor that best represents the slope. It can be concluded that the presence of calcium salts on the surface of a parchment sheet leads to a stronger absorption of parchment in the terahertz region 45 – 85 cm⁻¹.

The fibrous structure (FS) is negatively correlated with the slope of the absorption coefficient (Figure 2c), i.e. the angle between FS and Slope vectors is greater than 90 degrees: this negative correlation implies that the lower value (0), associated with a very dense and homogeneous structure, corresponds to a steeper slope. Therefore a parchment sheet with a dense fibrous structure on both flesh and grain sides tends to absorb more terahertz light than a parchment sheet with a clear and loose network of fibres on either side, which allows for more terahertz light to be transmitted through. Given the correlation between the shrinkage temperature and the fibrous structure (i.e. acute angle between FS and ST vectors), it is possible that the fibrous structure parameter accounts for both the state of degradation of parchment, the animal species used for the skin and the process of the skin altogether.

Finally, although the absorption coefficient is already calculated using the thickness of the sheet, the slope of the absorption coefficient and the thickness still are strongly correlated (i.e. the angle between Slope and d vectors is almost zero), implying that thicker parchment sheets lead to a steeper absorption slope.

III. SUMMARY

The study of 32 historical parchments with terahertz time-domain spectroscopy, optical microscopy and infrared spectroscopy reveals that the thickness of a sheet, the three-dimensional fibre structure and the presence of calcium salts on both flesh and grain sides have a synergetic influence on the absorption properties of parchment in the terahertz region 45 – 85 cm⁻¹. Further studies are being undertaken to concentrate on the possible correlation between the shrinkage temperature of the parchment fibres and the absorption properties of parchment in the terahertz region, towards the development of a non-invasive method to assess the state of degradation of parchment. Such studies involve terahertz time-domain spectroscopy of thermally degraded parchment samples from the same historical document (i.e. same fibrous structure, thickness and chemical composition), as well as further terahertz time-domain spectroscopic measurements of historical parchment sheets.

IV. REFERENCES