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POLARISED-ATR-FTIR CHARACTERISATION OF CELLULOSIC FIBRES IN RELATION TO HISTORIC ARTIFACTS

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Summary

The utility of polarised attenuated-total-reflectance (ATR) FTIR spectroscopy was investigated for the identification of cellulosic fibres and characterisation of their state of degradation.

Turning the polariser so that the electric vector is parallel (E_{pll}) or perpendicular (E_{prp}) provides a means of assessing the orientational crystallinity of cellulose from the polarised spectra of aligned plant fibres. Analysis of the spectra can reveal both the angle of microfibrillar wind and its directionality. Here, the best fits to the data suggest: flax 7°/S-spiral; sisal 25°/Z-spiral; coir 70°/S-spiral, where the predominant twist is given for the outer cell-wall regions sampled.

Polarised-ATR-FTIR also allows degradation of the amorphous component of cellulose to be highlighted, by recording spectra with the optimum alignment of fibre and polariser. Changes observed on thermal ageing of flax in air at 190 °C are consistent with oxidation of amorphous cellulose and formation of carbonyl and carboxylate moieties; the non-dichroic nature of the carbonyl band confirms that the ordered crystalline regions were not primarily involved.

Keywords: Polarised-ATR-FTIR, cellulose, microfibril, crystallinity, ageing, degradation

Polarised-ATR-FTIR Characterisation of Cellulosic Fibres in Relation to Historic Artifacts

by PAUL GARSIDE AND PAUL WYETH

INTRODUCTION

Plant fibres are the principal components of older cellulosic artifacts. Paper and textiles may contain flax, hemp, cotton fibres etc. Characterisation of the fibres has some merit, not only from a historic perspective but also for enabling informed conservation. The different fibres may show singular deterioration patterns and warrant customised approaches to treatment.

Vibrational spectroscopy has found its place amongst the variety of fibre micro-identification methods [1,2] and presents the additional advantage that the products of cellulose degradation can be monitored [3-7].

In following deterioration, particular emphasis has been placed on the value of the technique in revealing carbonyl and carboxyl moieties in cellulose, corresponding to oxidation and acid promoted dehydration during ageing. For example, both FTIR-attenuated total reflectance (ATR) and photoacoustic spectroscopy have confirmed that surface photo-oxidation of cellulose, with carboxylic acid generation, is predominant after short-term accelerated ageing [8,9].

Acid hydrolysis of cellulose may also cause an increase in crystallinity [10], and besides monitoring the chemistry, various FTIR-based methods have been proposed for quantifying such changes and monitoring crystal modification [11], such as the derivation of the $\frac{1372}{2900}$ crystallinity index [12]. Plane-polarised infrared radiation has been used to highlight other bands which reflect crystallinity and to aid in band assignment [13].

The relative cellulose crystallinity and orientation have a significant bearing on the strength of plant fibres [14]. The structural braces of plant cell walls are wound at a characteristic angle and sense around the fibre axis; those in the primary walls of cells tend to be less crystalline and somewhat disordered, while secondary wall microfibrils are generally well ordered and crystalline [14]. A detailed polarised FTIR microspectroscopy study on microfibril orientation in wood has been completed [15]. However, currently, the orientational crystallinity of fibres within historic artifacts and associated changes with ageing have not been investigated, despite the correlation with fibre strength.

In furthering this aspect of the analyses, we have assessed the utility of polarised attenuated-total-reflectance (ATR) FTIR spectroscopy and have shown it to have value in determining the angle of microfibrillar wind within the cell walls and to have some potential in revealing differential ageing within the amorphous and crystalline regions of the cellulose of flax fibres.

POLARISED FTIR-ATR AND MICROFIBRIL ORIENTATION

With the standard ATR accessory, samples are pressed against the surface of a prism and the infrared beam probes the interface. The simplicity and reproducibility of sampling by the ATR technique, its robustness when using a diamond prism [16] and, for example, its value in probing a paper surface layer of just a few microns [9] have been noted. For the experimental arrangement employed here the penetration depth was calculated to increase from 0.7 μm at 4000 cm^{-1} to 4.0 μm at 700 cm^{-1}.

Experimental method

Spectra were recorded on a BioRad 135 FTIR spectrometer and a Graseby Specac Golden Gate single reflection ATR accessory (diamond prism with 45° incident angle, sapphire anvil, sampling area 600 μm diameter). Each spectrum was averaged over 32 scans for the region 4000-700 cm^{-1}, with a resolution of 4 cm^{-1}, and was ratioed to the background. Spectral baselines were corrected in Grams 5 software assuming zero absorbance at 3700, 2500, 1800, 1185 and 770 cm^{-1}. Flax samples were single fibres or threads taken from linen cloth; sisal and coir samples were unprocessed fibres. In assessing orientational crystallinity, spectra were recorded with the fibres rotated successively by 7.5° from 0° to 180°; samples were renewed after each 45° rotation to avoid potential problems with repeated stress. Polarised spectra are designated as E_{pll} (i.e p-polarised) or E_{prp} (i.e. s-polarised), indicating the direction of polarisation of the electric field vector as either parallel or perpendicular to the plane of incidence of the infrared beam at the diamond/fibre interface. For the determination of peak heights close baselines were drawn.

Oriented crystallinity

Figure 1

The ATR spectrum of flax fibre is dominated by that of cellulose. The intensities of some of the bands change when the polariser is introduced (Fig. 1). For flax the most marked differences are seen in the E_{prp} spectra, when the fibre is moved from 0° to 90° (i.e., respectively, parallel and perpendicular to the electric field vector in the diamond crystal/ fibre interfacial plane). Randomly oriented crystalline cellulose and amorphous cellulose will contribute to the underlying absorption at all positions of the fibre. The dichroic bands are associated with ordered cellulose structures, i.e. the spiraling microfibrils [13].

The polymer chains in the cellulose I crystallites of flax run almost parallel to the fibre axis. With the electric vector parallel to the chain direction (fibre 0°) the most prominent dichroic peaks correspond to a δ CH_2 scissoring motion (1425 cm^{-1}), δ CH deformations (1372, 1360 cm^{-1}) and a ν antisymmetric ring breathing mode (1160 cm^{-1}); the ν COC symmetric glycosidic stretch or a ring stretching mode (1105 cm^{-1}) is also moderately responsive. Peaks due to δ OH deformation and δ CH_2 wagging (1335, 1315 cm^{-1}) are the more prominent when the interfacial plane electric vector is perpendicular to the chain direction. In the main, these results are consistent with those of Blackwell and co-workers [13] for *Valonia ventricosa* cellulose I crystallites (band assignments are taken from this reference). While no peaks are truly non-dichroic, for the ATR spectra the most appropriate normalisation reference appears to be the very weakly dichroic 1060 cm^{-1} band (ν CO secondary alcohol).

Figure 2

The intensities of the dichroic bands change gradually as the fibre is turned through 180°; this is illustrated for the band at 1160 cm^{-1} (Fig. 2). Theoretical fits are also shown to three simplistic models in which the variation in band intensity is related to the change in projection of the electric field vector onto the microfibrils of a flattened fibre, as the fibre is rotated. In each case, the oriented microfibrils are taken to spiral at an angle of 7° to the fibre axis. The data fit is improved somewhat if it is assumed that the twist is not only S, but that there is a 20% contribution from Z-spiraling microfibrils. The depth of sampling is about 2μm, and the results suggest that, in terms of the oriented components, two layers of opposite twist are being probed, consistent with a thin, outer Z-spiraling layer covering a thicker, S-spiraling layer. The results hint at the possibility of determining both the angle of microfibrillar wind and, by taking advantage of the shallow penetration afforded by ATR, the sense of wind in the outer layers of walls of other fibres.

Figure 3

Similar experimental data is shown for sisal and coir fibres, with overlaid best fit theoretical plots. These suggest winding angle values of 25° and 70° respectively, with predominant Z spiral and S spiral winding in the outer layers of the cell walls.

APPLICATION TO THERMALLY DEGRADED FLAX

Spectral features may be accentuated by recording the polarised-ATR spectrum with the optimum alignment of fibre and polariser. Since deterioration of cellulose will proceed from the amorphous zones, selecting the polariser orientation to reduce the contribution of the ordered crystalline regions may serve to emphasise such degradation .

Experimental method

Suspended flax cloth was heated in air at 190 °C for up to 43 hours. Humidity was not controlled but individual threads were removed for polarised ATR analysis soon after treatment.

Degree of crystallinity

The apparent $\frac{1372}{2900}$ crystallinity index (non-polarised ATR spectra) decreased gradually from 0.61 to 0.40 over the course of thermal ageing. The values are not directly comparable with those reported by Nelson and O'Connor [12], since, besides other considerations, in ATR spectroscopy the sampling volume is wavelength dependent. While some caution must be exercised in applying this analysis for degraded material, the changes observed in a second crystallinity index, $\frac{1425}{895}$, are quite similar, lending some confidence to the interpretation. However, since the relevant bands show dichroism the determination of the indices from the polarised spectra is not so appropriate.

Chemical modification

Heating cellulose in air is expected to induce depolymerisation, with cleavage of glycosidic bonds in the accessible regions, leading to a decrease in tensile strength; carbonyl and carboxyl groups are formed through oxidation [17].

Figure 4

The use of polarised ATR may emphasise those changes occurring in the more susceptible, amorphous regions of the cell wall. This can be seen the more clearly in the E_{prp} spectra, where the sense and degree of dichroism is such as to highlight the 1300-1350 cm^{-1} peaks in the amorphous region in the fibre 0 spectra, while band changes in the 1350-1500 cm^{-1} region are evident in the fibre 90 spectra (Fig. 4). Progressive changes in intensity are seen (which are rather less evident in the non-polarised spectra): decreases at 1455 cm^{-1} (δ OH primary and secondary alcohol), 1425 cm^{-1} (δ CH_2), 1335 cm^{-1} (δ OH) and 1315 cm^{-1} (δ CH_2) besides the increased absorption in the carbonyl region (1600 - 1800 cm^{-1}), all consistent with degradative thermal oxidation. A similar analysis of the E_{pll} spectra is not so revealing for the lower wavenumber range, since this relates to perpendicular bands, and the electric field vector has a perpendicular component relative to the interface. For the fibre 0 spectra, however, the parallel component of the electric field vector is at right angles to the fibre axis, so that parallel bands in the 1350-1500 cm^{-1} region are minimised, once again highlighting the amorphous or randomly oriented crystalline cellulose.

The carbonyl absorption at 1720 cm^{-1} progressively grows during thermal ageing. There is coincidence in the plots of peak intensities of the normalised carbonyl peaks versus treatment time for the E_{pll} and E_{prp} spectra (Fig. 5). This indicates the non-dichroic nature of the carbonyl band and confirms that the ordered crystalline regions were not primarily involved.

Figure 5

CONCLUSION

Our results suggest that polarised attenuated-total-reflectance (ATR) FTIR spectroscopy has some utility in the study of cellulosic fibres.

The orientational crystallinity of cellulose is highlighted in the polarised spectra of aligned plant fibres. Analysis of the spectra can reveal both the angle of microfibrillar wind and its directionality. Here, the best fits to the data suggest: flax 7°/S spiral; sisal 25°/Z spiral; coir 70°/S spiral, where the predominant direction of wind is indicated for the outer cell-wall layer of each.

Ageing of the amorphous component of cellulose can be highlighted by recording spectra with the optimum alignment of fibre and polariser. Changes observed on thermal ageing are consistent with oxidation of amorphous cellulose and formation of carbonyl and carboxylate moieties; the non-dichroic nature of the carbonyl band confirms that the ordered crystalline regions were not primarily involved.

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FIGURE LEGENDS

Figure 1: E_{prp} polarised-ATR-FTIR spectra of flax (1500-800 cm^{-1}) normalised to the 1060 cm^{-1} peak. Spectra are shown for two fibre orientations, 0° and 90°, respectively, parallel and perpendicular to the electric field vector component in the diamond crystal/ fibre interfacial plane.

Figure 2: Illustrations of the 1160 cm^{-1} peak intensity change (E_{prp} spectra) during the rotation of flax fibres. The data is normalised with respect to the peak intensities at 1060 cm^{-1}. The solid line overlays are theoretical fits to three simplistic models. In (a) the oriented microfibrils are taken to spiral at an angle of 7° to the fibre axis with an S twist. The data fit is improved somewhat if there is a 20% contribution from Z-spiraling microfibrils (b), but not if there is an equal contribution (c). The following equation was used in the calculations:

$I = [x\{\cos(\rho + \alpha)\} + y\{\cos(\rho - \alpha)\}]/(x+y)$, where I is the relative band intensity, x and y are the relative contributions of the two layers sampled, ρ = angle of fibre orientation, and α = winding angle.

Figure 3: Plots of the normalised intensities of the band at 1160 cm^{-1} (R) in E_{prp} spectra of flax, sisal and coir fibres versus fibre orientation. The lines represent the expected trends for the model in which two outer layer are sampled, with 80%:20% contributions.

Figure 4: Stacked E_{prp} polarised-ATR-FTIR spectra of flax (1800 - 1100 cm^{-1}) recorded after various times of thermal ageing at 190 °C: (a) Fibre 0° orientation, (b) Fibre 90° orientation.

Figure 5: Plots of the normalized 1720 cm^{-1} carbonyl absorption intensity from the non-polarised, E_{prp}/Fibre 0° and E_{pll}/Fibre 90° ATR spectra of thermally aged flax fibres, plotted against treatment time.