

OXIDATIVE AND HYDROLYTIC PATH OF PAPER DEGRADATION STUDIED BY IN-SITU FTIR TRANSMISSION SPECTROSCOPY

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1. Motivations

Millions of books worldwide are menaced by paper disintegration due to malignant and inevitable degradation of cellulose chains caused by acid catalysed hydrolysis of glycosidic bonds. In order to prevent this process mass deacidification programmes have been launched. These now go hand in hand with research which should deepen our understanding of the observed phenomena.

According to the most recent findings, cellulose degradation should be regarded in terms of oxidative and hydrolytic mechanisms¹⁻³ where the two reaction paths are autocatalytically accelerated by active oxygen species and protons, respectively. Notwithstanding, paper degradation kinetics is still based on formal rate laws^{4,5} which are with better or worse results, used to generate kinetic curves representing accelerated ageing of cellulose.

Typically, paper degradation progress is traced by mechanical or physical properties of paper such as tensile strength, fold endurance^{1,6}, dynamic modulus or mechanical loss tangent⁷. However, these properties provide only macroscopic information. Another implemented parameter has been the degree of polymerisation representing an average polymerisation state of cellulose chains. Even though of paramount and practical importance, these parameters do not give a real insight into molecular behaviour during the degradation process. By contrast, highly sensitive to structural changes in materials, vibrational spectroscopy seems still to have an unexploited potential in modelling of kinetics of cellulose degradation, in spite of copious amount of published material.

The goal of this work is a verification of oxidative and hydrolytic paths in cellulose degradation mechanism to finally combine them in a formalism of mixed-controlled kinetic model⁵. In particular, it concentrates upon refining an in situ FTIR transmission technique to study accelerated ageing of paper materials. The most essential advantage it has over other IR techniques is that the technique provides information from the same sample area and allows us to observe real time chemical changes in material under controlled conditions. Due to the spectral complexity our focus in this work has been the 1400-1800 cm⁻¹ region where CO groups of different degrees of freedom occur. However, there are controversies in the literature concerning band assignment even in such a limited range.

2. Experimental

For the kinetic studies, we used model paper (P1) samples: bleached sulphite softwood cellulose paper with 99.5 wt % cellulose content (grammage: 78 g/m², BET: 1.21 m²/g) obtained from the Netherlands⁸. In order to collect transmission spectra thin paper plates were prepared from P1.

The spectra were recorded by a FTIR spectrometer (Bruker Equinox 55) with a MCT detector at an optical resolution of 2 cm⁻¹ and 2 level zero-filling. For the accelerated ageing tests the quartz reaction chamber with ZnSe optic windows was placed in the sample compartment of the spectrometer. The chamber was equipped with an electric furnace enabling heating in the broad temperature range (to 900°C) and with a gas supplying and evacuating system.

3. Results

Benefiting from the above mentioned advantages offered by the *in situ* experimental setup we have proposed methods of paper spectra standardisation:

1. Spectra normalisation using an internal standard defined as an integral absorbance of the CH 1900 cm⁻¹ band in the range 3000-2800 cm⁻¹, and denoted as standard absorbance;
2. Removal of water molecular vibrations from carbonyl vibration region by preliminary desorption of H₂O from samples and by recording the spectra at elevated temperatures;
3. Introduction of the oxidation index, defined as a ratio of integrals of bands at 1730 cm⁻¹ to that at 1620 cm⁻¹.

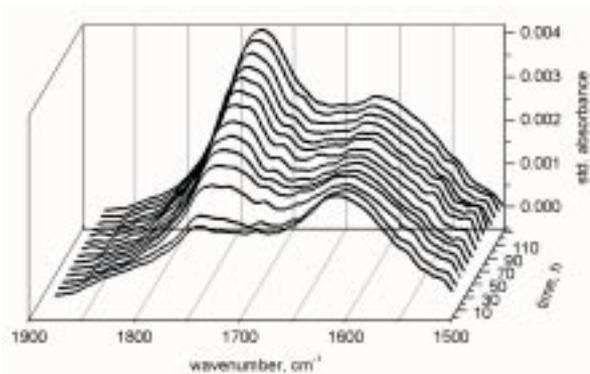


Figure 1: Isothermal oxidation of model paper (P1) sample in the dry air atmosphere at 150 °C monitored every 10 h by in situ FTIR measurements.

Complementarily, to remove water vibrations from the CO spectrum region, isotope exchange was applied and optimised. The applicability of this method for ageing experiments is, however, limited, because the properties of D-exchanged samples are different from original protonated samples.

The boundary conditions of experiments selected by us proved to be able to discriminate between hydrolysis of glycosidic bond and oxidation of carbon atoms in glycopyranose anomers. Accordingly, under the conditions of various gas mixtures (dry air, water vapour, humid air) two types of experiments were performed: (i) short ageing tests at three selected temperatures (100, 150, 250 °C) and (ii) longer isothermal tests. Following the changes in spectra in the carbonyl range as they increased with oxidation time (an example in Figure 1), various intermediates of cellulose oxidation were distinguished starting from the least oxidised monocarbonyl groups, through diketones to aldehydes and carboxyles.

The band assignment was supported by the spectra fitting by mixed Lorentzian-Gaussian function optimization and literature data. The changes in band intensities during paper oxidation were found to correspond to a parallel-consecutive mechanism. In the first approach a simple model taking into account both band positions, and presumed reaction mechanism, is proposed and is schematically presented in Figure 2.

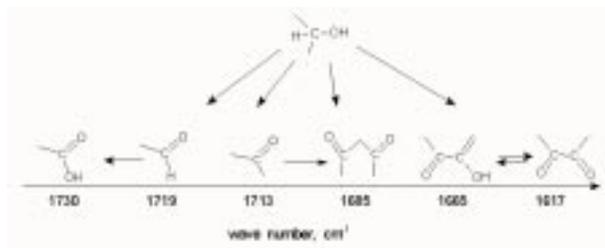


Figure 2: Consecutive-parallel mechanism of partial oxidation of cellulose, where intermediate products are represented by functional groups included in monomers and associated with frequencies of their vibrations.

The assumptions were verified by independent experiments. The position of -COOH stretching mode at 1730 cm⁻¹ was confirmed by the experiment utilizing the acidic groups neutralization with a dilute KOH solution (Figure 3). As a result of the reaction with KOH, the intensity of vibrations at 1730 cm⁻¹ weakened (curve b). At the same time the sub-bands coming from other intermediate products of cellulose oxidation revealed.

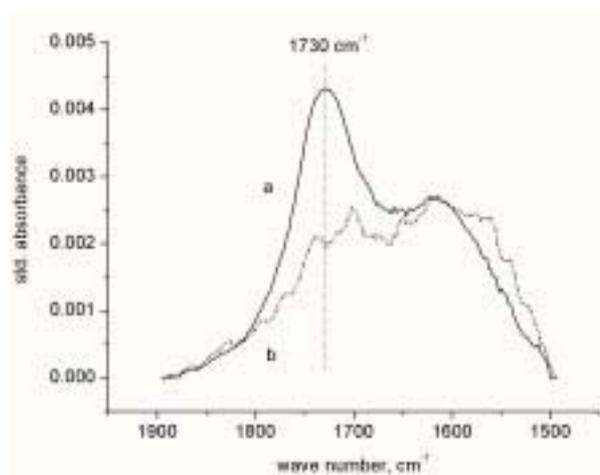


Figure 3: Model paper (P1) sample: a) aged for 110 h in dry air at 150 °C, b) then neutralised with 5×10^{-2} mol/dm³ KOH solution and washed with distilled water.

4. References

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