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Cellulose oxidative and hydrolytic degradation: In situ FTIR approach

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Abstract

This study concentrated upon refining an in-situ FTIR method to study accelerated ageing of paper under controlled conditions. The standardisation method applying the CH band at 2900 cm^{-1} allowed comparison of different samples from various experiments. To distinguish the features present in the spectra in the carbonyl region coming from carbonyl vibrations not disturbed by water vibrations, bound water present in paper was desorbed and the spectra were recorded at an elevated temperature. An oxidation index of paper defined as a ratio of integrals of bands at 1730 cm^{-1} to that at 1620 cm^{-1} has proved amenable to follow the degradation of cellulose aged under various conditions. The boundary conditions of experiments selected by us were able to discriminate between hydrolysis of glycosidic bonds and oxidation of carbon atoms in a glycopyranose anomer. Following the changes of the spectrum in the carbonyl range proceeding with oxidation time various intermediates of the cellulose partial oxidation were distinguished starting from the least oxidized monocarbonyl groups, through diketones to aldehydes and carboxyls. Assuming a parallel–consecutive mechanism of the cellulose oxidation the spectra were resolved by fitting with multiple Gaussian–Lorentzian functions.

Keywords: In-situ FTIR; Cellulose; Paper; Ageing; Carbonyl vibrations; Deconvolution

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1. Introduction

Millions of books worldwide now are menaced by paper disintegration through malignant and inevitably progressive degradation of cellulose chains due to acidic hydrolysis of glycosidic bonds. This problem is specific to the paper produced over around 150 years between the mid-19th century and the late 20th century. Although cellulose conformation of β-D-glycopyranose polymer is thermodynamically highly stable, it has appeared that the addition of aluminium sulphate into paper pulp acts as a catalyst of hydrolysis, which en mass exerts a detrimental effect on the cellulose durability. Long-term consequences of the modification in the paper-making technology utilising cheap groundwood raw material and sizing additives were not recognised or ignored for years, but it was not until the past two decades that the alkaline-sized paper technology replaced the acidic one, practically eliminating acidic paper from current archivistic use. In order to solve the immediate problems associated with retrospective collections, mass book deacidification programmes have been launched to protect those volumes which have

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not been completely damaged yet and to inhibit the cellulose degradation. At present, the paper preservation tasks are being aided by the research on the mechanisms of cellulose degradation which is aimed at deepening our understanding of the degradation phenomena to thus, in return, improve the existing conservation methods.

According to the most recent findings, cellulose degradation should be regarded in terms of mixed oxidative and hydrolytic mechanisms [1–3], where the two reactions are autocatalytically accelerated by active oxygen species and by protons, respectively. Presently, the paper degradation kinetics is based on formal rate laws [4,5], which with better or worse results are used to reproduce kinetic curves representing accelerated ageing of cellulose.

Typically, paper degradation is monitored by the mechanical or physical properties of paper, such as tensile strength, folding endurance, tear index [1,6], dynamic modulus or mechanical loss tangent [7]. Another parameter is the degree of polymerisation representing an average polymerisation state of cellulose chains [1]. Even though of paramount and practical importance, these parameters provide only macroscopic information on the paper condition and do not give a molecular insight into the mechanism of the degradation in cellulose-based materials. Notwithstanding numerous examples of the use of vibrational spectroscopy to resolve cellulose structure, crystalline phases [8], hydrogen bond network [9,10], vibrational spectroscopy, highly sensitive to structural changes in materials, seems still to have an unexploited potential in the modelling of kinetics of cellulose degradation. A great many sampling techniques have been used so far to study paper materials [8]: transmission spectra through KBr pallets [2,11,12], reflectance spectra using ATR [13] or DRIFT techniques [3,6,14]; each of them, however, suffers from several serious drawbacks. Various sampling techniques have also been tested by our group in the first approach to the problem of cellulose degradation [15,16]. The preparation of KBr pellets is rather time consuming as far as kinetic experiments are concerned, and not very representative of the environment in which the molecules react. The ATR and DRIFT techniques provide information restricted to the surface region of the samples, DRIFT giving high specular reflection.

Therefore what we propose herein is the application of in situ transmission FTIR measurements to directly look into the real time changes in cellulose structure during the degradation. This part of the study concentrates upon testing and refining the experimental set-up which will serve further as an effective tool for the kinetic studies involving mixed-controlled mechanisms [5]. The only example found of an interesting application of the similar in-situ method is the work by Zhou et al. [17]. Using a combined FTIR and viscometric measurements, the authors surveyed the correlations between modifications in mechanical properties and the structure in cellulose upon temperature- and water vapour-accelerated ageing.

Since the IR spectrum of cellulose is fairly unresolved in the finger print region due to the associated vibrations [15,16], and because the carbonyl region is relatively free from other vibrations, our focus is on the changes in the range between 1400 and 1800 cm^{-1} to finally associate them with the degradation of cellulose. A broad range of reaction conditions have been applied to distinguish between possible carbonyl vibrations and to set boundary conditions for the maximum changes in this region of the cellulose spectrum. A serious obstacle appears to be adsorbed or so called "bound" water [15], whose bending vibrations are observed around 1640 cm^{-1} and interfere with carbonyl bands, making the interpretation of the spectrum much more difficult or sometimes impossible (see examples in Refs [3,18]). Thus, another challenge is how to "clean up" the carbonyl vibrations range.

2. Experimental

2.1. Material

In this approach we decided to use the paper samples made almost exclusively of cellulose to observe the structural changes proceeding in glycopyranose rings. Model paper: bleached sulphite softwood cellulose paper with 99.5 wt% cellulose content (78 g/m^2, BET: 1.21 m^2/g), denoted as P1 was obtained from TNO, Netherlands [19]. The same kind of paper is used in our group for the kinetic studies utilising other experimental techniques. Moisture content related to a total mass the original P1 sample is 7.47% (23 °C, 50% RH). Little impurities found in this material were assigned to lignin and oligosaccharides [20]. For reference, in selected experiments we used samples of pure cellulose (JNO Pine 90, bleached softwood craft pulp) obtained from Botnia, Finland. The samples used for temperature tests were thinned mechanically to reduce the paper grammage by around 50 wt% thus allowing the satisfactory transmittance through the paper sheets.

2.2. Equipment

The spectra were recorded on a Brucker Equinox 55 spectrometer with an MCT detector at an optical resolution of 2 cm^{-1} and two level zero-filling. For the accelerated ageing tests a quartz reaction chamber with ZnSe optical windows was placed in the sample compartment of the spectrometer. The chamber was equipped with an electric furnace enabling heating in the