

**STUDY ON THE MECHANISM OF HYDROLYTIC AND
OXIDATIVE DEGRADATION OF PAPER
USING IN-SITU FT-IR METHOD**

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INTRODUCTION

Degradation of millions volumes of books and archives has become one of the main humankind problem of the beginning of 21st century. The change of papermaking technology in the mid 19th century, in particular, the addition of aluminium sulphate to a pulp leads to well-known aging effects such as yellowing and loss of paper strength. As the addition of Al₂(SO₄)₃ follows fall of pH and the degradation of the main paper ingredient, cellulose, undergoes rapidly. The mechanism of this process is based mainly on hydrolysis of β-1,4 glycosidic bonds in cellulose chains. However, according to the recent studies, the share of oxidation of the glucopyranose units in the process of degradation is significant [1,2]. While the mechanism of acid hydrolysis of cellulose is well known, the oxidation is still under studies. The aim of this work is to put forward the mechanism of mixed hydrolytic and oxidative degradation of cellulose chains using in-situ FTIR method.

EXPERIMENTAL

The object of the studies was the model paper assigned as "P1" imported from TNO Netherlands with 99,5% of cellulose content (78 g/m², BET: 1.21 m²/g), made from bleached sulphite softwood. Prior to studies, the samples had been thinned to the grammage about 25 g/m². This process made them transparent to infrared radiation. The spectra were recorded on a Bruker Equinox 55 spectrometer with a MCT detector at an optical resolution of 2 cm⁻¹ and 2 level zero-filling. The tests were carried out at higher temperatures (up to 250°C) in a special measurement cell equipped with a furnace, a gas supplying and evacuating systems.

The experiments were performed in two ways. In the first, the spectra dependence of various temperature and gas content was measured. The reaction temperatures were chosen to observe step-wise dehydration (100°C), oxidation of functional groups in glucopyranose units (150°C) up to their pyrolysis (250°C). Three different gas compositions (humid atmosphere, humid air atmosphere and dry air atmosphere) were used to discriminate between hydrolytic and oxidative routs of cellulose degradation. Gasses were supplied to maintain 1 atm. inside the cell (except the humid atmosphere, with the pressure of saturated vapour of water). In the second experiment, oxidation under constant temperature (150°C) in dry air atmosphere was monitored for up to 110 hours. After that an attempt to deconvolute the C=O range was made.

RESULTS AND DISCUSSION

From the mid-IR spectrum of paper, the range of 1500 cm⁻¹ – 1850 cm⁻¹, seemed to be helpful for understanding the process of oxidation of cellulose. In that range one can observe, among others, the C=O stretching vibrations from aldehyde, ketone and carboxyl groups. However, a wide and intense band with a maximum at 1640 cm⁻¹ from the bending vibration of water overlaps with other vibrations. That water, adsorbed by the paper is called "bound" water [3]. Moreover, according to our studies, water

desorbed at higher temperature while cooling process adsorbs it again by the paper. As it turned out, the solution of the readsorption problem was collecting spectra at the temperature used for accelerated aging. That is why the in-situ FTIR apparatus turned out to be useful to the experiments.

Another difficulty was the normalization of the spectra to compare them regardless of the thickness of the samples. For this purpose the band assigned to the C-H stretching vibration (with maximum around 2900 cm^{-1}) was chosen as the internal standard. The intensity of this band is practically constant during the accelerated aging tests.

Experiments conducted at temperatures 100°C and 150°C at the very short time (up to 2 hours) did not reveal any significant changes in the IR spectra, apart from removing of adsorbed water. However, as shown in *Fig. 1A* at the temperature 250°C after 2 hour reaction, the changes become significant.

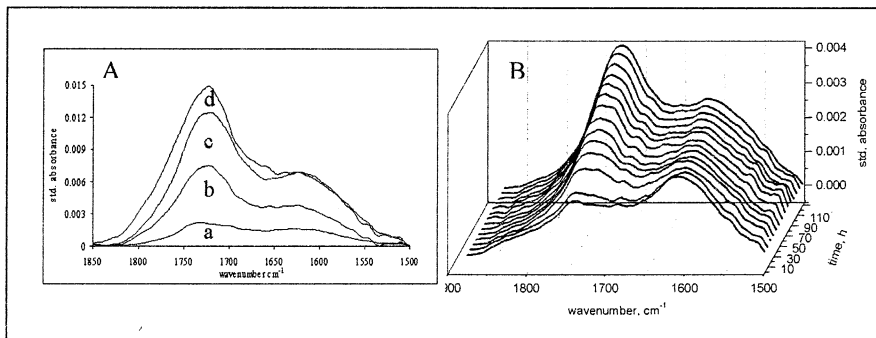


Fig. 1.A) FTIR in situ spectra of the CO region of the P1 sample studied at 250°C , at various gas content a – humid atmosphere; b – humid air atmosphere; c – dry air atmosphere; d – reference sample of cellulose in humid air atmosphere. B) Isothermal oxidation of P1 sample in the dry air atmosphere at 150°C monitored every 10 h by in situ FTIR measurements.

As one may have expected, the largest changes in the spectrum are observed at the dry air atmosphere where oxidation was the most intensive. Oxidation is also a dominant reaction at the air humid atmosphere unlike at the pure humid atmosphere. There two small broad maxima (1740 and 1620 cm^{-1}) may arise from CHO groups on glycosidic bonds cleavage. Dehydration and followed changes of conformation of glucose units are possible in all three cases. The observation of degradation up to 110 h at 150°C (*fig. 1B*) brought similar results. Moreover, one can additionally notice that the band with the maximum around 1730 cm^{-1} increases the most. In addition, spectra collected up to 110 h seem to be more complex (with more component bands) than the previous ones. The experiments mentioned above supported by the literature data allow to postulate a model of oxidative degradation of paper [4]. This model assumes existence of a number of consecutive and parallel reactions, example of which is showed in *Fig. 2*.

Oxidation may occur both with an opening of glucopyranose ring and without it. In both cases carbon atoms with hydroxyl groups are the most susceptible to the oxidation process which may proceed directly to obtain carboxyl groups or by one or more intermediate products. These products (like aldehydes, ketones, enols), if present,

are visible for infrared radiation, among others, at the "C=O" region of the spectrum. That is why we carried out peak fitting in that range. The fitting was simulated with the GRAMS/AI 7.00 program. The maxima of fitted peaks were optimised in a fairly narrow frequency range (up to 5 cm^{-1}) according to literature data for the C=O and C=C vibrations in the different environment [4,5,6]. The result of fitting showed in Fig. 3. is

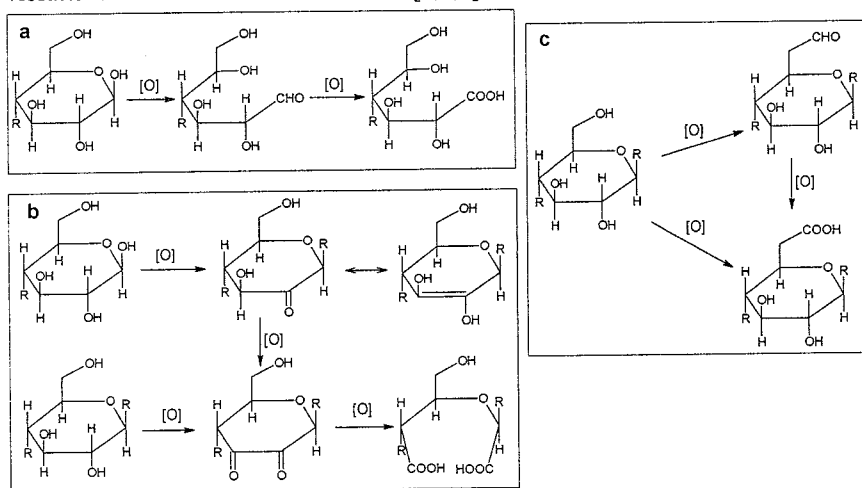


Fig.2. Some of postulated paths of cellulose oxidation: a) oxidation of terminal glucopyranose group, b) oxidation of the carbon atoms C2 and C3 of internal glucopyranose units with different intermediate steps (i.e. enol forms), c) direct and indirect possibilities of oxidation of carbon atom C6 to carboxyl group.

an example of such fitting of the spectrum collected in the dry air atmosphere at 150°C after 80 hours. Table 1 includes the parameters of fitting mixed Lorentzian-Gaussian functions to four more spectra. These spectra were obtained under the same conditions as the previous one, collected up to 110 hours. The most evident change is monotonous increase of absorption 2 and 3, which are the main components of the broad band with maximum at 1730 cm^{-1} . Those peaks are preliminary assigned to the stretching vibrations of carboxyl and carbonyl groups, what is in accordance with assumed model

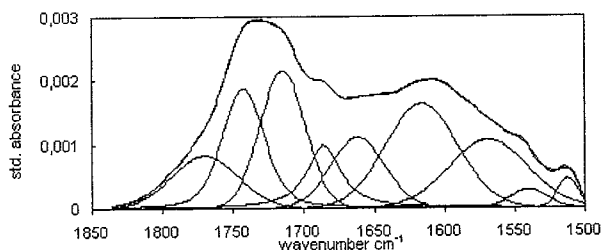


Fig.3. Fitting of nine potential peaks to C=O region of the spectrum of aged paper (dry air, temperature 150°C , 80 hours of aging).

of oxidation, where polycarboxylic acids are the final products of all reactions. Moreover, spectrum of aged paper next treated with KOH solution and washed with distilled water shows decrease in absorbance of the band mentioned above. This neutralisation with

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KOH causes shifting of vibration at the IR spectrum. This experimental fact confirms that intense absorbance in that region as deriving from COOH vibrations.

Table 1. Parameters of fitted peaks to the five chosen spectra: centre of the peak, full width at the half high and area of the peak

time, h	Fitting parameters	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
0	center	1778	1743	1707	1685	1663	1618	1574	1538	1513
	FWHH	65	40	40	23	40	58	55	28	20
	std. integral	0.0251	0.0454	0.0362	0.0096	0.0309	0.1004	0.0653	0.0109	0.0064
10	center	1780	1745	1713	1685	1665	1617	1571	1538	1513
	FWHH	50	40	40	26	48	63	60	32	19
	std. integral	0.0251	0.0645	0.0536	0.0185	0.0419	0.1044	0.0654	0.0102	0.0066
40	center	1773	1738	1710	1686	1662	1612	1564	1536	1511
	FWHH	55	40	31	25	47	65	51	37	16
	std. integral	0.0454	0.0795	0.0505	0.0283	0.0530	0.1220	0.0446	0.0149	0.0071
80	center	1770	1743	1715	1686	1662	1616	1569	1540	1512
	FWHH	55	35	38	29	45	60	66	30	17
	std. integral	0.0484	0.0777	0.0864	0.0409	0.0531	0.1046	0.0741	0.0091	0.0081
110	center	1770	1743	1716	1685	1661	1619	1571	1539	1514
	FWHH	54	39	41	36	41	59	58	23	19
	std. integral	0.0456	0.0917	0.0990	0.0598	0.0435	0.1120	0.0744	0.0080	0.0069

Concluding briefly, “in-situ” FTIR is a promising method to obtain step by step information about the process of accelerated aging. Removing water and choosing C-H band as the internal standard turn out to be essential for semi-quantitative standardization of collected spectra, what makes the results comparable and allows their repetition in the future. Obtained results allowed to postulate the mechanism of hydrolytic and oxidative degradation of cellulose; however, particular reaction paths proposed in this work has to be still confirmed.

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