FT-IR and FT-Raman study of hydrothermally degraded groundwood containing paper

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Abstract

Accelerated aging test of paper is used to understand mechanisms of acidic hydrolysis and oxidative degradation of cellulose, hemicellulose and lignin. In recent years FT-IR and FT-Raman spectroscopy have been used together with mass spectrometry and nuclear magnetic resonance as well as chemometrics methods to characterize degradation products of paper. In this work we present FT-IR and FT-Raman spectra of hydrothermally treated sample of acid paper (Paper 3—bleached sulfite softwood pulp) in extreme humid conditions (100% humidity and 100 °C). Degradation reaction is monitored mainly based on C=O stretching vibrations formed during the process of carbonyl compounds, however, some changes in C=C stretching vibrations are also noticed. We showed that in these conditions paper undergoes oxidation process in which at least three new carbonyl species that can be characterized by their C=O stretches are formed. Additionally, during this process, one can observe disappearance of the C=C stretching that can be associated with changes that involve, for example, coniferyl alcohol. We also show that water molecules play very important role in this process. Thus, we report here, changes caused by hydrothermal treatment of groundwood containing paper mainly associated with the appearance of new carbonyl species, besides others, as well as rearrangement of existing hydrogen bond network. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the oldest information carrying media is paper that was invented in China in the beginning of the 2nd century [1]. It consists mostly of cellulose fibers obtained from different plant sources such as cotton and linen rags, maize and bamboo grasses, manilla and sisal leaves or flax, hemp, ramie or jute and recently from wood [1,2]. Each cellulose fiber from these sources has its own characteristic properties influencing permanence and stability of paper. Cellulose from native wood exhibits degree of polymerization up to 10,000, while that from native cotton can reach up to 15,000 [3]. In 19th century increasing demand for paper directed attention to the most abundant, inexpensive and promising source of cellulose, wood. Since then, several processes for manufacturing paper from wood have been

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developed. However, used technology (mechanical wood grinding, pulping, bleaching and sizing) caused that paper being manufactured from the middle of 19 century till the end of this century was less durable to such extent that a large number of manuscripts, book, maps, etc. printed on this paper cannot be used today due to the high degree of deterioration caused mainly by the oxidation of lignin that in turn influenced mechanical stability of the paper. Nowadays, paper-making processes are of high quality, however, low quality pulps are still used to produce a short life span paper for newsprint, packing or carton boxes [4].

Paper undergoes natural aging processes that cause molecular degradation of its main component, cellulose, that in turn cause loss of fiber strength. This is manifested in lower mechanical stability that may lead, sometimes, to full disintegration of paper sheets [1,5]. These degradation processes of cellulose and/or lignin polymers are related to the presence of moisture, different acids, oxidative agents, traces of transition metal ions (Fe(III), Cu(II), Cr(III)), light as well as microorganisms [1,4,6–8]. As many as over 140 volatile compounds (alcohols, aldehydes, ketones, carboxylic acids, aliphatic and aromatic hydrocarbons, esters, terpenoids and terpenes) can be released from paper sheets during degradation processes depending upon paper chemical compositions [9–12].

Acid catalyzed hydrolysis of cellulose was recognized to be the primary reaction that accelerated deterioration of the paper [1,13,14]. To save millions of books and other archive materials produced on the so-called 'acid paper,' different technologies of deacidification, fiber strengthening and microorganisms removal have been invented in recent years [15]. However, in order to fully understand paper degradation processes, many careful studies of well-defined natural polymers (cellulose, hemicellulose, lignin) and their model compounds have been undertaken using different approaches [4,16–22]. In our recent work, we have studied the influence of hydrothermal degradation of bleached sulphite softwood cellulose and cotton linters cellulose) by using FT-IR and FT-Raman spectroscopy [23]. It is widely accepted that these spectroscopic methods are perfectly suited to study changes in structure and bonding of paper components [24–26]. Based on observed changes in frequencies and intensities of some characteristic

bands, we arrived at the conclusion that the acid catalyzed hydrolytic cleavage of the β(1-4)-glycosidic bonds that form cellulose structure forces rearrangement of the hydrogen bond system that in turn changes vibrational pattern of certain bending motions of characteristic molecular groups. Thus, water molecules play crucial role in deterioration of chemical integrity of cellulose fibers and then in stabilization of reaction products through the formation of hydrogen bond network. We also noticed that higher temperature and relative humidity accelerate aging processes by both oxidative and hydrolytic degradation reactions. This observation was in general agreement with other data that have been published thus far [1,7,12,27–29]. Also it was clear that presence of traces of Fe(III) ions in softwood cellulose in investigated sample promoted acidic hydrolysis of this polymer that proceeded much faster than degradation of Fe(III)-free cotton cellulose studied at the same conditions.

In this work, which is a continuation of our efforts to use the artificial accelerated paper aging tests, we present for the first time results obtained for hydrothermal deterioration of groundwood-containing paper by using FT-IR and FT-Raman techniques. The main goal of this work is to show, how the presence of lignin polymer influences degradation process that was previously studied by us for pure celluloses obtained at the same experimental conditions (see Section 2 for details).

2. Experimental

2.1. Materials and methods

The so-called, 'Paper 3' (P3) was obtained from TNO (Center for Paper and Board Research), Delft (The Netherlands). A fiber composition of P3 is 75% of groundwood and 25% of bleached sulfite softwood pulp. Kaolin (around 20%) and alum–rosin are used as filler and sizing materials, respectively [2]. The pH of the cold paper extract is 5.9, thus the alkaline reserve of it is zero.

The artificial accelerated aging tests were performed at 100 °C and relative humidity of 100% (RH = 100) by using previously described procedure [23,30]. Briefly, teflon vessels with capacity of 1 dcm^3
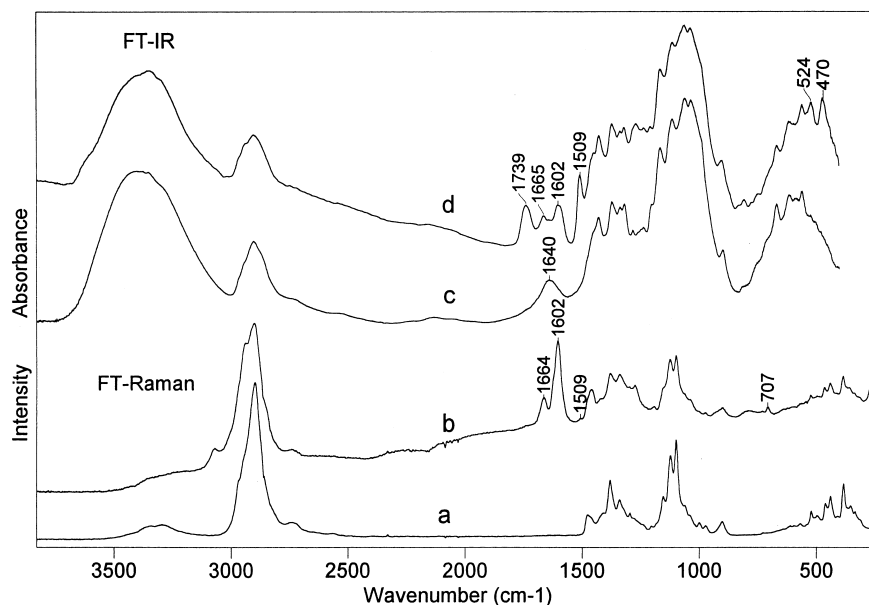
Fig. 1. FT-Raman spectra of bleached sulphite softwood cellulose paper (trace a), paper P3 (trace b), FT-IR spectra of bleached sulphite softwood cellulose paper (trace c) and paper P3 (trace d).

were filled with 0.1 dcm^3 of water. Paper strips were cut and inserted into the vessels the way that maintained no direct contact with water. Then vessels were moved to a dryer and closed tightly after reaching desired temperature of 100 °C. The temperature stability of ±0.5 °C was kept. After the assumed time of aging had been attained the vessels were cooled to room temperature, opened and paper strips were removed, conditioned for 24 h at 23 °C and RH = 50% and transferred to commercially available polyethylene bags with zippers. These conditioned paper strips were measured as quickly as possible.

2.2. Spectroscopic measurements

The middle FT-IR spectra were recorded on a Bio-Rad interferometer model FTS-60v with the 4 cm^{-1} resolution. The straightforward transmission technique was used. Thus, a cut piece of a strip of the paper P3 was mounted into the special holder, placed in the pass of the infrared beam and intensity of the transmitted radiation was measured. A total of 512 scans were collected for each sample. FT-Raman spectra were measured on a Bio-Rad model FTS-6000 Raman Accessory equipped with germanium liquid nitrogen cooled detector. Samples were excited with

1064 nm line from a diode-pumped 1 W Nd:YAG Spectra-Physics laser. Power at the sample was maintained at 300 mW. As many as 4000 scans with the 4 cm^{-1} resolution were collected for each sample. Three different spots in each paper strip were measured to assure reproducibility of the experiment in both FT-IR and FT-Raman methods.

3. Results and discussion

Fig. 1 shows FT-IR spectra of Paper P3 (trace d) and cellulose (trace c). Also, FT-Raman spectra of the same samples are included in the figure (P3—trace b and cellulose—trace a). IR and Raman spectra of cellulose, presented here, are 'typical' for this polymer that is a linear polysaccharide composed exclusively of β-D-glucopyranose monomers linked together by β-(1-4)-glycosidic bonds [1,18,19,26]. These chains are held together by intermolecular hydrogen bonds in which water molecules play a very important role. The hydrogen bond network causes aggregation of cellulose into crystalline forms. Thus, differences in fiber structure can be monitored by vibrational studies. Mainly FT-IR methods have been used together with chemometrics techniques

(principal component analysis (PCA), soft independent modeling of class analogies (SIMCA), discriminant analysis (DA), and others) to show that even subtle changes in frequencies and/or intensities can be traced and assigned [31–35].

3.1. Band assignment

Vibrational assignment of cellulose bands is based on comparative analysis of experimental and theoretically calculated spectra of elementary carbohydrates [36–40]. It is impossible to identify all spectral features since, for example, just for a single α-anomer of D-glucose, 18 normal modes are expected in the 1200–1500 region [40]. No wonder that observed vibrational patter of cellulose is very complex in the 500–1500 cm^{-1} range, where stretching and deformation modes of various groups couple. Thus, it is generally accepted, that below 900 cm^{-1} complex modes involving deformation and torsional vibrations of CCC, CCO, COC, OCO, and COH (configurational and conformational changes of the ring) are expected. The range between 900 and 1200 cm^{-1} covers the CO and CC stretching, antisymmetric in-phase ring stretching, antisymmetric bridge COC as well as CCH and OCH deformation vibrations. COH in-plane bendings, CCH, OCH, and CCH deformation stretchings as well as HCH bending and wagging are observed in the 1200–1500 cm^{-1}. In the 1650 cm^{-1} region HOH bending vibrations of adsorbed water molecules is expected.

IR and Raman spectra of P3 (traces d and b) differ from that of cellulose spectra (traces c and a) that reflects the complexity of the sample, where hemicellulose, lignin, fillers and sizing material are additional components to cellulose to make paper. Hemicellulose is a natural polymer that is built from not only glucose monomers but also other monosaccharides such as xylose, mannose, arabinose and galactose [6]. It forms branched skeleton with amorphous structure that adsorbs water much easier than cellulose. Lignin is a very complex polymer of phenylpropane units. It is formed by dehydrogenative polymerization, promoted by the peroxidase in the presence of hydrogen peroxide, of three alcohols: *p*-coumaryl (*trans*-3-(4-hydroxyphenyl)-2-propen-1-ol), coniferyl (*trans*-3-(3-methoxy-4-hydroxyphenyl)-2-propen-1-ol), and sinapyl (*trans*-3-(3,5-

dimethoxy-4-hydroxyphenyl)-2-propen-1-ol) [4,6, 22]. Also natural resinous material and aluminum sulphate (alum–rosin sizing) and kaolin (filler) are present in paper.

The main difference in Raman spectra (traces a and b) is the observation of new bands at around 700 (medium weak), 1509 (very weak), 1602 (very strong) and 1664 cm^{-1} (medium). The first three are assigned easily to phenyl ring vibrations, while the band at 1664 cm^{-1} is due to the C=O stretching vibration, ν(C=O), overlapped with C=C stretching vibrations from coniferyl alcohol of lignin [18,41–43]. According to Takayama et al. [43], the Raman band observed at 1594 cm^{-1} can be used as guaiacyl (3-methoxy-4-hydroxyphenyl) and that at 1599 cm^{-1} syringyl (3,5-dimethoxy-4-hydroxyphenyl) marker band. The syringyl to guaiacyl ratio calculated from the integrated intensities of these markers can be used for quantitative determination of lignin structure.

There are also many slight changes in band positions and intensities in the range of 400–1500 cm^{-1} that have to be expected from the composition of the P3 sample since this spectrum is a Raman spectrum of cellulose superimposed on lignin and hemicellulose spectra. Thus, observed changes compared to cellulose spectrum are due to lignin and small amount of hemicellulose presence in the paper. Concentration of rosin and aluminum sulphate is too small to be observed. Additionally, kaolin does not exhibit any strong Raman band in this range, however, a broad band at around 800 cm^{-1} can be associated with this filler.

Presence of lignin is clearly manifested in IR spectrum (trace d) as two bands at 1509 and 1602 cm^{-1} that are due to phenyl ring vibrations [1, 6,38]. Since all substituted phenyl groups that appear in lignin possess *C*1 point group symmetry thus, all expected vibrations are both Raman and IR active. No wonder that these two clearly observed IR bands have their counterparts in Raman spectrum (trace b). Somehow surprisingly, Takayama et al. [43] stated that "…due to the difference in the selection rule for infrared and Raman spectroscopies, ν(C=C) vibration is only active in Raman scattering, which is specific for lignin-derived aromatic skeleton". Additionally, the presence of carbonyl moieties that are formed in lignin during pulping processes can be seen in IR spectrum (trace a) as characteristic broad bands at
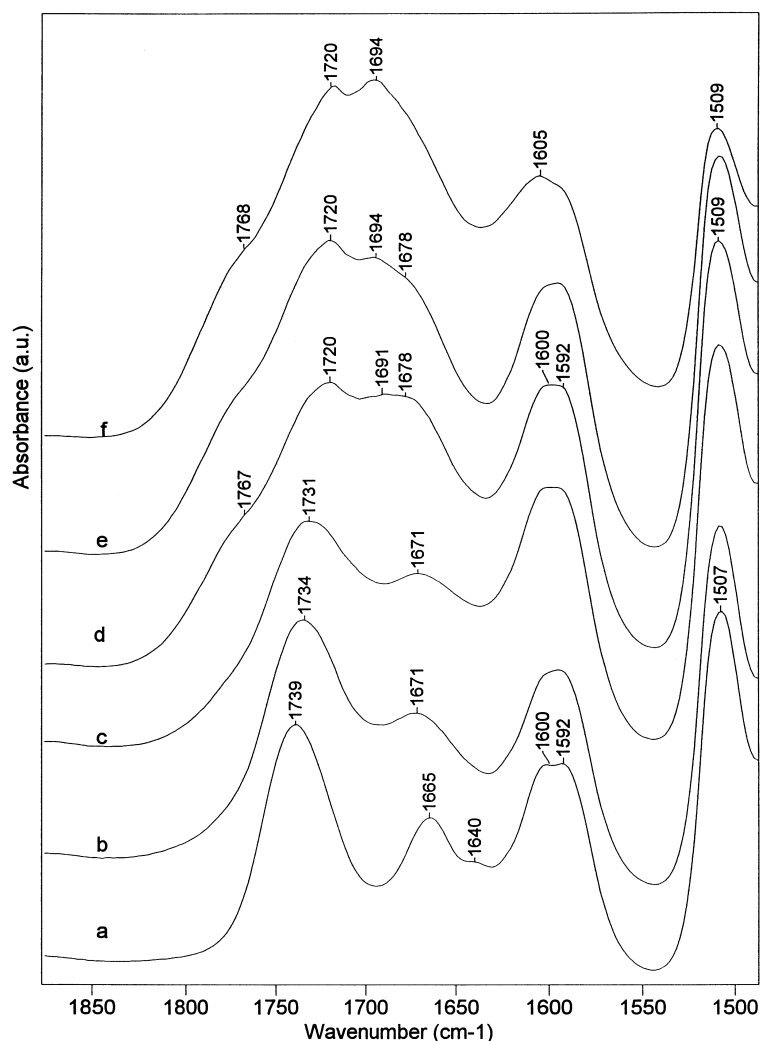
Fig. 2. FT-IR spectra of hydrothermally degradated (humidity 100%, temperature = 100 °C) P3 sample: starting sample (a), after 2 days (b), after 8 days (trace c), after 10 days (trace d), after 12 days (trace e), after 15 days (trace f).

1665 (mainly form conferyl aldehyde) and 1739 cm^{-1} (ester vibrations) that are due to ν(C=O) of different species [1,18,22]. The most likely, a band at 1640 cm^{-1} can be assigned to the H−O−H bending vibration of water molecules. From the reasons discussed earlier, also in the IR spectrum of P3, when compared to cellulose spectrum presented in trace b, there are many slight changes in band positions and intensities in the range shown in Fig. 1. It has to be emphasized also that additional to lignin and cellulose, some hemicellulose bands are expected to be seen in the spectra of P3. However, its

concentration is rather low since the characteristic IR band at 815 cm^{-1} is not seen [2].

Kaolin's presence in the sample is manifested in IR spectrum (trace d) by two bands at 470 and 524 cm^{-1}, while there are no clear indications of the presence of alum−rosin sizing and resin materials. Their characteristic bands are hidden in the IR spectrum due to their low concentration.

3.2. Accelerated aging

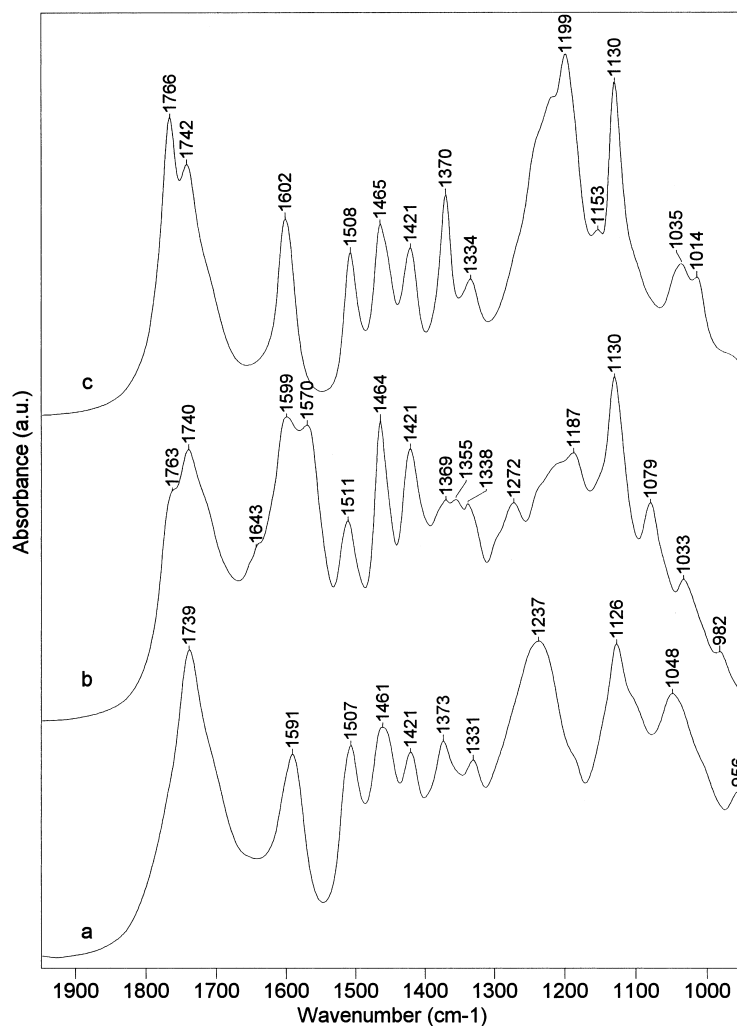The influence of accelerated aging process on IR

Fig. 3. FT-IR spectra of lignin standards from Aldrich a) organosolv. acetate (cat. no. 37,102-5), b) organosolv. propionate (cat. no. 37,103-3), c) organosolv. 2-acetoxyethyl ether (cat. no. 37,106-8).

spectra of paper P3 is shown in Fig. 2. The 1509 cm^{-1} band and the 1592/1600 cm^{-1} doublet are assigned to phenyl ring vibrations (vidè supra). The former band does not change during the aging process and can be used as an internal standard. A doublet that can be used as a guaiacyl/syringyl marker of the lignin structure, as proposed for Raman spectra [43], changes its shape (trace f) with time of exposure of paper strip to humid conditions. These spectral changes are due to increasing amount of water molecules being adsorbed and/or absorbed by paper and also due to possible changes in crystalline state

that are due to the degree of lignin oxidation. The 1640 cm^{-1} band disappears by going from trace a to f but this band is growing in intensity causing broadening and loss of symmetrical shape of the 1592/1600 cm^{-1} doublet. That is why we postulated that this band should be assigned to the H−O−H bending vibration of water molecules.

Very complex changes are observed in the band structures of the 1665 and 1739 cm^{-1} IR modes that are associated with the ν(C=O) vibrations. With aging time, a band at 1665 cm^{-1} diffuses with the maximum shifted to 1671 cm^{-1} just after 2 days (trace b). Then
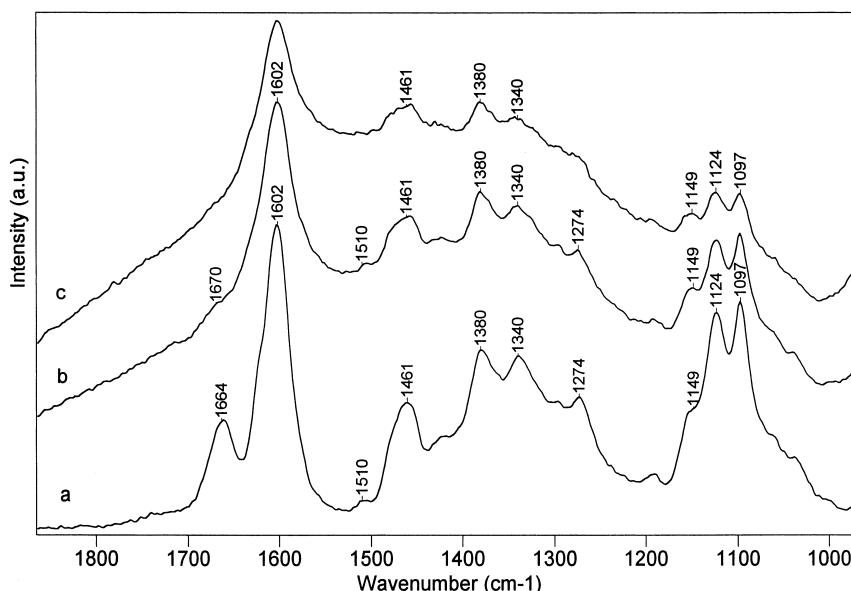
Fig. 4. FT-Raman spectra of hydrothermally degraded (humidity 100%, temperature = 100 °C) P3 sample: starting sample (a), after 10 days (trace b), after 15 days (trace c).

two other bands can be seen at 1678 and 1691 cm^{-1} after 10 days (trace d), while a band at 1665 cm^{-1} is loosing its intensity and practically is not observed in the spectrum. However, it seems reasonable that this band is hidden underneath the band envelope. The 1739 cm^{-1} band is shifting towards lower frequencies and reaches 1720 cm^{-1} after 10 days of experiment. In addition to the reported changes, a new species emerges after 5 days of accelerated degradation that is characterized by a shoulder at 1767 cm^{-1} (trace c). This shoulder is more pronounced in trace d, i.e. in IR spectrum taken 8 days after starting the experiment (trace c).

Some changes in IR pattern have been noticed in the range below 1500 cm^{-1}. However, this range is too crowded with bands from many components, so subtle changes caused by oxidation reaction are too small to be clearly interpreted in terms of structural changes. Previously we showed [19] that hydrother-mal degradation of cellulose can be seen in vibrational spectra in the 1200–1500 cm^{-1}. Based on changes of C–C–H, O–C–H, C–O–H, and H–C–H in-plane bending and H–O–H bending vibrations of water molecules we postulated that hydrothermal oxidation reaction of cellulose affects its polymeric structure causing rearrangement in hydrogen bond network.

With no doubt, also in the additional presence of lignin and hemicellulose in P3, oxidation reaction forces a new arrangement of hydrogen bond system in addition to the formation of new species. This process can be observed mainly based on changes in the ν(C=O) vibrations. The band at 1739 cm^{-1} is shifting down while the oxidation reaction progresses. It means that the C=O bond is getting weaker probably due to its engagement in new hydrogen bond system. During accelerated oxidation process one of the new species that is formed possesses characteristic ν(C=O) frequency at 1768 cm^{-1} and is observed as a high-frequency shoulder on the 1739 cm^{-1} band. As seen in Fig. 3, acetate and propionate groups in lignin show a doublet with frequencies at 1742 and 1766 cm^{-1} (traces b and c). In addition, a standard lignin with 2-acetoxyethylether groups gives rise to a strong single IR band at 1739 cm^{-1} (trace a), i.e. a frequency that is exactly the same as that observed in Fig. 2a. Thus, it is reasonable to propose that both these bands are associated with acetate or propionate group vibrations that can be formed either in lignin or hemicellulose chains. The origin of the band at 1665 cm^{-1} is not clear at this time. However, we propose that the 1665 cm^{-1} band is associated with either keto- or aldehyde group that oxidizes during the

reaction and gives rise to several new species. One has been already discussed earlier. Oxidation of either ketone or aldehyde that usually are in para position to hydroxyl group on phenyl ring [4,6,18,22,43] will lead to the formation of carboxylic acid or its ester. This is consistent with observed changes. So, the 1665 cm^{-1} bend is losing its intensity and new species appear with their ν(C=O)s at higher frequencies. Thus, additionally to the band at 1768 cm^{-1} discussed earlier these species exhibit characteristic frequencies at 1678 and 1694 cm^{-1}. We also assume that they are involved in the formation of complex hydrogen bond system.

Fig. 4 shows Raman spectra of P3 original sample (trace a) and that measured after 8 and 15 days of hydrothermal treatment. ν(C=O)s are not enhanced strongly in Raman spectra. The 1664 cm^{-1} Raman band can be assigned to the C=C stretch (coniferyl alcohol) that overlaps with C=O stretch of conferaldehyde [18]. This band corresponds to the IR band at 1665 cm^{-1} that is mainly assigned to C=O stretch. With the degradation time progressing this band becomes a shoulder on the 1602 cm^{-1} band and moves towards higher frequency by 7 cm^{-1}, the behavior being expected from previously discussed IR data. This band is still clearly seen in the Raman spectrum (trace b) while it is hidden in IR spectrum (Fig. 2). This band almost disappears from Raman spectrum measured after 15 days of accelerated aging. A small fluorescence background is observed together with broadening of Raman bands. This fluorescence can be due to traces of Fe(III) ions presented in the sample [2]. This is possible even if excitation line is in infrared region. Diffusion of bands shows that crystalline structure of the sample is slowly getting amorphous with the time of the reaction.

In conclusion, observed changes in paper structure that are caused by accelerated aging reaction in extreme humid conditions are mainly due to oxidation (hydrolysis) processes of lignin and possible hemicellulose. There are no clear indications that hydrolysis influences cellulose fibers also since this information is hidden in the spectra in the presence of lignin. This hydrolysis is effectively monitored in FT-IR and FT-Raman spectra in the range, where the ν(C=O) vibrations are expected. Thus, the oxidation leads to formation of new carbonyl species and causes rearrangement of existing hydrogen bond network.

References

[1] J.B.G.A. Havermans, Environmental Influences on the Deterioration of Paper, Barjesteh, Meeuwes and Co, Rotterdam, 1995.
[2] J.B.G.A. Havermans, Restaurator 16 (1995) 209.
[3] D.A.T. Goring, T.E. Timel, Tappi 45 (1962) 454.
[4] O. Lanzalunga, M. Bietti, J. Photochem. Photobiol. B: Biol. 56 (2000) 85.
[5] C. Fellers, T. Iversen, T. Lindström, T. Nilsson, M. Righahl, Ageing/degradation of paper, A literature survey, Report No. 1E, The Swedish Research and Development Project for Paper Preservation, Stockholm (Sweden), 1989.
[6] A. Johannson, Air pollution and paper deterioration, PhD thesis, Göteborg University, Göteborg, 2000.
[7] C.J. Shahani, Accelerated Aging of Paper: Can it Really Foretell the Permanence of Paper, Preservation Research and Testing Series No. 9503, Library of Congress, Washington, 1995.
[8] B.L. Browning, Analysis of Paper, Marcel Dekker, New York, 1977.
[9] G. Buchbauer, L. Jirovetz, M. Wasicky, A. Nikiforov, J. Pulp Pap. Sci. 21 (1995) J398.
[10] S. Soares, Proc. Int. Symp. Nat. Polym. Compos. 2 (1998) 181.
[11] J.B.G.A. Havermans, M. de Feber, W. Genuit, G. van Velzen, 12th Triennial Meeting, Lyon, France, ICCOM Committee for Conservation, Preprints, II, 1999, p. 513.
[12] T. Doering, P. Fisher, U. Binder, J. Liers, G. Banik, Adv. Print. Sci. Technol. 27 (2002) 27–39.
[13] A.C. Sclawy, J.C. Williams, Tappi 64 (1981) 49.
[14] F. Daniel, F. Flieder, P. Kolseth, Mass deacidification effects of three different methods in the effects of air pollutants on the accelerated ageing of cellulose containing materials—paper, EC/DGXII/STEP Project CT 90-0100, BU3.94/JH, TNO Delft, The Netherlands, 1994.
[15] J. Dufour, J.B.G.A. Havermans, Restaurator 22 (2001) 20.
[16] H.A. Carter, J. Chem. Edu 66 (1989) 883.
[17] H.J. Pork, Snelheid van papierverval, De betrouwbaarheid van prognoses op basis van kunstmatige-ver-ouderingstests, Koninklijke Bibliotheek, Haga, 1999.
[18] U.P. Agarwal, in: D.S. Argyropoulos (Ed.), Advances in Lignocellulosics Characterization, Tappi Press, New York, 1999.
[19] U.P. Agarwal, S.A. Ralph, Appl. Spectrosc. 51 (1997) 1648.
[20] M. Ali, E.M. Emsley, H. Herman, R.J. Heywood, Polymers 42 (2001) 2893.
[21] B. Saake, D.S. Argyropoulos, O. Beinhoff, O. Faix, Phytochemistry 43 (1996) 499.

[22] O. Faix, in: V. Lin, W. Dence (Eds.), Lignin Chemistry, Springer, Berlin, 1992, Chapter 4.1.

[23] L.M. Proniewicz, C. Paluszkiewicz, A. Wesełucha-Birczyńska, H. Majcherczyk, A. Barański, A. Konieczna, J. Mol. Struct. 596 (2001) 163.

[24] M. Mathlouthi, J.L. Koenig, Adv. Carbohydr. Chem. Biochem. 44 (1986) 7.

[25] U.P. Agarwal, R.H. Atalla, Surface Analysis of Paper, CRC Press, New York, 1995, Chapter 8.

[26] N. Duran, R. Angelo, Appl. Spectrosc. Rev. 33 (1998) 219.

[27] I. Frojd, Preservation Research and Development: Round Table Proceedings, September 28–29, 1992, Library of Congress, Washington, DC, 1993.

[28] M.C. Jarvis, Carbohydr. Res. 325 (2000) 150.

[29] Y. Marechal, H. Chanzyl, J. Mol. Struct. 523 (2000) 183.

[30] A. Barański, R. Dziembaj, A. Konieczna, A. Kowalski, J.M. Łagan, L.M. Proniewicz, Technologia Chemiczna na Przełomie Wieków, Wyd. Stałego Komitetu Kongresów Technologii Chemicznej, Gliwice, Poland, 2000, p. 411 in English.

[31] J. Ziçba, Kriminal. Forens. Wiss. 77,78 (1990) 58.

[32] C. Gilbert, S. Kokot, U. Meyer, Appl. Spectrosc. 47 (1993) 741.

[33] C. Gilbert, S. Kokot, Vib. Spectrosc. 9 (1995) 161.

[34] M. Mascarenhas, J. Dighton, G.A. Arbuckle, Appl. Spectrosc. 54 (2000) 681.

[35] A. Kher, M. Mulholland, B. Reedy, P. Maynard, Appl. Spectrosc. (2002) 55 in press.

[36] P.D. Vasco, J. Blackwell, J.L. Koenig, Carbohydr. Res. 23 (1972) 407.

[37] G. Longhi, G. Zerbi, G. Paterlini, L. Rigard, S. Abbate, Carbohydr. Res. 161 (1987) 1.

[38] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Graselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, San Diego, CA, 1991.

[39] R.G. Zhbankov, H. Andrianov, H. Ratajczak, M. Marchewka, Zh. Fiz. Khim. 69 (1995) 553.

[40] D.K. Buslov, N.A. Nikonenko, N.I. Sushko, R.G. Zhbankov, Spectrochim. Acta, Part A 55 (1999) 229.

[41] R.H. Atalla, U.P. Agarwal, Science 227 (1985) 636.

[42] U.P. Agarwal, R.H. Atalla, J. Wood Chem. Technol. 14 (1994) 227.

[43] M. Takayama, T. Johjima, T. Yamanaka, H. Wariishi, H. Tanaka, Spectrochim. Acta, Part A 53 (1997) 1621.