



Changes in chromophoric composition of high-yield mechanical pulps due to hydrogen peroxide bleaching under acidic and alkaline conditions

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ABSTRACT

The effects of bleaching of high-yield mechanical pulps (TMP, CTMP) with hydrogen peroxide under acidic and alkaline conditions were studied using different spectroscopic analytical methods. Diffuse reflectance laser flash photolysis (DRLFP) showed the differences in photochemical behavior reflecting transformation of chromophores upon treatment with acidic hydrogen peroxide. FT IR spectroscopic studies allowed to differentiate between the effects of the alkaline peroxide treatment with various stabilizing agents. FT-Raman technique provided additional information on localization of chemical changes after treatment under acidic and alkaline conditions, especially concerning the removal of coniferaldehyde-type groups.

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1. Introduction

Hydrogen peroxide is widely used in the environmentally friendly bleaching technologies of the paper-making industry [1]. Standard bleaching procedure of high-yield wood pulps (TMP – thermomechanical pulp, CTMP – chemothermomechanical pulp) is carried out as a single- or double-stage process under alkaline conditions. In fact, the main bleaching agent is the hydroperoxide anion (O_2H^-), formed upon hydrogen peroxide dissociation in an alkaline medium [2]. The optimum basicity of the bleaching slurry, securing high final brightness of the pulp, is close to pH = 11 [3]. During bleaching in non-delignifying conditions at 70 °C the hydroperoxide anion first of all reacts with the lignin-related chromophoric structures, such as conjugated carbonyl groups, stilbenes and quinones [4–6]. Hydrogen peroxide in alkaline medium does not exhibit such strong oxidative properties as other oxygen-based

bleaching agents – ozone or peracids, used in industrial practice and research. The enhancement of peroxide bleaching efficiency can be attained by the use of an acidic medium at the first (preliminary) bleaching stage. The two-stage hydrogen peroxide bleaching under acidic and then alkaline conditions has advantages both as regards peroxide consumption and the final brightness, at the same time maintaining the high pulp yields [2,7–10]. Hydrogen peroxide is relatively stable in the acidic medium, therefore, transition metal catalysts are used for its activation [3]. The transition metal ions decompose peroxide into free-radical products, including the very reactive hydroxyl radical (OH^\bullet) that shows low selectivity toward pulp structural components (lignin and carbohydrates) [3,7]. Hydroxyl radicals may influence negatively the pulp strength and even contribute to formation of new chromophoric structures [11]. In order to control the catalytic activity at the second (main) alkaline bleaching stage, stabilizers such as magnesium sulfate and/or sodium silicate are added [12–14]. The latter stabilizing agent is an additional source of alkali, thus preventing a decline in bleaching efficiency due to lowering basicity of the bleaching slurry occurring during the treatment [15].

The reactions of alkaline hydrogen peroxide with lignin and carbohydrates are relatively well-known. However, there is a lack

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of information concerning the influence of acidic conditions of the peroxide bleaching treatment on chemical pulp components, and especially on its chromophoric structures, affecting color and brightness. Authors describing an improved efficiency of a two-stage process as compared to standard one-stage alkaline process suggested that acidic hydrogen peroxide affects the pulp brightness indirectly, modifying its chromophores in a way which renders them more susceptible to elimination in the second alkaline step [7].

The specificity of research on pulp bleaching is accompanied by the heterogeneous nature of the process. The final pulp brightness results from reactions between active species (e.g. ions, free radicals) dissolved in the bleaching liquor, and chromophoric structures accessible mostly at the fiber surface. The observed changes in brightness of the pulp bleached with acidic hydrogen peroxide do not reflect the treatment parameters only, because the ISO method is also sensitive to light scattering. Thus, the ISO brightness measurement makes possible comparison of the total absorbing species concentration, while not allowing to localize them or to determine the nature of the light-absorbing chromophores, such as lignin or carbohydrate. Therefore, to better understand the chemistry of hydrogen peroxide bleaching under acidic and alkaline conditions we utilized a combination of spectroscopic methods, which allowed us to assess the influence of different treatment factors (e.g. change of pH of the bleaching slurry from acidic to alkaline, dosage of stabilizers) upon the pulp and its main constituents – lignin and carbohydrates.

2. Experimental

2.1. Pulp bleaching

Two unbleached high-yield spruce pulps obtained from International Paper – Kwidzyn/Poland mill were used in this work, namely, a thermomechanical pulp (TMP) with 28.3% initial lignin content and 47.2% ISO brightness and chemothermomechanical pulp (CTMP) with 53.6% ISO brightness and 27.6% initial lignin content. The third sample, softwood kraft pulp after oxygen delignification with less than 2.4% residual lignin (IP Kwidzyn), was used for comparative studies only (Raman spectroscopy).

All experiments on pulp bleaching were made in zip-lock PET bags placed in a thermostatic water bath. The pH of the peroxide solution was adjusted with the use of H_2SO_4 (P_{ac} bleaching stage, pH 2.5 or 4.5) and 2% NaOH on o.d. pulp (P bleaching stage, pH 10.8–11). The conditions of the bleaching were as follows: pulp concentration – 10%, H_2O_2 charge – 3% on o.d. pulp, temperature – 70 °C, treatment time 30 min at the acidic stage and 120 min at the alkaline stage. Cu (II) ions as a catalyst were used at the acidic stage as an aqueous solution of CuSO_4 in some of the bleaching experiments, corresponding to 0.037 $\mu\text{g}/\text{cm}^3$ of Cu^{+2} ions in the bleaching slurry. Depending on the type of experiments, the following stabilizers were dosed into the alkaline medium: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.25% on o.d. pulp) and Na_2SiO_3 (3% on o.d. pulp). After bleaching or additional chemical treatment the pulps were washed with deionised water to neutral reaction and dried at room temperature.

The chelation stage (Q) used 1% solution of EDTA at 50 °C and pH 4.5 for 20 min.

The reduction (B) of carbonyl groups with NaBH_4 was done at room temperature in the following conditions: pulp concentration 1%, 3% NaBH_4 on o.d. pulp (the total amount of this reagent was introduced into the reaction vessel as a single doze), pH 10.0, time of treatment 18 h.

Analytically pure chemical reagents and deionised water were used in this work.

The abbreviations for the treatments used in the present work are listed in Table 1.

Table 1
Abbreviations for the treatments used.

Ref.	No treatment
P_{ac}	Hydrogen peroxide bleaching under acidic conditions
$P_{\text{ac}}(\text{Cu}^{+2})$	Hydrogen peroxide bleaching under acidic conditions with Cu^{+2} catalyst
P_{ac}/P	Two-stage treatment: (1) hydrogen peroxide bleaching under acidic conditions; (2) hydrogen peroxide bleaching under alkaline conditions
$P_{\text{ac}}(\text{Cu}^{+2})/P(\text{Mg}^{+2})$	Two-stage treatment with Cu^{+2} catalyst under acidic conditions and magnesium sulfate (Mg^{+2}) stabilizer under alkaline conditions
$P_{\text{ac}}(\text{Cu}^{+2})/P(\text{SiO}_3^{-2})$	Two-stage treatment with Cu^{+2} catalyst under acidic conditions and sodium silicate (SiO_3^{-2}) stabilizer under alkaline conditions
$P_{\text{ac}}(\text{Cu}^{+2})/P(\text{Mg}^{+2}; \text{SiO}_3^{-2})$	Two-stage treatment with Cu^{+2} catalyst under acidic conditions and magnesium sulfate (Mg^{+2}) with sodium silicate (SiO_3^{-2}) stabilizers under alkaline conditions
B	Reduction of carbonyl groups with NaBH_4
Q	Chelating stage

2.2. Carbonyl and carboxyl groups

The carbonyl group contents in the pulps were determined using potentiometric titration following the modified Lewin and Epstein method [16]. The carboxyl groups were determined with the Wilson's acidimetric method [17]. The aldehyde groups were found as the difference between carboxyl groups determined before and after the oxidation of the pulp with sodium chlorite (0.3 M sodium chlorite in 2 M acetic acid, 48 h of treatment).

The following standard control indices (results not shown) were determined after the pulp treatment: hydrogen peroxide consumption by iodometric titration using saturated ammonium molybdate as a catalyst, pulp yield was determined on the basis of humidity measurements by drying samples to constant weight, brightness of the paper sheets was tested by L&W ELREPHO 2000 spectrophotometer following ISO 2470 standard method (R457 with C-illuminant) [18].

2.3. Spectroscopic methods and equipment

Time-resolved diffuse reflectance laser flash photolysis (DRLFP) experiments were made using the systems available at the IST Lisbon, and were performed at room temperature, in the front-face arrangement. A diagram of the system has been presented in Ref. [19]. The system uses the 337.1 nm pulse of a N_2 laser (Photon Technology Instruments, Model 2000, ca. 600 ps FWHM, ~ 1.3 mJ/pulse) as the excitation source. The light arising from the irradiation of solid samples is detected by a gated intensified charge coupled device (ICCD, Oriel Model Instaspec V). The system was used in the time-resolved mode by using a delay box (Stanford Research Systems, model D6535) and a suitable gate width. The ICCD has high-speed (2.2 ns) gating electronics and an intensifier, and covers the 200–900 nm spectral range. Time-resolved absorption spectra are available in the nanosecond to second time range [19,20].

FT IR spectra were obtained using the KBr pellet technique. Transmission spectra in MIR were recorded on a Mattson Infinity spectrophotometer in the range from 550 to 4000 cm^{-1} with 2 cm^{-1} resolution. The number of scans was 128, and a blank reference was subtracted from the sample spectra. The absorbance spectra were standardized – a baseline correction was performed between 1900 and 836 cm^{-1} and from 3900 to 2250 cm^{-1} .

All of the spectra were normalized by the y-axis expansion algorithm of the spectrophotometer in such a way that the absorption

of the dominant band equaled 1.00. The band intensities of the normal spectra were determined by the baseline method for each of the separate bands. The relative band intensities were related to the intensity of the bands close to 2907 and 1507 cm^{-1} , respectively, which were used as internal references. The intensities were calculated using the appropriate peak heights, with the baseline determined as proposed by Faix [21] and by Kimura et al. [22].

In order to reduce the influence of residual humidity of pulps on FT IR spectroscopic results, the samples were kept in a vacuum desiccator (5×10^{-2} mbar) using phosphoric anhydride (P_2O_5) at room temperature for 2 weeks. Next, normal pressure in the desiccator was restored by introduction of dry air passing through a washer filled with D_2O . After 2 days, the pulp samples were transferred for 2 weeks to a second desiccator with D_2O solution (100% RH, room temperature), thus substituting H_2O by D_2O . The FT IR measurements were carried out at room temperature and in ambient atmosphere.

The FT-Raman spectra were recorded by using a System 2000R spectrometer (Perkin-Elmer) with a liquid-nitrogen-cooled germanium detector. The samples were exposed to the 1064 nm (9394.7 cm^{-1}) line from an Nd:YAG laser source. The power at the sample was maintained at 250 mW. The spectra were collected at 4 cm^{-1} resolution. At least three different zones on each sample were probed in order to ensure reproducibility of the experimental results. Data collection and transfer were managed through Perkin-Elmer Spectrum software.

3. Results and discussion

Mechanical high-yield pulps, such as TMP or CTMP, are fibrous raw materials, containing not only all of the structural wood constituents (hemicelluloses, cellulose, lignin), but also extractives, such as tannins and waxes. Although all of these components determine to some extent the optical properties of pulp, it is the presence of lignin chromophoric structures that is mainly responsible for its brightness and susceptibility toward light-induced yellowing [23,24]. Chromophores and chemical molecules liable for photochemical behavior of pulps occur there both as “native” chemical species and reaction products generated during technological operations (e.g. pulping, high-temperature refining of wood chips, and defibration). This justifies the importance of knowledge of the optical properties of a pulp after each of the technological operations or bleaching stages. The oxidative treatment of lignocellulosics by hydrogen peroxide forms carbonyl and carboxyl groups whose content may be used as indicators of the bleaching agent activity in variable reaction conditions. The content of carbonyl groups in pulps increased as a result of acidic hydrogen peroxide bleaching step (P_{ac}) as compared to carboxyl groups (Fig. 1). A majority of the CO groups is transformed upon treatment under alkaline conditions, with the resulting share of ketone and aldehyde CO groups higher in pulps processed under acidic as opposed to alkaline conditions. The predominance of acidic products due to oxidation of CO into COOH groups is notable after treatment with alkaline hydrogen peroxide (stage P), with the content of reductive (aldehyde) groups very much reduced as a result of this treatment.

The results of ISO Brightness measurements (Table 2) show that acidic hydrogen peroxide actively affects the chromophoric structures in a fibrous material (TMP). Even the brightness loss after treatment under acidic conditions at lower pH 2.5 and the brightness recovery upon borohydride reduction (B) prove such activity

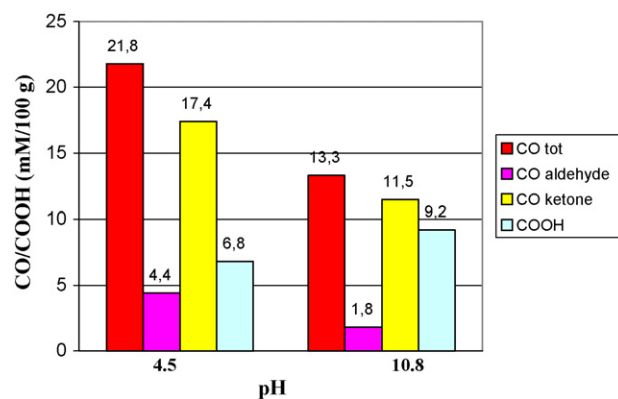


Fig. 1. Content of carbonyl and carboxyl groups in TMP bleached with hydrogen peroxide under acidic and alkaline conditions.

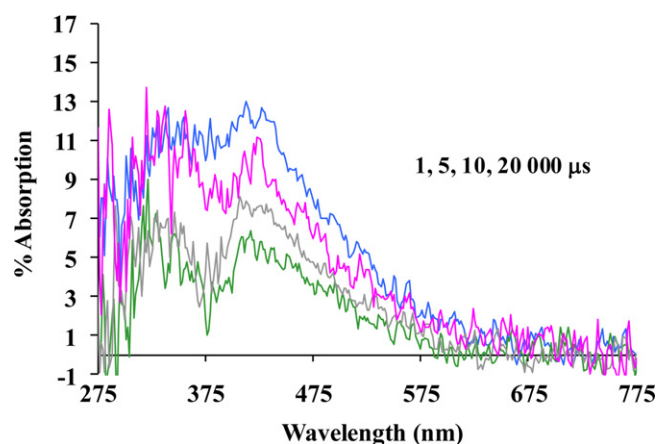


Fig. 2. Diffuse reflectance laser flash photolysis spectra of pulps (CTMP): one-stage hydrogen peroxide treatment under acidic conditions: stage P_{ac} , pH 2.5, Cu^{+2} catalyst; air-equilibrated sample, room temperature. Note the decay of transient species from the first (blue line) to the last (green line) of the spectra shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

through creation of new chromophores, including CO groups. These results show the role of CO groups, also produced on carbohydrate chains under acidic conditions, in their interaction with light resulting in color of the pulp. The efficiency of chromophore elimination increased upon a second (alkaline) hydrogen peroxide bleaching step (P_{ac}/P). These effects were more pronounced when catalyst (Cu^{+2}) was used at the first (acidic) bleaching stage and stabilizers (Mg^{+2} , SiO_3^{-2}) at the second (alkaline) stage. Addition of chelating agents (Q) removing metal ions from the bleaching slurry after the first acidic stage did not alter the pulp brightness. As follows from Table 2, a relatively short acidic treatment of the pulp (30 min) is sufficient for activation of the chromophores, which thereby become prone to elimination by hydrogen peroxide in alkaline medium, while the presence of a catalyst is efficiently neutralized by stabilizers.

The already mentioned difference of hydrogen peroxide activity under acidic and alkaline conditions was confirmed by diffuse reflectance laser flash photolysis (DRLFP), providing direct observations of the changes in the interaction of light with the

Table 2

The effect of different CTMP treatments on ISO Brightness (P_{ac} – pH 2.5; P – pH 10.8).

Ref.	P_{ac}	B/ P_{ac}	P_{ac}/P	$P_{ac}(\text{Cu}^{+2})/P(\text{Mg}^{+2}, \text{SiO}_3^{-2})$	$P_{ac}(\text{Cu}^{+2})/Q/P(\text{Mg}^{+2}, \text{SiO}_3^{-2})$
53.6	52.3	54.9	58.5	63.8	63.4

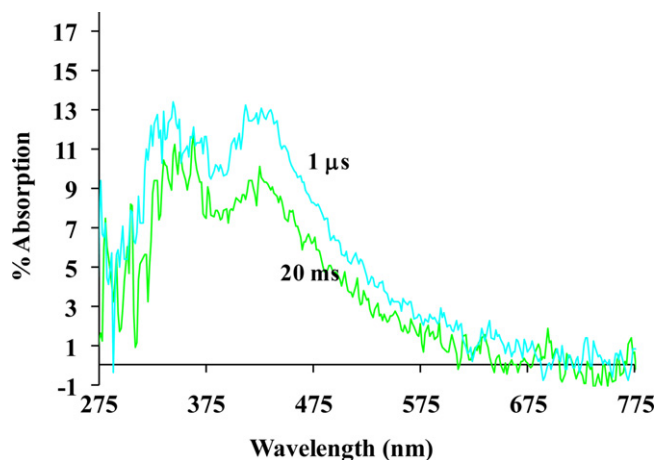


Fig. 3. Diffuse reflectance laser flash photolysis spectra of pulps (CTMP): two-stage bleaching under acidic (stage P_{ac} , pH 2.5, catalyst Cu^{+2} introduced) and alkaline conditions (stage P, pH 10.8, Mg^{+2} and SiO_3^{-2} stabilizers introduced).

chromophoric units in the form of transient absorption spectra. Figs. 2 and 3 show the transient absorption spectra of short-lived transient species, generated in the pulps by laser flash excitation. The spectra were recorded in a very wide range of times from 1 μs to 20 ms after the laser pulse. The general shape and the distinct maximum at about 450 nm with a broad structureless tail extending beyond 750 nm is common to both pulps studied. Thus, we assume that similar transient species appear upon laser excitation of pulps after acidic (P_{ac} – Fig. 2) and alkaline oxidative treatments (P_{ac}/P – Fig. 3). However, the photochemical behavior of the two pulp samples is quite different, reflecting differences in chromophoric structures formed/modified upon bleaching (Figs. 2 and 3). These differences become very pronounced at longer times, for instance, comparing the spectra recorded 20 ms after excitation. Indeed, the spectra of pulp treated under acidic conditions (Fig. 2) show a distinct instability of the transient species that exhibits a faster decay already evident after 5 μs and continuing at longer times. On the other hand, the spectra of transient species recorded in the pulp treated under acidic and then alkaline conditions (Fig. 3) exhibit a much slower decay, remaining almost unchanged even at 20 ms after the laser excitation pulse. Thus, we conclude that short-lived transient species, present in the pulp bleached in the one-stage process under acidic conditions (P_{ac}), are absent in the two-stage bleached pulp (P_{ac}/P). The recorded transient spectra reflect the complex nature of the studied pulps including all of the possible chemical components, such as lignin, cellulose and hemicelluloses, which makes it difficult to attribute the observed transient absorption to any specific chemical group. However, it is widely accepted that the absorption in the 300–400 nm range belongs predominantly to lignin-related chromophoric groups. Several authors interpreting transient spectra of similar pulp samples (spruce TMP) proposed that conjugated α -carbonyl groups strongly contribute in the above-mentioned spectral absorption range [8,25,26]. Comparison to the spectroscopic data (absorption maxima and decay kinetics) obtained for the black spruce thermomechanical pulp shows that in our case the respective transient could be interpreted as aromatic carbonyl triplet state [25]. However, identification of chromophoric quinone and hydroquinone groups proves the possible complexity of the studied pulp samples (TMP and CTMP), with the transient absorptions probably belonging to several chemically distinct species [5,27].

The FT IR spectra allowed us to better understand reactions of the pulp constituents or its specific chemical groups with hydrogen peroxide under different conditions (acidic vs. alkaline media, addition of stabilizers at the second bleaching stage). The spectra

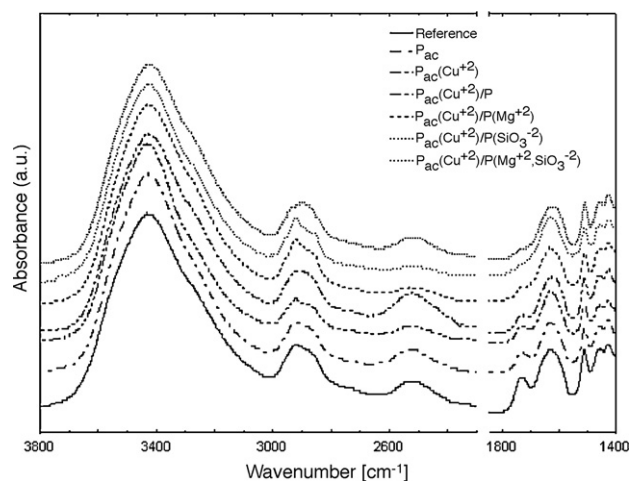


Fig. 4. FT IR spectra of CTMP's bleached with hydrogen peroxide under acidic and alkaline conditions with various additives (P_{ac} – pH 2.5; P – pH 10.8) (samples after D_2O sorption). Note that different spectra were arbitrarily shifted along the vertical axis, for visual separation.

are quite complex, which is typical for lignocellulosics; moreover, there may be cases of more than one species absorbing at the same characteristic frequency (Fig. 4). Taking into consideration the chemistry of hydrogen peroxide bleaching treatment and the results of CO/COOH analysis (Fig. 1), molecular changes should be observable mainly in the bands around 1600–1750 cm^{-1} [28]. This spectral range is relatively free of distinct vibrations belonging to other functional groups, therefore the band at 1729 cm^{-1} is commonly assigned to stretching vibrations of carbonyl groups, predominantly belonging to acid and ester functional groups of hemicelluloses [29,30]. However, an important obstacle to semi-quantitative measurements of the carbonyl group band is the so-called “bound water” adsorbed into the pulp fibers. Indeed, the bending vibrations of H_2O molecules occur at around 1640 cm^{-1} and may interfere with the CO band, making quantitative interpretation more difficult [28–30].

Therefore, we made efforts to remove bound water from the pulp samples, by drying in vacuum and at raised temperature, with subsequent isotopic exchange using heavy water D_2O [28]. The spectra in Fig. 5 show the effects of D_2O penetration into the pulp samples. Contrary to expectations, no distinct shift of the 1640 cm^{-1} band towards lower frequencies was observed, which would confirm the process of “cleaning up” of the carbonyl vibrations range. However, at least part of the adsorbed water molecules

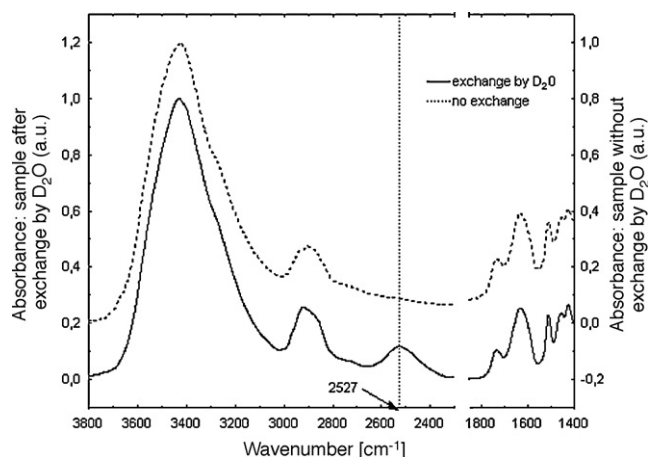


Fig. 5. FT IR spectra of CTMP's before and after D_2O sorption.

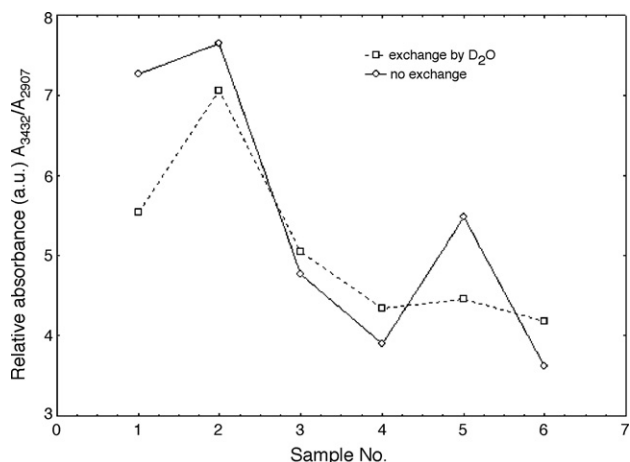


Fig. 6. Relative FT IR absorbances of the CTMP's treated under various conditions – samples before and after D₂O absorption: 1 – reference, 2 – P_{ac}, 3 – P_{ac}(Cu²⁺)/P, 4 – Pac/P (Mg²⁺), 5 – Pac(Cu²⁺)/P (SiO₃²⁻), 6 – Pac(Cu²⁺)/P(Mg²⁺, SiO₃²⁻).

was exchanged or eliminated from this spectral range, as demonstrated by the appearance of the 2527 cm⁻¹ band arising from the O–D stretching vibrations. Note, however, that other authors also found it impossible to obtain isotopic exchange at more than 40% using the same procedure [28]. The response of the pulp samples towards D₂O exchange was non-uniform. Namely, the pulps treated under acidic conditions (Fig. 6, samples 1 and 2) show an increase of relative absorbance at 3432 cm⁻¹, which may be explained by the exchange of O–H for O–D groups, confirmed by the shift of the absorption band up to 2527 cm⁻¹. The spectroscopic behavior of the pulp samples bleached under alkaline conditions is different, marked by a generally increased relative absorbance (Fig. 6, samples no 3, 4, 6). The only exception is the pulp bleached in the presence of Na₂SiO₃ as a stabilizer, which may form a persistent residue on the fibers making the interpretation difficult (Fig. 6, sample no 5) [15]. The observed increase in the relative absorbance of the pulp samples bleached at alkaline medium results probably from the lowering of OH functional groups content of the oxidized carbohydrates and lignin. The phenyl OH groups of lignin origin along with COOH/COONa groups created on carbohydrates are known to react under alkaline conditions, undergoing further degradation (e.g. splitting) [31,32]. Another possibility is that bleaching under alkaline conditions might change the pulp in a way that it binds H₂O molecules stronger, making it more difficult to exchange them for D₂O, as happened in acidic hydrogen peroxide treated pulp samples. However, independently of the reference used, the change pattern of the relative absorbances for two different internal references (1507 and 2907 cm⁻¹) is nearly the same, confirming the correct choice of the reference bands (Fig. 7).

To obtain a better understanding of the structural transformations due to different bleaching stages, we calculated the relative absorbances at 1729 cm⁻¹ for the two above-mentioned internal references (Fig. 8), concluding that they change in a manner almost independent on the reference used. Noting that the band at 1507 cm⁻¹ is attributed to the phenyl ring stretching modes, we conclude that its stability confirms the non-delignifying character of the bleaching treatment, as the aromatic lignin successfully resisted the hydrogen peroxide treatment. As seen in Fig. 8, the absorption at 1729 cm⁻¹ decreased after peroxide treatment in alkaline medium, which we believe results from the splitting of the ester groups of hemicelluloses due to alkaline hydrolysis [33]. The relative absorbance already decreased after treatment under alkaline conditions (Fig. 8, sample no 3) but it was the addition of magnesium sulfate that improved the technologic efficiency of the peroxide treatment resulting in higher brightness values but

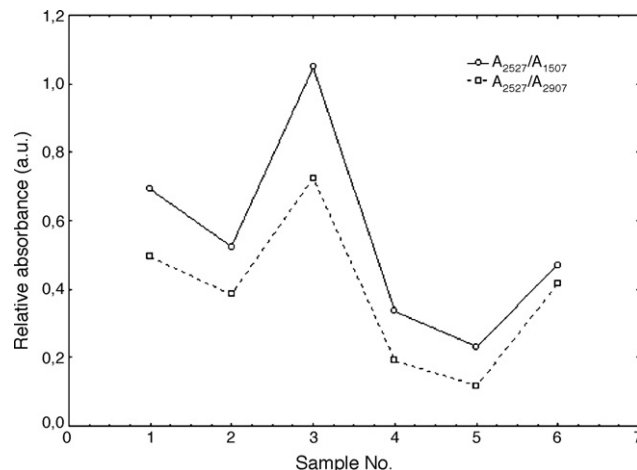


Fig. 7. Relative FT IR absorbances of the CTMP's treated under various conditions – samples after D₂O absorption: 1 – reference, 2 – P_{ac}, 3 – P_{ac}(Cu²⁺)/P, 4 – Pac/P (Mg²⁺), 5 – Pac(Cu²⁺)/P (SiO₃²⁻), 6 – Pac(Cu²⁺)/P(Mg²⁺, SiO₃²⁻).

also the lower relative absorbance (Fig. 8, sample no 4) [10]. Taking into consideration that the same alkali charge was used at the second stage (P) both with and without magnesium sulfate, the question whether the observed changes of absorption arise from better general conditions of the peroxide oxidative treatment deserves further studies [34]. The bleaching reactions that reduce the relative absorbance even more proceed further when sodium silicate is present (Fig. 8, sample no 5). Hydrolysis of this stabilizer produces additional alkali, preventing the decrease of pH of the bleaching slurry due to acidic products formed upon oxidation, and thus increasing bleaching efficiency [15]. Such treatment conditions are favorable also for alkaline hydrolysis of ester functional groups of hemicelluloses. The case of pulp bleached in presence of two stabilizers (SiO₃²⁻, Mg²⁺) is more complex (Fig. 8, sample no 6). As it was shown earlier [9,10], the joint usage of these two stabilizing agents during bleaching improves ISO Brightness and other technological factors (hydrogen peroxide consumption, pulp yield), involving a change in the stabilization mechanism. According to Lapiere et al. [13], magnesium sulfate transforms into magnesium hydroxide in alkaline medium, creating bonds with carboxyl groups formed during pulp bleaching and thus protecting them against splitting. Several mechanisms have been proposed for the sodium silicate stabilizing effect [14,15], although none of these involves

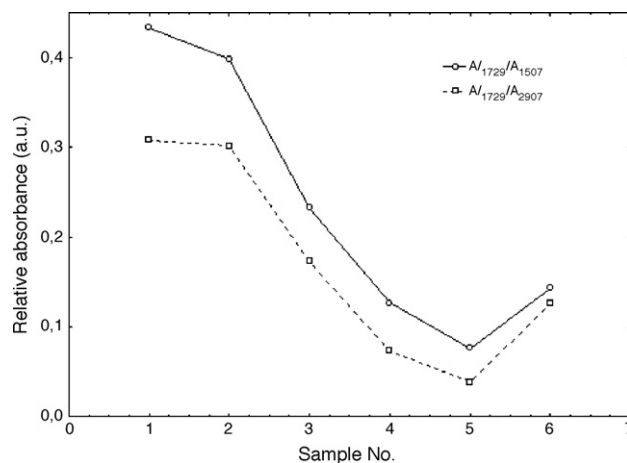


Fig. 8. Relative FT IR absorbances of the CTMP's treated under various conditions – samples after D₂O absorption: 1 – reference, 2 – P_{ac}, 3 – P_{ac}(Cu²⁺)/P, 4 – Pac/P (Mg²⁺), 5 – Pac(Cu²⁺)/P (SiO₃²⁻), 6 – Pac(Cu²⁺)/P(Mg²⁺, SiO₃²⁻).

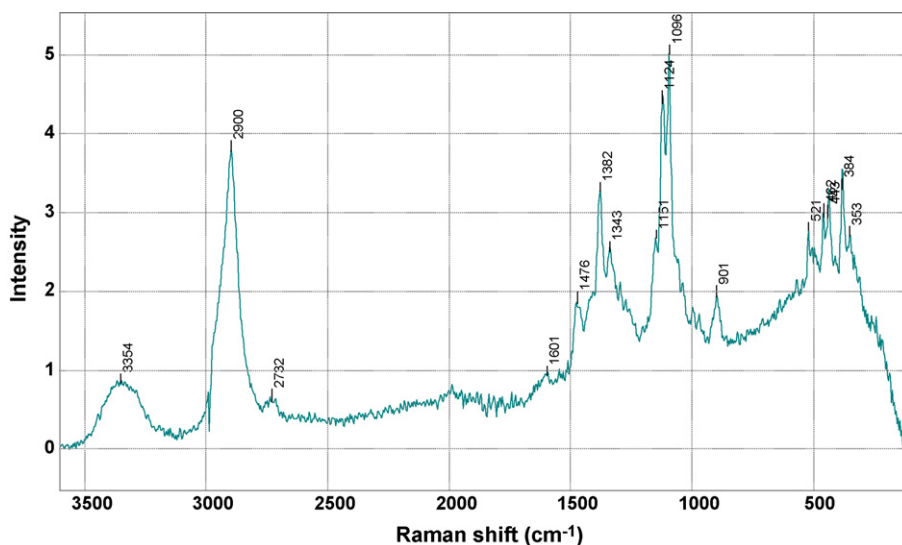


Fig. 9. FT-Raman spectrum of oxygen-delignified kraft softwood pulp.

interaction with carboxylic groups, which to some extent explains similarity between the relative absorbance values of the pulp samples treated by magnesium sulfate only (sample no 5, Fig. 8) and jointly by magnesium sulfate and sodium silicate (sample no 6, Fig. 8).

Conventional Raman spectroscopy applying laser excitation in the visible region is not suitable for plant material analysis because of fluorescence emission interfering with Raman measurements and possible sample damage caused by high laser power. The application of near-infrared excitation allows to reduce these inconveniences [5,27,33,34]. The other advantage of FT-Raman spectroscopy is that the time needed to record a spectrum has been seriously shortened [35,36] (Fig. 9). Besides, as opposed to the FT IR measurements, the moisture in the sample affects the FT-Raman spectra only very weakly and the presence of adsorbed water does not trouble in analysis [36,37]. The important thing is that FT-Raman and IR methods supply complementary data.

The complex nature of the pulp samples, comprising carbohydrates (cellulose and hemicellulose) and lignin would suggest that their spectra will present contributions from all these structural

components, making it difficult to assign spectral bands to specific vibrational modes. In fact, cellulose has got chemical bonds similar to those of hemicellulose, and that is why the latter is not easily detectable [35]. However, according to Agarwal and Ralph, who identified contributions of lignin and carbohydrates in the FT-Raman spectrum of black spruce pulp [35], few of the detected bands could be assigned to both cellulose and lignin. It is generally accepted that bands below 520 nm belong predominantly to cellulose, although for example the peak at 492 nm is attributed to both carbohydrates and lignin [35]. The sharp and intense peaks at 901, 1100, 1127, 1339, 1382 and 1460 cm^{-1} , visible in the spectrum of unbleached spruce pulp (Fig. 10), have strong resemblance to similar features assigned to carbohydrate components (mostly cellulose) by Agarwal and Ralph [35]. The weak band at 2740 cm^{-1} may also be attributed to cellulose [35], while the distinct asymmetric band close to 2900 cm^{-1} belongs to aliphatic $\nu(\text{C-H})$ stretch mode of cellulose [38]. The broad band around 3350 cm^{-1} is interpreted as $\nu(\text{O-H})$ stretching mode of the OH groups associated with hydrogen bonds [39].

However, the bands most interesting in terms of changes introduced by bleaching are those exclusively assigned to lignin-derived

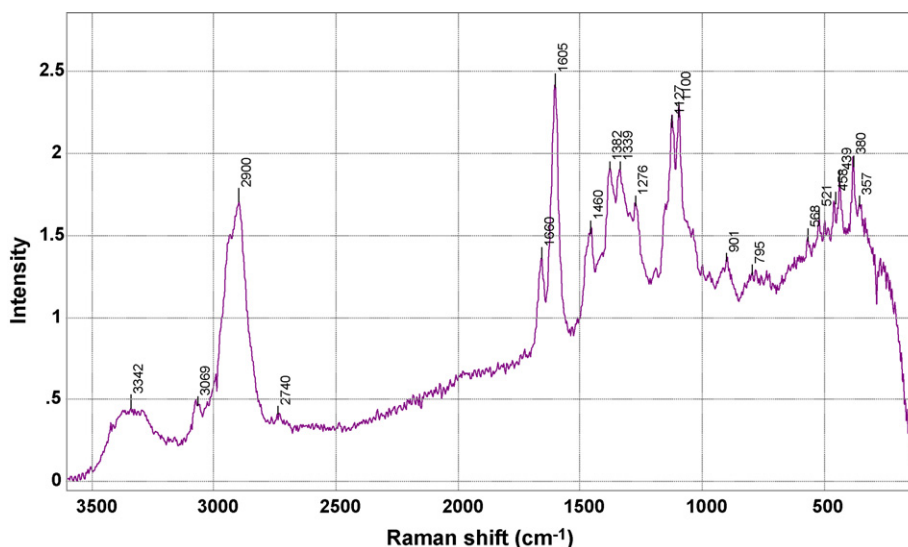


Fig. 10. FT-Raman spectrum of softwood CTMP.

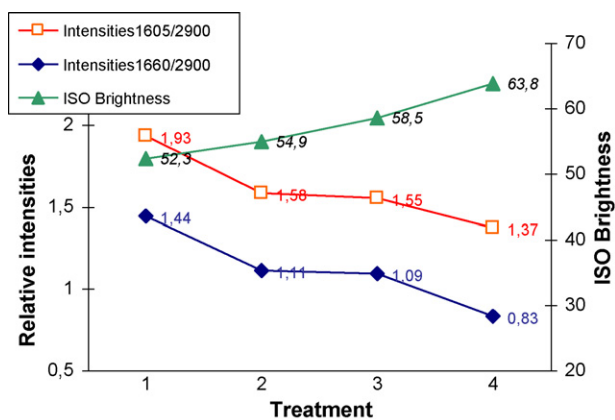


Fig. 11. Relative FT IR Raman intensities of the stretching vibrations at 1605 and 1660 cm^{-1} calculated in relation to the internal reference band at 2900 cm^{-1} and ISO Brightness of the TMP samples bleached in various conditions: 1 – P_{ac} , 2 – $\text{P}_{\text{ac}}/\text{P}$, 3 – $\text{P}_{\text{ac}}/\text{P}/\text{B}$, 4 – $\text{P}_{\text{ac}}(\text{Cu}^{+2})/\text{P}(\text{Mg}^{+2}, \text{SiO}_3^{-2})$.

structures. Changes due to the bleaching treatment are observed mainly in the “chromophoric” lignin bands at 1605 and near 1660 cm^{-1} (Fig. 10). The first band is associated with aryl ring stretching vibrations and the second one originates from the C=O stretch in coniferaldehyde or ring-conjugated C=C of coniferyl alcohol [38]. Both these bands are characteristic for the lignin-rich high-yield pulp and sensitive to bleaching. Only one of them (1601 cm^{-1}) is probably observed in the reduced form in the spectrum of oxygen-delignified softwood kraft pulp having less than 2% of residual lignin, with the peak at 1660 cm^{-1} being absent (Fig. 9). There was another band detected at near 1620 cm^{-1} , appearing as a weak shoulder (better visible in the spectrum of a similar TMP see Fig. 5 from Ref. [10]). The shoulder arises due to coniferaldehyde groups of lignin and is also susceptible to bleaching [4,5,35]. However, the studied pulp is not typical, as it was produced using a non-pressurized refiner (adapted from Brite-Chem technology), therefore its chromophoric system and to some extent spectral characteristics differ from standard CTMP produced using a thermo-defibrator. This was the reason why we focused our attention on the two above-mentioned intense “chromophoric” bands. As shown in Fig. 11, both “chromophoric” bands show a loss of the relative intensity (calculated as the ratio to the band at 2900 cm^{-1} , used as an internal reference) depending on the bleaching treatment. The values of the relative intensities for the pulp samples treated by oxidative and reductive bleaching agents may be ordered as follows: $\text{P}_{\text{ac}} > \text{P}_{\text{ac}}/\text{P} > \text{P}_{\text{ac}}/\text{P}/\text{B} > \text{P}_{\text{ac}}(\text{Cu}^{+2})/\text{P}(\text{Mg}^{+2}; \text{SiO}_3^{-2})$. Importantly, these spectroscopic data correlate well with the ISO Brightness measurements (Fig. 11). An observed drop in intensity of the chromophoric bands confirms that the usage of activated hydrogen peroxide under acidic conditions, followed by a second alkaline stage, can improve elimination of the chromophores. The reduction of carbonyl groups by the borohydride reduced the chromophore concentration in the pulp still further. The lowest relative intensities and the highest ISO brightness were obtained when catalyst at the first acidic step and stabilizers at the second alkaline bleaching stage were used. The treatment of pulp with hydrogen peroxide under acidic conditions, particularly in presence of a catalyst, may activate potential chromophores on the fiber surface that are subsequently eliminated at the alkaline bleaching stage.

4. Conclusions

The usage of different spectroscopic methods made possible the monitoring of changes in chromophoric system of high-yield pulps

(TMP and CTMP), bleached by hydrogen peroxide under acidic and alkaline conditions with various additives such as catalysts and stabilizers. Diffuse reflectance laser flash photolysis (DRLFP) demonstrated that pulp chromophores or their chemical environment are transformed already at the preliminary acidic peroxide stage, facilitating their subsequent bleaching by alkaline peroxide. FT IR spectroscopy confirmed the non-delignifying character of the process and allowed to differentiate the effects of bleaching between pulp samples treated under acidic and alkaline conditions. Distinct differences were observed when monitoring relative absorbance changes at 1729 cm^{-1} of pulps bleached with magnesium sulfate and sodium silicate, used as stabilizers. FT-Raman spectroscopy allowed to localize the observed transformations of the chromophores. Spectroscopic data describing vibrations in lignin-related coniferaldehyde units correlated well with the ISO Brightness measurements.

References

- [1] R.W. Allison, K.L. Graham, *J. Pulp Pap. Sci.* 15 (1989) 145–151.
- [2] G.C. Hobbs, J. Abbot, *J. Wood Chem. Technol.* 14 (1994) 195–225.
- [3] J. Abbot, G.C. Hobbs, *J. Pulp Pap. Sci.* 18 (1992) 67–70.
- [4] U.P. Agarwal, L.L. Landucci, *ISWPC International Symposium of Wood and Pulp- ing Chemistry S EPPG Saint Martin d’Heres (Ed.) Proceedings*, vol. 3, Nice France, 2001, pp. 563–567.
- [5] U.P. Agarwal, L.L. Landucci, *J. Pulp Pap. Sci.* 30 (2004) 269–274.
- [6] L. Lapiere, J. Bouchard, R.M. Berry, B. van Hierop, *J. Pulp Pap. Sci.* 21 (1995) J268–J273.
- [7] G.C. Hobbs, J. Abbot, *J. Wood Chem. Technol.* 11 (1991) 225–246.
- [8] A. Wójciak, M. Sikorski, R. Gonzalez-Moreno, J.L. Bourdelande, F. Wilkinson, *Wood Sci. Technol.* 36 (2002) 187–195.
- [9] E. Sikorska, I.V. Khmelinskii, A. Krawczyk, A.S. Oliveira, L.F.V. Ferreira, A. Wójciak, M. Sikorski, *J. Photochem. Photobiol. A* 184 (2006) 66–72.
- [10] A. Wójciak, H. Kasprzyk, I. Khmelinskii, A. Krawczyk, A.S. Oliveira, L.F.V. Ferreira, A. Weselucha-Birczyńska, M. Sikorski, *J. Phys. Chem. A* 111 (2007) 10530–10536.
- [11] D.G. Brown, J. Abbot, *Appita* 47 (1994) 211–220.
- [12] L. Lapiere, R. Berry, J. Bouchard, *Holzforchung* 54 (2000) 279–286.
- [13] L. Lapiere, R. Berry, J. Bouchard, *Holzforchung* 57 (2003) 627–633.
- [14] J.L. Colodette, S. Rothenberger, C.W. Dence, *J. Pulp Pap. Sci.* 15 (1989) 45–50.
- [15] J.L. Colodette, S. Rothenberger, C.W. Dence, *J. Pulp Pap. Sci.* 15 (1989) J3–J10.
- [16] M. Lewin, J.A. Epstein, *J. Polym. Sci.* 58 (1962) 1023–1037.
- [17] K. Wilson, *Tappi* 44 (1961) 131–137.
- [18] ISO 2470, Paper and Board – Measurement of Diffuse Blue Reflectance Factor. (ISO Brightness), 1997.
- [19] A.M. Botelho do Rego, L.F.V. Ferreira, in: H.S. Nalva (Ed.), *Handbook of Surfaces and Interfaces of Materials*, Academic Press, New York, 2001, p. 275.
- [20] L.F.V. Ferreira, I.F. Machado, A.S. Oliveira, M.R.V. Ferreira, J.P. da Silva, J.C. Moreira, *J. Phys. Chem. B* 106 (2002) 12584–12593.
- [21] O. Faix, *Holzforchung* 40 (1986) 273–280.
- [22] F. Kimura, T. Kimura, D.G. Gray, *Holzforchung* 46 (1992) 529–532.
- [23] H. Takagi, I. Forsskahl, H. Perakyla, S. Omori, C.W. Dence, *Holzforchung* 44 (1990) 217–222.
- [24] K. Fischer, M. Beyer, H. Koch, *Holzforchung* 49 (1995) 203–210.
- [25] J.A. Schmidt, C. Heitner, G.P. Kelly, P.A. Leicster, F. Wilkinson, *Ist European Workshop on Lignocellulosics and Pulp – Proceedings*, Hamburg-Bergedorf, 1990, p. 266.
- [26] J.A. Schmidt, C. Heitner, G.P. Kelly, P.A. Leicster, F. Wilkinson, *J. Pulp Pap. Sci.* 16 (1990) J111–J117.
- [27] U.P. Agarwal, *J. Wood Chem. Technol.* 18 (1998) 381–402.
- [28] J. Łojewska, P. Miśkowiec, T. Łojewski, L.M. Proniewicz, *Polym. Degrad. Stabil.* 88 (2005) 512–520.
- [29] L.M. Proniewicz, Cz. Paluszkiwicz, A. Weselucha-Birczyńska, H. Majcherczyk, A. Barański, A. Konieczna, *J. Mol. Struct.* 596 (2001) 163–169.
- [30] L.M. Proniewicz, Cz. Paluszkiwicz, A. Weselucha-Birczyńska, A. Barański, D. Dutka, *J. Mol. Struct.* 614 (2002) 345–353.
- [31] J. Marton, in: K.V. Sarkanen, C.H. Ludwig (Eds.), *Lignins, Occurrence, Formation, Structure and Reactions*, Wiley-Interscience, 1971, p. 651.
- [32] A. Meller, *Holzforchung* 14 (1960) 78–83.
- [33] U.P. Agarwal, J.P. Mc Sweeney, *J. Wood Chem. Technol.* 17 (1997) 1–26.
- [34] R.H. Atalla, in: D. Burton, K. Nakanishi, O. Cohn (Eds.), *Comprehensive Natural Product Chemistry*, Elsevier Science, Oxford, UK, 1999, p. 529.
- [35] U.P. Agarwal, S.A. Ralph, *Appl. Spectrosc.* 11 (1997) 1648–1655.
- [36] U.P. Agarwal, I.A. Weinstock, R.H. Atalla, *Tappi J.* 1 (2003) 22–26.
- [37] J.J. Workman, *J. Appl. Spectrosc. Rev.* 36 (2001) 139–168.
- [38] U.P. Agarwal, in: D.S. Agrypoulos (Ed.), *Advances in Lignocellulosic Characterisation*, TAPPI Press, 1999, p. 201.
- [39] M. Takayama, T. Johjima, T. Yamanaka, H. Wariishi, H. Tanaka, *Spectrochim. Acta* 53 A (1997) 1621–1628.