Direct Characterization of Hydrogen Peroxide Bleached Thermomechanical Pulp Using Spectroscopic Methods

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The effects of thermomechanical pulp (TMP) bleaching with hydrogen peroxide under acidic and alkaline conditions were studied using different spectroscopic analytical methods. The results of hydroxyl radical determination in bleaching solutions, analyses of carbonyl and carboxyl groups contents in the pulp, and the cellulose fiber surface analysis by X-ray photoelectron spectroscopy (XPS) elucidate the chemistry of the hydrogen peroxide treatment. Diffuse reflectance laser flash photolysis (DRLFP) method showed the differences in the photochemical behavior that reflect the changes of the chromophoric system after the preliminary peroxide bleaching stage under acidic conditions. Fourier transform infrared (FTIR) spectroscopy confirmed the non-delignifying character of the bleaching process. Suppression of carbonyl and formation of carboxyl groups in the case of the two-stage peroxide bleaching performed in the presence of catalysts and stabilizers was also confirmed. FT-Raman studies showed the removal of coniferaldehyde groups after treatment under acidic and alkaline conditions.

1. Introduction

Hydrogen peroxide is commonly used in the paper-making industry as an environmentally friendly, easy-to-operate reagent for non-delignifying bleaching of high-yield pulps.[1] The bleaching is carried out as a single-stage process under alkaline conditions, which is in agreement with the phenomenon of enhancement of the final pulp brightness accompanying the increase of the basicity of the bleaching slurry up to approximately pH = 11.[2] The essential feature of the non-delignifying process is the elimination of the chromophores from the pulp without any chemical loss of pulp constituents, such as lignin or carbohydrates. In this way high fiber yields are assured.

Because of the relatively high treatment costs, many attempts have been made to improve peroxide bleaching by varying the process conditions, including the use of acidic medium at an additional first stage.[2−4] Two-stage peroxide bleaching under acidic conditions at the first and alkaline at the second stage has beneficial effects both on peroxide consumption and on the final brightness, at the same time conserving the high pulp yields.[5−9] Hydrogen peroxide is relatively stable in the acidic medium; therefore, metal catalysts are used for its activation. The increase of the hydrogen peroxide activity toward pulp is ascribed to its decomposition into free-radical products or formation of transient complexes with metals.[10] High efficiency of the peroxide bleaching in alkaline media is sustained by added stabilizers, such as magnesium sulfate and sodium silicate.[11−13]

The reactions of alkaline hydrogen peroxide with lignin and carbohydrates are well-known. However, there is a lack of information concerning its reactivity with the chemical constituents of pulp under acidic conditions.[14] Acidic hydrogen peroxide has been reported not to influence the pulp brightness.[2] Improvement of the ISO brightness values recorded after an acid−alkali two-stage treatment suggests that even though the chromophores are not removed from the pulp under acidic conditions, they are nevertheless modified in such a way that renders them more susceptible for elimination in the alkaline stage.[2,15] In our previous investigations, we studied the interactions of light with chromophores of thermomechanical pulp (TMP) bleached by hydrogen peroxide under acidic and alkaline conditions, using different spectroscopic methods.[15] In all of the spectroscopic methods we have used (UV−vis, time-resolved fluorescence and emission spectroscopy, and diffuse reflectance laser flash photolysis (DRLFP)), the recorded spectra differed from sample to sample in function of treatment, which suggests significant changes in the chromophoric system due to the treatments. The results of our studies confirm that activated acidic hydrogen peroxide does affect the chromophores, as revealed by the relatively small changes in the ISO brightness. Standard ISO brightness measurements indicate the occurrence of some changes in the chromophoric system; however, they are unable to give any information on the respective chemistry and do not allow one to trace the changes to the respective components of the pulp fiber (lignin, carbo-

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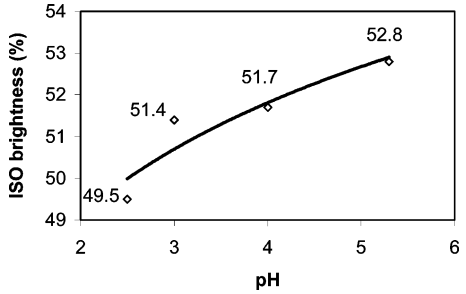

Figure 1. Effect of pH of acidic hydrogen peroxide solution on spruce TMP brightness (49.9% ISO brightness, untreated pulp).

hydrates) in the same way as the spectroscopic methods do. Clearly, practical usage of activated acidic hydrogen peroxide at a preliminary bleaching stage in the industrial practice requires a far deeper understanding of its reactivity with the pulp chromophores.

The specific character of the studies on bleaching of the pulp fibers results from the heterogeneous nature of the process. The final brightness is determined by the reactions of active species, such as anions and free radicals present in the bleaching slurry, with the chromophoric structures and functional groups existing in lignin or carbohydrates—the main chemical components of wood fibers. The brightness is the effect of interaction of light with the surface of fibers, being an indirect indicator of the concentration of the absorbing species. Therefore, to understand hydrogen peroxide bleaching reactions under acidic and alkaline conditions, we presently applied a combination of analytical methods, which allowed us to evaluate the importance of various treatment factors, with regard to both the bleaching slurry and the pulp. The concentration of hydroxyl radicals in the presence of catalyst and stabilizers in peroxide solution and carbonyl and carboxyl groups content in the pulp were determined using wet chemistry techniques. Direct spectroscopic methods were applied to study the interaction of pulp with light (DRLFP), its surface chemical composition (X-ray photoelectron spectroscopy (XPS)), and structural changes (Fourier transform infrared (FTIR) and FT-Raman).

2. Experimental Section

2.1. Pulp Bleaching. Unbleached thermomechanical spruce pulp (TMP) with 28.3% initial lignin content and 47.2% ISO brightness, obtained from International Paper—Kwidzyn/Poland mill, was predominantly used in this work, except for the TMP samples shown on Figure 1 with 49.9% ISO brightness.

All experiments on the TMP bleaching were made in zipper-sealed polyethylene terephthalate (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 = 4.5 if not indicated otherwise) and NaOH (P_{alk} bleaching stage, pH = 10.8−11). The bleaching conditions were as follows: pulp consistency, 10% (30 g of oven-dried (o.d.) pulp were used in such experiments); H_2O_2 charge, 3% on o.d. pulp; temperature, 70 °C; 30 min treatment time at the acidic stage and 120 min at the alkaline one. The Cu^{2+} ions were introduced at the acidic stage as a catalyst in the amount of 0.0556 μM as an aqueous solution of $CuSO_4$. The concentration of Cu^{2+} ions in the bleaching solution was 0.037 μg/cm^3. Depending on the type of experiments, the following stabilizers were dosed into the alkaline medium: $MgSO_4 \cdot 7H_2O$ (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 distilled water to neutral pH and dried at room temperature.

The reduction of carbonyl groups with $NaBH_4$ after the chosen peroxide stages was made at room temperature in the following conditions: pulp consistency, 1%; $NaBH_4$ charge, 3% on o.d. pulp (the total amount of this reagent was introduced to the reaction vessel at once); pH = 10.0; 18 h treatment time. The abbreviations for the treatments used are listed in Table 1.

2.2. Hydroxyl Radicals. Hydroxyl radicals were determined by the colorimetric method using the *N*,*N*-dimethyl-4-nitrosoaniline (DMNA) solution (2.5×10^{-5} M) at the wavelength of 440 nm.[16] The investigations were performed in a water bath in PET bags with zippered seals. The hydrogen peroxide concentration was 1.2% on o.d. pulp, while the concentration of the charged catalysts in the form of aqueous solutions of $CuSO_4$ was 0.00371 μM on o.d. pulp. The pulp consistency was 1% (1 g of o.d. pulp was used in the experiment). The reagent concentrations used in the blank runs, without any pulp added, were the same as those for the pulp consistency of 1%. The sequence of the addition of reagents was as follows: water; DMNA; catalyst; H_2O_2; pH correction. Colorimetric tests were made with the use of a SPECORD M-40 spectrophotometer.

Analytically pure chemical reagents and deionized water were used throughout.

2.3. Carbonyl and Carboxyl Groups. The carbonyl groups content in the pulps was determined using potentiometric titration following the modified Lewin and Epstein method.[17] The carboxyl groups were determined with the Wilson's acidimetric method.[18] 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 standard deviations calculated for CO and COOH determinations in five oxidized pulp samples were equal to 0.57 and 0.46, respectively (mM/(100 g of o.d. pulp)).

Standard control indices were determined after the pulp treatment: hydrogen peroxide consumption by iodometric titration using saturated ammonium molybdate as a catalyst; brightness of the paper sheets tested by L&W ELREPHO 2000 spectrophotometer following ISO 2470 standard method (R457 with the C-illuminant).

2.4. Spectroscopic Methods and Equipment. X-ray photoelectron spectroscopy measurements were performed using a VG Scientific ESCALAB-210 spectrometer. A Mg Kα radiation source operated at 300 W (15 kV, 20 mA) was used. Vacuum in the analysis chamber was below 8×10^{-9} mbar during all measurements. The spectrometer binding energy scale was calibrated by the Ag $3d_{5/2}$ peak at 368.27 eV and Ag M_4NN peak at 895.75 eV. The survey spectra were recorded at 100 eV analyzer pass energy, 0.4 eV increment, and analyzer axis normal to the surface. Detailed high-resolution scans were recorded with CAE = 20 and 0.1 eV increment. All binding energies (BE) were referred to the C 1s carbon peak at 286.73 eV. Data were analyzed using the Avantage program, including satellite subtraction, Shirley background subtraction, and fitting procedure, using a Gauss-to-Lorentz constant ratio of 0.3. Quantification was made using common Scofield sensitivity factors.

Time-resolved diffuse reflectance laser flash photolysis (DRLFP) experiments were made using the systems available in IST Lisbon and were performed at room temperature, in the front-face arrangement. A diagram of the system is presented in ref 19. The system uses a 266 nm pulse of a Nd:YAG laser (B.M.Industries (Thomson-CSF), Model Saga 12-10, ca. 6 ns full width at half-maximum (fwhm), ~10−30 mJ/pulse) as the excitation source. The light arising from the irradiation of solid

TABLE 1: Abbreviations for the Treatments Used

abbreviation	description
ref	reference sample, no treatment
P_{ac}	hydrogen peroxide bleaching under acidic conditions
P_{alk}	hydrogen peroxide bleaching under alkaline conditions
$B_{red.}$	sodium borohydride reduction
$P_{ac}(Cu^{2+})$	hydrogen peroxide bleaching under acidic conditions with Cu^{2+} catalyst
$P_{alk}(Mg^{2+};SiO_3^{2-})$	hydrogen peroxide bleaching under alkaline conditions with stabilizers (Mg^{2+}; SiO_3^{2-})
P_{ac}/P_{alk}	two-stage treatment: (1) hydrogen peroxide bleaching under acidic conditions; (2) hydrogen peroxide bleaching under alkaline conditions
$P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+};SiO_3^{2-})$	two-stage hydrogen peroxide bleaching with Cu^{2+} catalyst under acidic conditions and stabilizers (Mg^{2+}; SiO_3^{2-}) under alkaline conditions

TABLE 2: ISO Brightness of the TMP after Different Treatments

sample	treatment	ISO brightness	sample	treatment	ISO brightness
1	ref.	47.2	5	$P_{ac}/B_{red.}$	55.1
2	$B_{red.}$	54.0	6	P_{alk}	57.0
3	P_{ac}	52.7	7	P_{ac}/P_{alk}	57.7
4	$P_{ac}(Cu^{2+})$	51.5	8	$P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+},SiO_3^{2-})$	69.2

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]

FTIR 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 4000 to 2400 cm^{-1}, and the spectrum was normalized by the *y*-axis expansion algorithm of the spectrometer in such a way that the absorption of the dominant band equalled 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 standards. The intensities were calculated using the appropriate peak heights with the baselines determined as proposed by Faix and by Kimura et al.[21,22]

The FT-Raman spectra were measured on a Bio-Rad FT-Raman accessory (based on a FTS 6000 spectrometer) with a liquid-nitrogen-cooled germanium detector. The samples were excited with the 1064 nm line of a diode-pumped Nd:YAG Spectra-Physics laser, model T10-8S. The power at the sample was maintained at 200 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.

3. Results and Discussion

3.1. Effect of Acidic and Alkaline Hydrogen Peroxide on Optical Properties of Pulp. There are many chromophoric units and functional groups in the pulp originating predominantly from lignin, but only a few of these are precisely known. Hydrogen peroxide as an excellent bleaching reagent is active toward most of them in alkaline media, bleaching both the (most important) lignin chromophores and the chromophoric groups bonded to carbohydrates. However, the reactivity of hydrogen peroxide toward pulp is different in acidic and alkaline media, caused by differences in the amount and variety of the peroxide decomposition products. These changes in peroxide activity become more pronounced when catalysts are added in the acidic media and stabilizers in the alkaline media (Table 2). The lowering of the ISO brightness after treatment under acidic conditions, especially when catalyst was introduced into the reaction volume, followed by brightening of the pulp after borohydride reduction, suggests that the peroxide decomposition products may create new chromophoric structures including carbonyl groups. It is important from the technological point of view that a two-stage bleaching with hydrogen peroxide results in higher brightness values as compared to the standard one-stage alkaline treatment.

Note that the drop in brightness resulting at the acidic hydrogen peroxide stage depends on the pH of the bleaching slurry. This effect becomes stronger at pH < 2.5, which suggests an incidental creation of new chromophores during the treatment. At higher pH values, the growing tendency of hydrogen peroxide to dissociate into an ionic form correlates with the higher brightness (Figure 1).

The ISO brightness measurements indicate changes in the pulp chromoforic system. The usage of diffuse reflectance transient absorption spectroscopy provides direct observations of the changes in the interactions of light with the pulp chromophoric units. As seen in Figure 2, transient species are observed with an absorption maximum at about 400 nm and a broad structureless tail extending beyond 750 nm, with all of the bands decaying both in the reference sample and in the pulp treated under acidic conditions. The shape of the transient spectra of untreated and treated samples of TMP is essentially similar, which allows one to assume that the same transient species are involved in both pulps. However, as compared to the reference, the peroxide-treated sample spectrum shows a distinct difference of the photochemical behavior that reflects the changes of the chromophoric system due to the preliminary oxidative stage. Although the spectra taken 1 μs after laser excitation are nearly the same in the two samples, the differences are clearly seen when comparing the spectra recorded after 5 μs and 20 ms. The reference sample shows a distinct stability of the transient species, with the shapes of the spectra recorded immediately after the laser pulse (1 μs) and after 20 ms being very similar. The transient absorption spectrum of the peroxide-treated pulp exhibits a much faster decay of transient absorption: it decays significantly even after 5 μs and further after 20 ms, which indicates the presence of a short-lived species absent in the

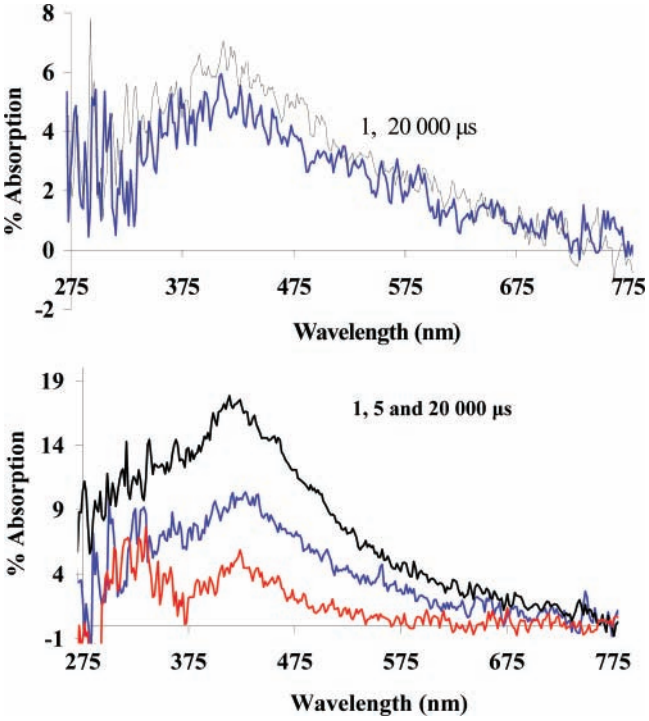

Figure 2. Diffuse reflectance laser flash photolysis spectra of pulps (TMP): reference and the sample bleached under acidic conditions (P_{ac}). The time delays are 1 μs and 20 ms (top panel) and 1 and 5 μs, and 20 ms (bottom panel). Note that the initial transient absorption is always the most intense, decaying with time in a non-exponential manner.

reference sample. The observed differences may be explained by changes of the reactivity of the chromofores or of their environment, caused by peroxide treatment under acidic conditions. The recorded spectra reflect the complexity of the samples containing all the chemical components, including lignin, cellulose, and hemicelluloses, which makes it difficult to assign the transient absorption to a definite structural group. However, it is generally accepted that transient absorption in the 300−400 nm region is due to lignin and previously a contribution of α-carbonyl groups to the transient absorption spectrum has been proposed.[23−25] Comparison of the spectroscopic data suggests that in our case the transient observed can also be assigned to aromatic carbonyl triplet states. However, this interpretation is uncertain as long as unquestionable evidence proving the presence of α-carbonyl groups in TMP remains unavailable.[26] Moreover, identification of chromophoric structures of quinone and hydroquinone type in the pulps indicates the possible complexity of their transient absorption spectra, with several chemically distinct species probably involved.[27,28]

Note that the presence of catalysts or stabilizers is an additional factor that influences the resulting pulp brightness. The activation mechanism of the acidic hydrogen peroxide solution by metal catalysts is similar to Fenton's reaction. Hydrogen peroxide decomposes releasing free radicals, e.g., hydroxyl radical. The results shown in Table 3 confirm the influence of catalysts and stabilizers on the concentration of hydroxyl radicals both in bleaching slurry and in blank runs. Hydroxyl radical, contrary to superoxide radical, had been reported to directly affect the chromophoric units in the pulp; therefore, it is the hydroxyl radical that should be responsible for such modifications in the pulp chromophores that facilitate peroxide bleaching at the second alkaline stage.[1,3] The main bleaching species under alkaline conditions is the peroxide anion, although hydroxyl and superoxide radicals also participate

TABLE 3: *N,N*-Dimethyl-4-nitrosoaniline, DMNA (10^{-4} M), Consumed during Hydrogen Peroxide Oxidation under Acidic and Alkaline Conditions in the Presence of Various Additives

	conditions		
sample	treatment	additive	DMNA consumed (10^{-4} M)
1	$P_{ac}(Cu^{2+})$	blank	4.29
2	$P_{ac}(Cu^{2+})$	pulp	5.22
3	$P_{alk}(Cu^{2+})$	blank	11.70
4	$P_{alk}(Cu^{2+};SiO_3^{2-})$	blank	11.25
5	$P_{alk}(Cu^{2+};Mg^{2+})$	blank	8.26
6	$P_{alk}(Mg^{2+};SiO_3^{2-})$	blank	4.85
7	$P_{alk}(Cu^{2+};Mg^{2+};SiO_3^{2-})$	blank	5.21

TABLE 4: Content of Carbonyl and Carboxyl Groups in the Spruce TMP Bleached with Hydrogen Peroxide under Acidic and Alkaline Conditions (mM/(100 g))

sample	treatment	CO ketone	CO aldehyde	COOH
1	ref	12.7	4.9	6.6
2	P_{ac}	21.8	4.4	6.8
3	$P_{ac}(Cu^{2+})$	27.0	3.8	7.3
4	P_{ac}/P_{alk}	12.5	2.7	8.2
5	$P_{ac}(Cu^{2+})/P_{alk}$	12.5	1.0	9.3
6	$P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+};SiO_3^{2-})$	13.2	1.8	8.7

in the process.[3] Nonselective free-radical chain reactions lead to a decrease in the DP of pulp carbohydrates and consequently to the loss of the fiber strength.[29] The addition of magnesium ions during the treatment limits the decomposition of hydrogen peroxide into hydroxyl radicals. The best results of the peroxide bleaching are obtained with the optimized charges of the two stabilizers combined: magnesium sulfate and sodium silicate (Table 3). Sodium silicate stabilizes hydrogen peroxide in the presence of the pulp and supplies an additional quantity of alkali during the treatment via hydrolysis. As we already noted, the catalysts and stabilizers affect the bleaching process; therefore, pulp samples bleached in their individual and combined presence were used in our spectroscopic studies.

3.2. Carbonyl and Carboxyl Groups of the Peroxide-Treated Pulp. The oxidation of lignocellulosics by hydrogen peroxide creates carbonyl and carboxyl groups, which may be used as probes for the bleaching agent activity changes due to reaction conditions (Table 4). Pulp treatment with acidic peroxide results in increased content of carbonyl in comparison to carboxyl groups. The ratio of ketone to aldehyde carbonyl groups is higher under acidic conditions (Table 4, samples 1−3). On the other hand, an increase in acidic products—carboxyl groups—is observed upon treatment under alkaline conditions, accompanied by a decrease in carbonyl groups (especially ketones) due to their oxidation into carboxyl groups (Table 4, samples 4−6).

Earlier spectroscopic studies have confirmed the influences of carbonyl groups on the pulp brightness.[15] Carbonyl groups are reduced by borohydride both before and after bleaching under acidic and alkaline conditions; this proves their presence not only in oxidized but also in the untreated (reference) pulp (Table 2, samples 2 and 5). We propose that treatment with acidic peroxide activates the chromophoric units potentially existing in the pulp, which are subsequently more easily eliminated or transformed into carboxyl groups under alkaline conditions. Therefore, two-stage peroxide bleaching under acidic and alkaline conditions results in higher brightness in comparison to the standard one-stage alkaline process (Table 2, samples 6−8). In comparison, the removal of chromophores in a one-

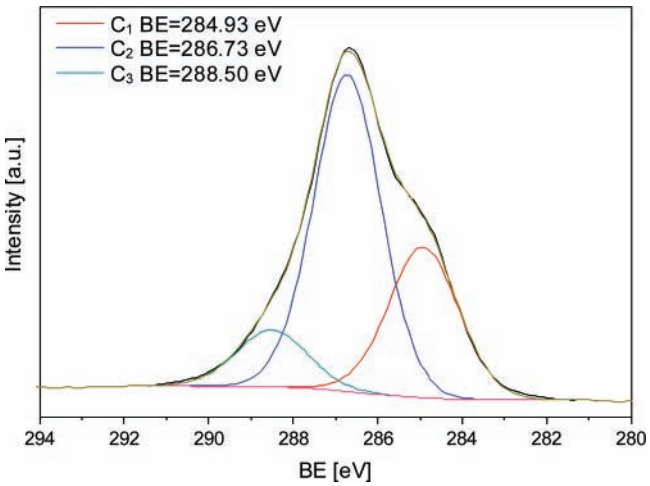

Figure 3. High-resolution XPS spectrum of C_{1s} electrons from carbon−TMP after two-stage hydrogen peroxide treatment with Cu^{2+} catalyst and stabilizers: $MgSO_4$ and Na_2SiO_3 $P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+};SiO_3^{2-})$.

TABLE 5: Atomic Percentage Ratios, O/C, C_1/C_2, $C_1/C_{tot.}$ and Atomic Percentage C_3 at the Surface of the TMP Samples, As Determined by XPS

sample	treatment	O/C	C_1/C_2	$C_1/C_{tot.}$	C_3
1	ref	0.49	0.51	0.21	3.64
2	P_{ac}	0.59	0.40	0.35	6.53
3	P_{ac}/P_{alk}	0.60	0.45	0.37	8.01
4	$P_{ac}/P_{alk}/B_{red.}$	0.58	0.48	0.41	7.10
5	$P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+};SiO_3^{2+})$	0.58	0.50	0.42	7.06

stage bleaching is limited to groups and units present in pulp at the moment of reaction, leaving other (potential) chromophores intact.

The hydrogen peroxide reaction with the structural constituents of the pulps occurs mainly at the surface of the fibers.[29] Therefore, the XPS method has been useful in the analysis of the changes occurring during the bleaching.[30,31] It has allowed quantitative determination of the percentage atomic composition at the pulp surface. It also enabled a quantitative estimation of types of existing chemical bonds, to a certain extent. Figure 3 shows a typical deconvoluted high-resolution spectrum of the C_{1s} peak (electrons ejected from the carbon atoms) of TMP after peroxide treatment. The appearance of all the other XPS spectra was quite similar, with the list of samples given in Table 5. The component peaks were marked C_1 to C_3, starting from the lowest binding energy (BE) for the analysis and discussion of the results. Three distinct component peaks were found in all spectra. These component peaks correspond to carbon bonds present in lignin and extractive substances (C_1 corresponds to the C−C bond) and in lignin and polysaccharides (C_2 corresponds to the C−OH bonds, C_3 corresponds to C═O bonds).[32] The C_4 component peak of the carboxyl groups was undetectable. Table 5 presents the oxygen to carbon ratio (O/C) as well as the relative contributions of components on the surface of the fibers, i.e., C_1/C_2 and $C_1/C_{tot.}$ (where $C_{tot.}$ denotes the total fraction of carbon atoms detected). The results obtained show that the peroxide treatment did cause significant changes in the chemical structure at the surface in all of the samples investigated. Note an increase of the O/C ratio for all of the treated samples and higher C_1/C_2 and $C_1/C_{tot.}$ ratios for the pulp that was brightened in the two-stage treatment, especially with catalyst and stabilizers.

These results confirm uncovering of the superficial lignin molecules, the previously postulated potential chromophores, resulting probably from the removal of weakly bound hemicelluloses from the fiber surface during bleaching. It has to be emphasized that the results of quantitative determination of the C_3 component did not correlate in all of the investigated samples with the results of carbonyl group concentrations as determined by potentiometric titration and shown in Table 4. The carbonyl group content at the fiber surface increased both after acidic treatment used in the first bleaching step (Table 5, sample 2) and after the alkaline step (Table 5, samples 3−5). Borohydride reduction performed after the two-stage treatment reduced the carbonyl group content slightly (Table 5, sample 4). The two-stage hydrogen peroxide treatment with catalyst and stabilizers did not seriously reduce the carbonyl group contents, as one would expect from earlier potentiometric studies. The principal reason of the differences noted between the results obtained by XPS and potentiometry is that XPS probes only a very thin surface layer, whereas potentiometry in solution detects almost all of the carboxylic groups existing at the surface and in the bulk.

3.3. FTIR and Raman Spectroscopy. To understand how TMP is affected during bleaching under different conditions (with or without catalyst and stabilizers in acidic and alkaline media), the pulp samples were treated in accordance with the sequences outlined in Table 6. FTIR spectra of TMP treated by hydrogen peroxide under acidic and alkaline conditions are shown in Figure 4. The spectra are very complex, which is typical for lignocellulosics; additionally, combinations of bands difficult for interpretation appear at some characteristic frequencies. However, important changes due to the reaction of carbohydrates are observed in the band structure around 1729 cm^{-1}.[33] Because the 1600−1750 cm^{-1} region of the spectrum is relatively free of distinct vibrations belonging to other functional groups, the band at 1729 cm^{-1} is commonly assigned to stretching vibrations of carbonyl groups, predominantly acid and ester functional groups of hemicelluloses.[26,33,34] Since the absorption at this band decreased after treatment in alkaline medium or reduction by sodium borohydride in alkaline environment, the observed changes can be interpreted as splitting of the ester groups of hemicelluloses. When we changed the treatment pH from acidic to alkaline (P_{ac} vs P_{ac}/P_{alk} treatment), the band lost its intensity and a shoulder appeared at the low-frequency side. This band shift can be explained by the influence of carboxyl groups formed during oxidation in the alkaline

TABLE 6: Relative FTIR Absorbances of the Stretching Vibrations at 1729 cm^{-1} Calculated in Relation to the Internal Standard Bands at 1507 and 2907 cm^{-1} and ISO Brightness of the TMP Samples Treated in Various Conditions

		absorbance relative to given internal standard bands			
sample	treatment	1507 cm^{-1}	2907 cm^{-1}	ISO brightness	H_2O_2 consumed (%)
1	ref	1	1	47.2	
2	P_{ac}	1.29	1.44	46.6	2.9
3	$P_{ac}(Cu^{2+})$	1.61	1.56	46.7	7.7
4	P_{ac}/P_{alk}	0.48	0.52	49.3	63.5
5	$P_{ac}/P_{alk}(Mg^{2+})$	0.43	0.40	51.9	55.8
6	$P_{ac}/P_{alk}(SiO_3^{2-})$	0.25	0.21	60.5	58.3
7	$P_{ac}/P_{alk}(Mg^{2+};SiO_3^{2-})$	0.32	0.27	57.3	52.4

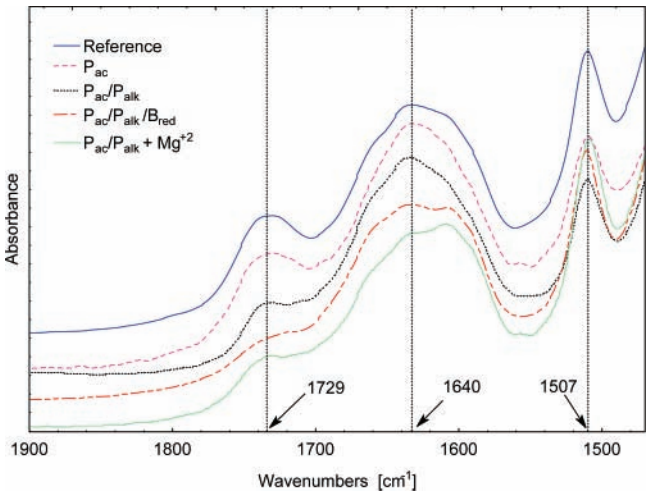

Figure 4. FT-IR spectra of TMPs: reference; bleached with hydrogen peroxide under acidic conditions (P_{ac}); after two-stage bleaching with hydrogen peroxide under acidic and alkaline conditions (P_{ac}/P_{alk}); after two-stage bleaching followed by borohydride reduction ($P_{ac}/P_{alk}/B_{red}$); after two-stage bleaching with the magnesium sulfate stabilizer ($P_{ac}/P_{alk}(Mg^{2+},SiO_3^{2-})$).

medium. This band shifts down both at higher pH values of the reaction and also as the oxidation reaction proceeds, as shown in Table 6, presenting the relative absorbances calculated at 1729 cm^{-1}. The increase of the relative absorbance after an acidic stage and its decrease after an alkaline stage correlates well with the determinations of carbonyl groups by potentiometric titration (Table 4). An addition of stabilizers in alkaline medium, which improves the technologic efficiency of the peroxide treatment, results in some reduction of the carbonyl band accompanied by a reduction in peroxide decomposition, and to some extent by higher resulting ISO brightness values. The latter observation will be discussed below. Thus, the carbonyl band allows one to differentiate between the effects of peroxide treatment with various additives.

Interestingly, the band at 1640 cm^{-1} changes when comparing the treatments under acidic (P_{ac}) and alkaline conditions (P_{ac}/P_{alk}). This band originates from the H−O−H bending vibration of water molecules.[33−36] The band increases in intensity and loses its symmetrical shape after alkaline peroxide treatment with magnesium ions (Figure 4). Since the same spectral region has contributions from oxygen-containing functional groups of lignin, we conclude that the observed changes result from the lignin oxidation. The absorption band at 1507 cm^{-1} associated with the phenyl ring-stretching modes was relatively stable, confirming non-delignifying character of the bleaching treatment.

To achieve a better understanding of the changes due to different oxidative treatments, we calculated the relative absorbances at 1729 cm^{-1} for two different internal standards: 2907 and 1507 cm^{-1} (Table 6). Independently of the standard used, the change pattern of the relative absorbances is nearly the same, which confirms the correct choice of the reference bands. Similar changes of the relative absorbance are observed for both internal standards, including the 1507 cm^{-1} band attributed to the phenyl ring, indirectly confirming that the aromatic lignin successfully resists the peroxide treatment. Sample 2 treated in acidic medium is an exception, presenting a distinctly lower relative absorbance at 1507 cm^{-1} (as compared to data calculated for 2907 cm^{-1}) in two independent series of experiments. A possible explanation is that the free-radical active species formed during the treatment in acidic medium form new functional groups, bonded to the lignin aromatic skeleton. Therefore, a FT-Raman study of the same pulp samples was undertaken. A number of studies have proved the usefulness of the FT-Raman technique in monitoring bleaching-related changes in mechanical pulps.[27,28,37] Presently, we focused on the chromophoric lignin bands at 1605 and 1655 cm^{-1}. As shown in Figure 5, the spectral changes in the pulp samples treated by hydrogen peroxide under acidic and alkaline conditions usually appeared as lower intensities in this region. Some other changes were also recorded, for example, those in the band that cannot be attributed with any certainty at ca. 900 cm^{-1}, associated with either cellulose or lignin. The Raman band at 1605 cm^{-1} is associated with aryl ring stretching vibrations and the band at 1654 cm^{-1} originates from the C═O stretch in coniferaldehyde or ring-conjugated C═C of coniferyl alcohol.[38] Both these bands are sensitive to bleaching, as clearly visible in Table 7, presenting ISO brightness and relative intensities calculated in relation to the band at 2893 cm^{-1} used as an internal standard and representing ν(C−H) stretch vibrations. The relative intensities of both "chromophoric" bands (1605 and 1655 cm^{-1}) for the samples treated by oxidative and

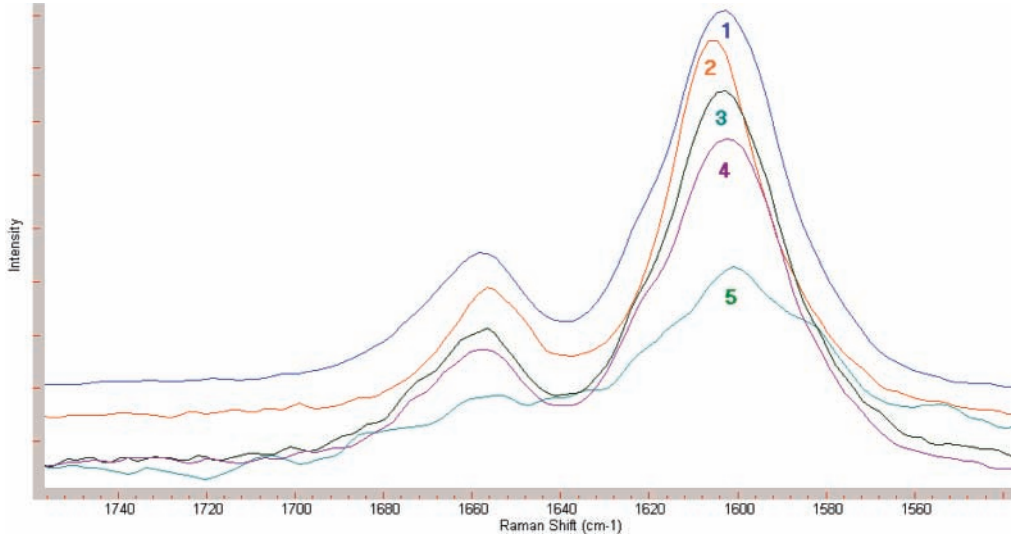

Figure 5. FT-Raman spectra of hydrogen peroxide bleached pulps (TMP): 1, reference; 2, acidic conditions (P_{ac}); 3, two-stage treatment under acidic and alkaline conditions (P_{ac}/P_{alk}); 4, two-stage treatment under acidic and alkaline conditions followed by borohydride reduction ($P_{ac}/P_{alk}/B_{red}$); 4, two-stage treatment under acidic and alkaline conditions with Cu^{2+} catalyst and stabilizers—$MgSO_4$ and Na_2SiO_3—($P_{ac}(Cu^{2+})/P_{alk}(Mg^{2+};SiO_3^{2-})$).

TABLE 7: Relative FT-IR Raman Intensities of the Stretching Vibrations at 1605 and 1655 cm^{-1} Calculated in Relation to the Internal Standard Band at 2893 cm^{-1} and ISO Brightness of the TMP Samples Treated in Various Conditions

		for given absorbance ratio		
sample	treatment	A_{1601}/A_{2893}	A_{1658}/A_{2893}	ISO brightness
1	ref	1	1	47.2
2	P_{ac}	0.93	0.92	48.0
3	P_{ac}/P_{alk}	0.84	0.83	50.6
4	$P_{ac}/P_{alk}/B_{red.}$	0.62	0.68	54.5
5	$P_{ac}/P_{alk}(Mg^{2+};SiO_3^{2-})$	0.84	0.84	57.6

reductive bleaching agents have decreased in comparison to the reference. This demonstrates that bleaching reactions in acidic (pH = 4.5) and alkaline media, and borohydride reduction resulted in chromophore removal in the region corresponding to coniferaldehyde. The decrease of intensities after treatment with acidic peroxide is lower than that after two-stage bleaching with alkaline peroxide in the second step. The lowest relative intensities were observed for samples treated by acidic and alkaline peroxide followed by borohydride reduction. It should be noted that the decrease of the relative intensities correlates well with an increase of ISO brightness except for the sample treated under acidic and alkaline conditions in the presence of catalyst and stabilizers. This proves the complexity of the rearrangement associated with the chromophoric units during the two-stage peroxide treatment. The bands at 1729 (IR) and 1655 (Raman) cm^{-1} are related to carbonyl groups originating respectively from carbohydrates (IR) and from lignin (Raman). The increased amount of carbonyl groups formed under acidic conditions (pH = 4.5) did not affect negatively the ISO brightness results, with an exception of the pulp treated by Cu^{2+}-activated peroxide (Table 2). In fact, the carbonyl groups are not distributed homogeneously in the fibrous structure of the pulp—the XPS studies showed an increased amount of carbonyl groups on the fiber surface after bleaching under alkaline conditions as compared to the pulps treated by acidic hydrogen peroxide, whereas the titration measurements revealed an opposite tendency. Therefore, the results of ISO brightness measurement that relies exclusively on the superficial phenomenon of scattering can differ from titrimetric and spectroscopic data probing the entire fiber structure. The reactions of hydrogen peroxide with pulp at lower temperatures (70 °C) primarily affect the surface layer. We believe that the treatment with hydrogen peroxide under acidic conditions, especially in the presence of a catalyst, may activate potential chromophores on the fiber surface that are subsequently eliminated at the alkaline bleaching stage. The superficial character of activation may explain differences in the ISO brightness results obtained between pulp samples with similar relative Raman intensities bleached under acidic and alkaline conditions with and without catalyst and stabilizers (Table 7, samples 3 and 5).

4. Conclusions

The use of different analytical methods made possible the monitoring of transformations of the TMP chromophoric system caused by the changes in the pH of the hydrogen peroxide solution used in the pulp processing. We conclude that acidic peroxide used at a preliminary bleaching stage activates the chromophoric units potentially existing in the pulp, such as the lignin-located ketone carbonyl groups, which are subsequently more efficiently eliminated at the principal bleaching stage under alkaline conditions. Therefore, the two-stage peroxide bleaching results in higher brightness of the pulp than the standard single-stage alkaline process. The determining role of the removal of the potential chromoforic units in the technological advances ensuing from the two-stage bleaching process was confirmed using DRLFP, FT-IR, and Raman spectroscopic techniques.

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