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ARE THE PULP FIBER WALL SURFACE LAYERS THE MOST RESISTANT ONES TOWARDS BLEACHING?

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The residues of the wood cell wall compound middle lamella affect the composition of the relevant pulp fiber surface layers and influence the fibers' bleachability. The objective of the present work was to separate the eucalyptus kraft and birch organosolv pulp fiber wall surface layers by hydromechanical peeling and to proceed with enzyme boosted bleaching of the separated fiber wall layers. The initial content of lignin and heteroaromatic compounds ("false" lignin) was determined by chemical methods and UV-spectra. The separated fiber wall surface layers representing the residues of the primary wall P and outer layer S_1 of the secondary wall, as well as the main part of the secondary wall were exposed to the bleaching sequence peroxide-xylanase treatment-alkaline extraction-peroxide $(P_1\text{-}X\text{-}E\text{-}P_2)$. Brightness measurements revealed significant distinctions between the preparations. The final brightness of the main part of eucalyptus kraft pulp fibers reached 67%, while the brightness of the surface layers attained only 50% ISO. Similar results were obtained for birch organosolv pulp. It was concluded that the main reason for the described phenomena is the discordant chemical composition of the different fiber wall layers.

INTRODUCTION

It is well known that the residual components of the wood cell walls' compound middle lamella affect the composition of the chemical pulp fiber wall surface layers consisting of the remnants of the primary wall P and outer layer S_1 of the secondary wall. A knowledge of the fiber wall structure and composition contributes to the understanding of the fundamental properties of papermaking fibres.

Among investigations of the lignin and hemicelluloses distribution's across the fiber wall, peeling procedures have taken quite a distinguished place. As early as in 1934, Elöd and Bielenberg introduced an interesting chemical peeling method, which was later used by Jayme and von Köppen (1950). Applying heterogeneous acetylation of pulp fiber wall and subsequent dissolution of the acetylated material, they investigated the differences in distribution of hemicelluloses between sulphite and kraft pulp fibers. After several years this kind of the study was repeated with more details and across the whole cell wall (Luce 1964).

A hydromechanical (mechanical) method of the separation of fiber wall outer layers was introduced in the 1960s (Kallmes 1960; Krause 1967). It is based on the fact that there are comparatively weaker bonds between the surface of secondary wall layers

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S_1 and S_2 due to the distinctions of cellulose fibril angle in relation to the fiber axis. An advantage of this fiber surface layers separation method is the possibility to isolate chemically unmodified fractions of the fiber wall. An extensive study has been performed in Sweden (Heijnesson et al. 1995) to determine the optimal mechanical treatment for removing the fiber surface material. It was concluded that a laboratory pulp disintegrator was the most suitable equipment for peeling process. At the Latvian State Institute of Wood Chemistry in Riga, the composition of different unbleached and bleached pulp fiber samples has been investigated during a number of years. Both the hydromechanical and the chemical fiber wall peeling methods have been applied. The first one was modified (Gromov et al. 1976) by adding ethanol to the fiber suspension in order to prevent the dissolution of hemicelluloses during the prolonged (30-60 h) mixing procedure in a laboratory disintegrator built according to the ISO standard 5263:1995. As regards the chemical peeling method, acetylation of fiber substance and subsequent dissolution of esterified matter in methylene dichloride, a decrease in the acetylation time, and the amount of catalyst was recommended (Purina et al. 1979). A new parameter – the degree of the exposure (DE) of the fiber wall S_2 layer – was introduced to characterize the openness of the main part of the secondary wall. Later the hydromechanical peeling procedure was upgraded (Treimanis 2006) by using a digital device, the "Fiber Tester" from Lorentzen&Wettre, Sweden, for evaluation of the quantity of fiber fines (fragments of the surface layers) created by peeling.

A representative part of our results on the residual lignin concentration in fiber surface layers is reflected in Fig. 1 (Gromov et al. 1977; Treimanis 1989, 1996; Treimanis et al. 1990).

It was confirmed that the residual lignin content in the fiber wall surface layers practically always was higher as compared to the average lignin content. In some samples (spruce sulphite pulp, hydrotropic birch pulp), the lignin content in the P-S_1 layers exceeded the average lignin values by 3 to 5 times. The distribution of residual hemicelluloses was established to be more even, except in the case of kraft pulp fibers. It was established (Treimanis 1989) that the residual xylan concentration in dissolving kraft pulp fibers from pine was almost twice as compared to its concentration in the main part of the secondary wall. Recently, an enzymatic peeling method was developed (Buchert et al. 1996). Separation of the pulp fiber surface material is followed by different analytical methods to establish its composition as well as structure. In a study (Hildén et al. 2005) endoglucanase preparations were used in the attempt to establish the correlation between the parameters of enzyme kinetics and mechanical properties of the paper produced from the corresponding pulp fibers. The authors conclude that the exact distribution of constituents on the surface of a fiber is still unknown.

There are not much data available on how the bleaching agents influence the chemical composition and brightness of the fiber wall surface layers as compared to the bulk fibers and main layer S_2 of the secondary wall. By means of the enzymatic peeling method (Buchert et al. 1995), it has been established that, during bleaching with ozone or chlorine dioxide, the hexenuronic acid side groups of xylan are degraded, whereas, after peroxide treatment, they are retained.
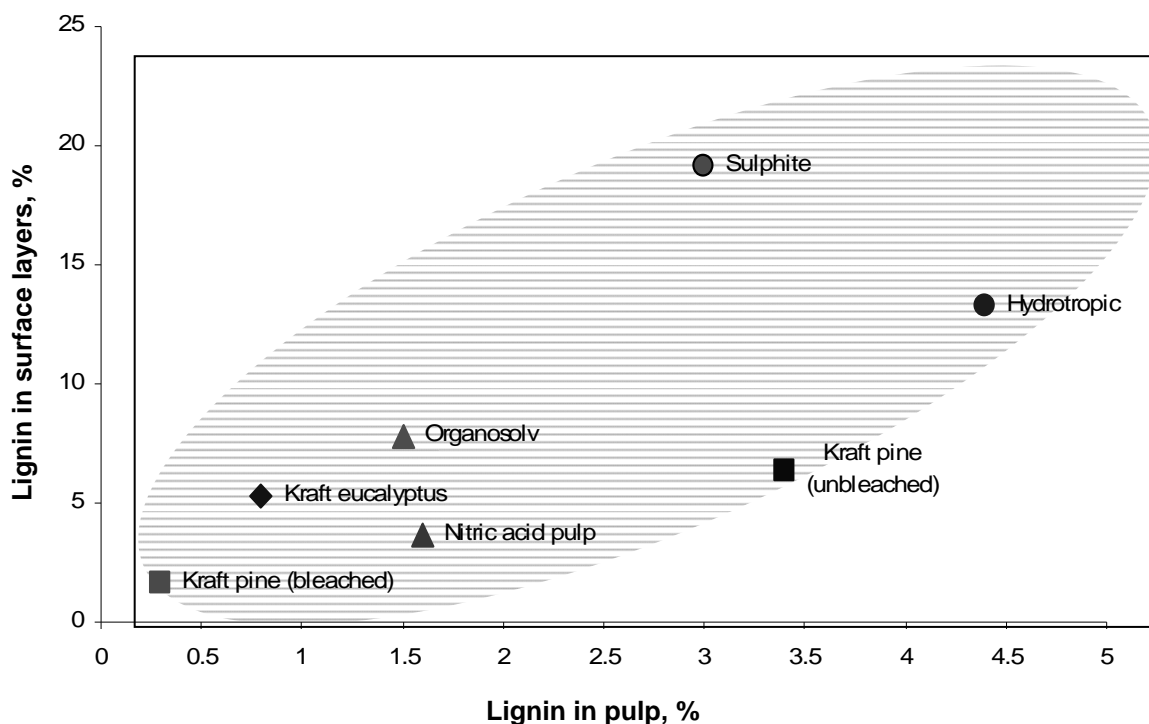
Fig. 1. Relationship between the lignin content in the pulp fiber surface layers (P-S$_1$) and in the bulk

Using electron spectroscopy for the chemical analysis (ESCA) method, the surface layers of the kraft pulp fibers after elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching have been characterized (Laine et al. 1996). The resulting depth of the fiber surface analysis was about 10 nm. It has been found that both the amount and reactivity of residual lignin vary in different morphological areas of fibers during bleaching. The fraction of the surface lignin removed by oxygen and peroxide treatment is much smaller than the total decrease in the lignin content. Ozone removes a significant amount of lignin independently of the location of the lignin in the fiber wall. It has been concluded that the strong enrichment of lignin in the surface layers of fibers retards the bleachability of kraft pulp fibers. Within a few years, another team of researchers (Kleen et al. 2002) have applied ESCA analysis and the mechanical peeling method in order to investigate the effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces. It has been confirmed that, for most pulps, the surface coverage by lignin is higher on unpeeled than peeled fibers. A comparatively higher lignin content on the fiber surface has been determined also after different bleaching stages. The concentration of extractives has been also found to be higher in the fiber surface layers.

The aim of the present work was to obtain data on the bleachability of the *separated* pulp fiber wall surface and central, main layers. A sufficient amount of the pulp fiber wall surface layers P-S$_1$ was isolated from the main fiber walls' part S$_2$-S$_3$ by means of the hydromechanical peeling, and the bleaching procedure was performed *directly* to these "genuine" fractions of the fiber wall.

EXPERIMENTAL

Birch *(Betula verrucosa)* wood 20x20x2 mm chips were cooked in laboratory stainless steel autoclaves according to the organosolv procedure: Stage 1 with CH_3OH/H_2O (1:1 by volume), 180^oC, 10 min; Stage 2 with CH_3OH/H_2O (3:7 by volume), NaOH 5% on the wood weight, 170^oC, 20 min. Eucalyptus *(Eucalyptus globulus)* wood was subjected to sulphate (kraft) delignification in industrial equipment, and unbleached fibers (before the oxygen delignification) were used as a sample for "integrated" analysis in different European laboratories in the framework of COST Action E41.

The pulp fiber walls were divided into two fractions – outer (surface) and central layers – by an upgraded hydromechanical peeling technique (Treimanis 2006). This method involves (Fig. 2) a continuous intense stirring of a 3% fiber-water (plus 50% ethanol) suspension, resulting in a partial removal of the primary wall (P) and the outer (S_1) layer of the secondary wall from the central part of the fiber walls. Before the peeling procedure the parenchyma cells, vessel fragments, and fiber debris were separated by screening of the fiber suspension. The intact fibers (approx. 90% by weight from total sample) were collected on the sieves with 600 and 400 µm holes and then combined. During the peeling process, the fibers were examined using a light microscope to establish the end of the process with regard to specific swelling forms in Cuoxam solution (in the case of the organosolv pulp fibers) and by using the fiber dimensions digital analysis equipment L&W "Fiber Tester" (sulphate pulp fibers). After the peeling the fiber surface layer fragments were collected by a screening process using sedimentation, centrifugation and freeze drying (Fig. 2). During the screening the fraction that passed the sieve with 400 µm holes was accumulated. The yield of fraction containing fiber surface material was determined to be approx. 5% by weight.

The DMF/DMSO solubility of pulp component followed by direct SEC analysis of extracts was carried out as described by Leite et al. (1995). A multi-wave UV detector in line with an RI-detector was applied to quantify lignin and hemicelluloses, and molecular mass (MM) determination, respectively.

Alkaline sequential extraction with 0.5% and 10% NaOH (both during 1 h at room temperature) followed by direct UV/VIS spectra and the 1st derivative analysis of extracts aiming at the simultaneous determination of lignin, furan resins and hexenuronic acid (HexA) were carried out as described previously (Bikova and Treimanis 2002). The HexA contents were determined by UV- analysis in cadoxen according to Evtuguin et al. (2002).

After the peeling process, the degree of the central S_2 layer exposure (openness) was estimated. In the first case (organosolv pulp), it was 75%; this means that approximately 75% of the surface layers P-S_1 were separated. For eucalyptus kraft pulp, the degree of the S_2 layer exposure reached approximately 25%, which means that the isolated P-S_1 fraction (surface layers) was very clean, while the fraction S_2-S_3 still contained fibers with unpeeled surface layers. The fractions of the fiber wall layers obtained were analysed by chemical (TAPPI standard methods) as well as chromatography, microscopy, and spectroscopic methods.
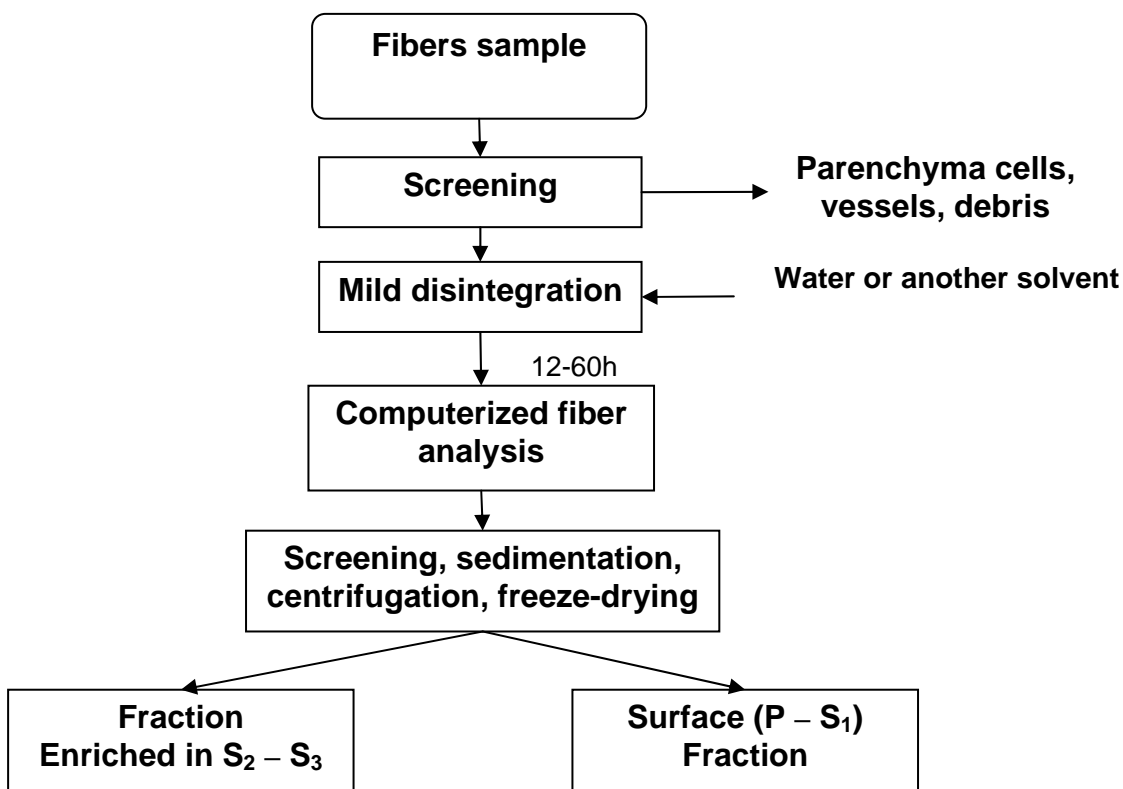
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Fig. 2. General scheme of the hydromechanical peeling of pulp fibers.

The bleaching of fiber wall fractions was performed according to the sequence peroxide (P_1) – enzyme treatment (X) – alkaline extraction (E) – peroxide (P_2). More detailed pulp bleaching conditions are shown in Table 1. As the xylanase, preparation *Pulpzyme HC* from Novozymes was applied.

Table 1. Pulp Fibers Bleaching Conditions

Bleaching stage	Consumption of chemicals, % on oven-dry pulp	Temperature, ^{o}C	Duration, min
P1	5% H_2O_2, 1.5% NaOH, 0.5% $MgSO_4$	80	90
X	Xylanase 2 U/g	60	180
E	1.5% NaOH	80	90
P2	3% H_2O_2, 1% NaOH	80	90

RESULTS AND DISCUSSION

Birch Organosolv Pulp Fibers

The bleaching experiments on birch organosolv pulp fibers have been partly described earlier (Leite et al. 1995), and only the main data are reflected in the present paper. As can be seen from Table 2, we have established a remarkable variation in the hemicelluloses and residual lignin contents as well as lignin/hemicelluloses ratio in the separated fiber wall layers.

Table 2. Birch Organosolv Pulp Fiber Wall Composition

Treatment	Lignin content, %		Xylan content, %		Brightness, % ISO	
	Surface layers	S_2-S_3	Surface layers	S_2-S_3	Surface layers	S_2-S_3
Unbleached	7.8	1.6	29.1	24.1	20.1	45.5
After bleaching	1.9	0.5	27.1	19.5	34.5	72.3

The data listed in Table 2 demonstrate that the surface (P-S_1) layers are characterized by a five times higher initial concentration of residual lignin and by a significant loss of lignin during bleaching. The content of lignin in the surface layers still remains comparatively high, namely, 1.9% *versus* 0.5% in the S_2-S_3 layers. The reduction of the xylan content is also more considerable in the latter part of the fiber wall. It is assumed that the hemicelluloses located in the surface layers are highly substituted by the uronic acid side chains. As can be seen from Table 2, the final brightness of the surface layers is only 34.5% ISO *versus* 72.3% ISO of the main part of the fiber walls.

The size exclusion chromatography (SEC) analysis reveals that the fiber wall surface layers have a ten times higher amount of the total lignin soluble in DMFA, DMSO, and DMSO/H_3PO_4, and approximately a 1.5 times higher amount of the hemicelluloses accessible by solvents, in comparison with the central part of fiber walls. No essential differences are revealed in the MM parameters of the hemicelluloses between the layers, while, at the same time, there is a remarkable difference in the lignin MM parameters. The high MM fraction soluble in DMSO/H_3PO_4 is the largest one in the surface layers and is 20 times as large as the corresponding fraction in the fiber wall main part (S_2-S_3 layers). We conclude that, in the surface layers, the lignin-carbohydrate complex (LCC) during the delignification is insignificantly destructed, whereas, in the central layers, there are almost lignin-free hemicelluloses.

Eucalyptus Kraft Pulp Fibers

Eucalyptus unbleached kraft pulp fibers were also subjected to hydromechanical peeling, and the two fractions were obtained: surface layers (P-S_1) and the main part of the fiber wall S_2-S_3 layers. In order to differentiate the UV-absorbance derived by residual lignin and oxypolysaccharides, two stage alkaline extraction with 0.5% and then

with 10% NaOH was applied. The total NaOH solubility was 40% by weight for the P-S$_1$ layers fraction and two times lower, namely, 19% for the main part of the fiber walls.
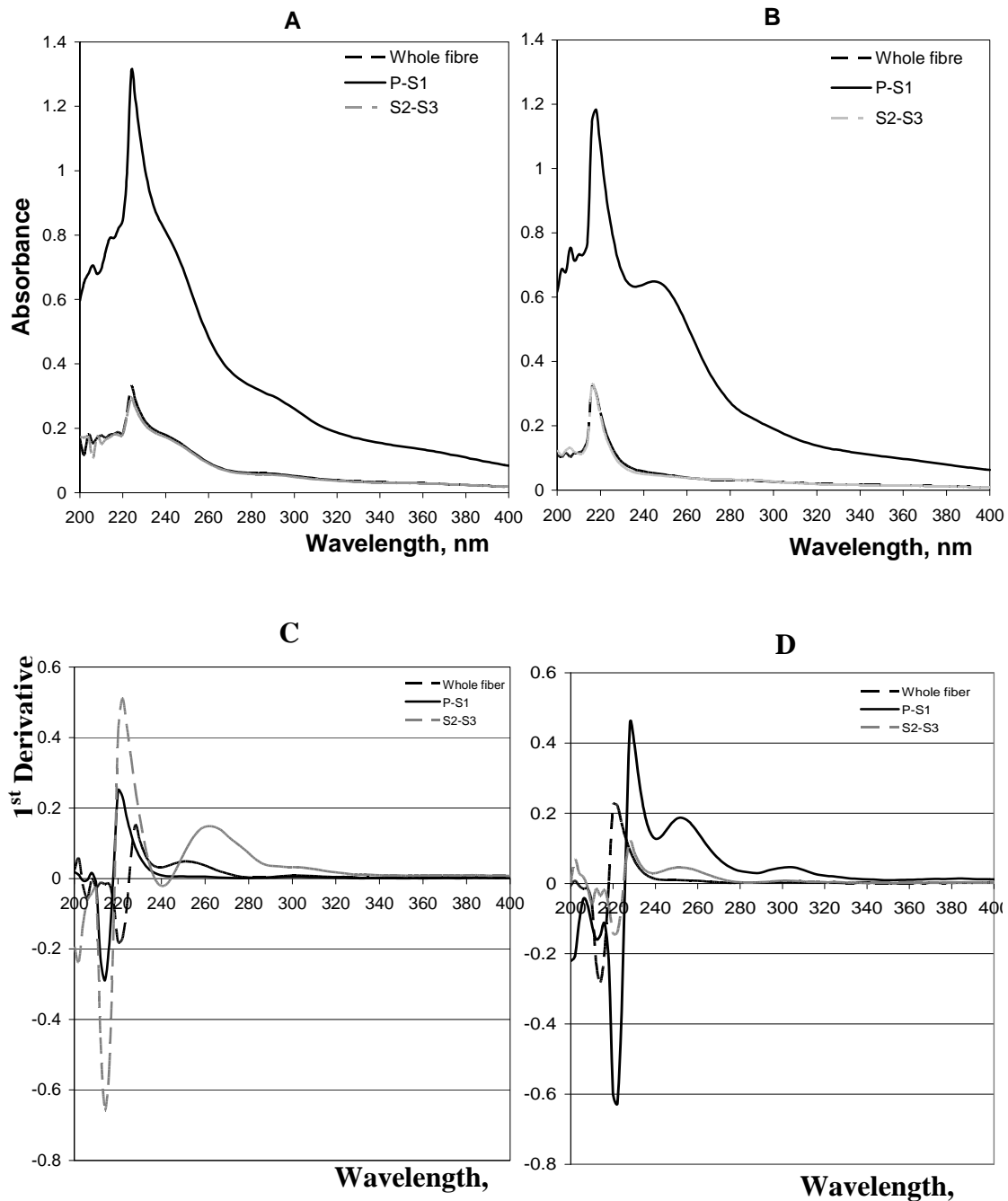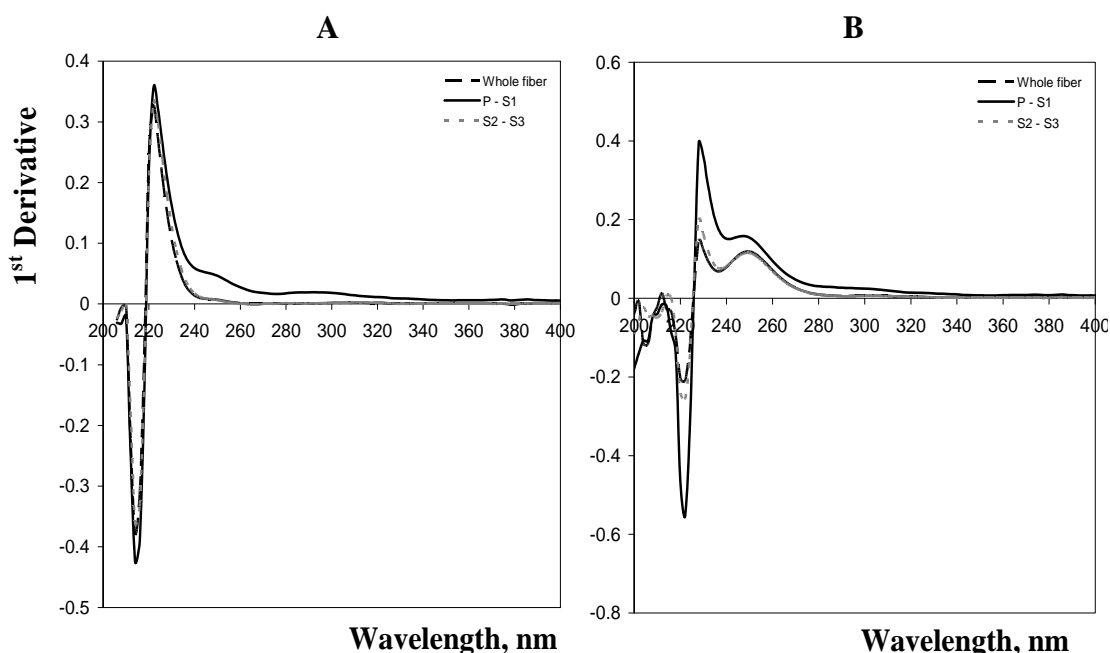

Fig. 3. The UV-spectra and their 1st derivative of the alkaline extracts from unbleached surface P-S$_1$ (upper curves) and S$_2$-S$_3$ fractions (lower curves) (A, C – 0.5% NaOH; B, D – 10.0% NaOH).

In order to elucidate the distinctions in the chemical composition of the fractions before bleaching, the UV-spectra (Fig. 3) and the 1st derivative of the spectra were analyzed. When 0.5% NaOH solution was applied, the absorbance values at 218, 290,

330, 350, 386 and 390 nm were attributed to lignin. Strong absorbance values of the alkaline extract from P-S$_1$ layers at 245 nm and rather weak UV-absorbance values at 244, 254, 266, and 276 nm for the alkaline extract of S$_2$-S$_3$ layers may indicate the presence of the heteroaromatic compounds of the furanoid (pyranoid) type. In 10% NaOH extracts, the absorbance at 240 nm is attributed to hexenuronic acids (HexA). The absorbance at above 280 nm can be explained by the presence of the oxidized hemicelluloses and polysaccharides containing conjugated heteroaromatic compounds as well as lignin.

UV-spectra analysis reveals that the content of lignin and HexA was 3-4 times higher in fiber wall surface layers as compared to the average values. The content of the heteroaromatic compounds (olygofuranoids/furan resins and oxypolysaccharides) was also estimated to be much higher in the P-S$_1$ layers.

Fig. 4. UV-spectra and their 1st derivative of the alkaline extracts from the bleached surface P-S$_1$ (upper curves) and S$_2$-S$_3$ fractions (lower curves) of eucalyptus kraft pulp fibers (A, C – 0.5% NaOH; B, D – 10.0% NaOH).

Figure 4 shows the UV-spectra of the alkaline extracts of the separated fractions after bleaching of eucalyptus kraft pulp fibers according to the sequence (P$_1$) – xylanase treatment (X) – alkaline extraction (E) – peroxide (P$_2$). It was established that the total NaOH solubility was 25% by weight for the surface (P-S$_1$) layers fraction and 15% for the main part of the fiber walls. Figure 5 illustrates the difference between the UV-absorbance spectra before and after the bleaching. The analysis of the spectra reveals that the decrease of the absorbance of the P-S$_1$ layers takes place in the whole range of the spectra. The absorbance drop at 218 nm and 250 nm by 45% and 63%, respectively, in

the 10% NaOH extract of the P-S_1 layers indicates the destruction of the heteroaromatic compounds, possibly incorporated in the so-called "furan resins". The decrease of absorbance at 280-300 nm and around 340-360 nm (not reflected in Fig. 5) indicates the elimination of both carbonyl groups =CO and double bond conjugated structures in the P-S_1 layers. The main part of the fiber walls, the S_2-S_3 layers, has lost most of the easily accessible fraction (in 0.5% NaOH) of hemicelluloses and HexA during the bleaching procedure. This is indicated by the decrease of absorbance around 240 nm.

Fig. 5. Differential UV-absorbance spectra of the alkaline extracts from whole fibers (curve 2 - 10% NaOH, curve 4 – 0.5% NaOH), S_2-S_3 (curve 1 – 10% NaOH, curve 3 – 0.5% NaOH), and surface P-S_1 fractions (curve 5 – 10% NaOH, curve 6 – 0.5% NaOH).

After the bleaching of the eucalyptus kraft pulp fibers, and the separate surface (P-S_1) and S_2-S_3 layers according to the sequence P_1-X-E-P_2, pulp brightness values were measured similar to those obtained for organosolv pulp fiber walls and the fractions (Fig. 6). In spite of the rather exhaustive changes in the chemical composition during the fiber wall layers bleaching, the ISO brightness of the fiber surface layers remained much lower as compared to the S_2-S_3 layers. A value of approximately 50% ISO was observed, as compared to the 67% ISO brightness for both S_2-S_3 layers and whole fibers.
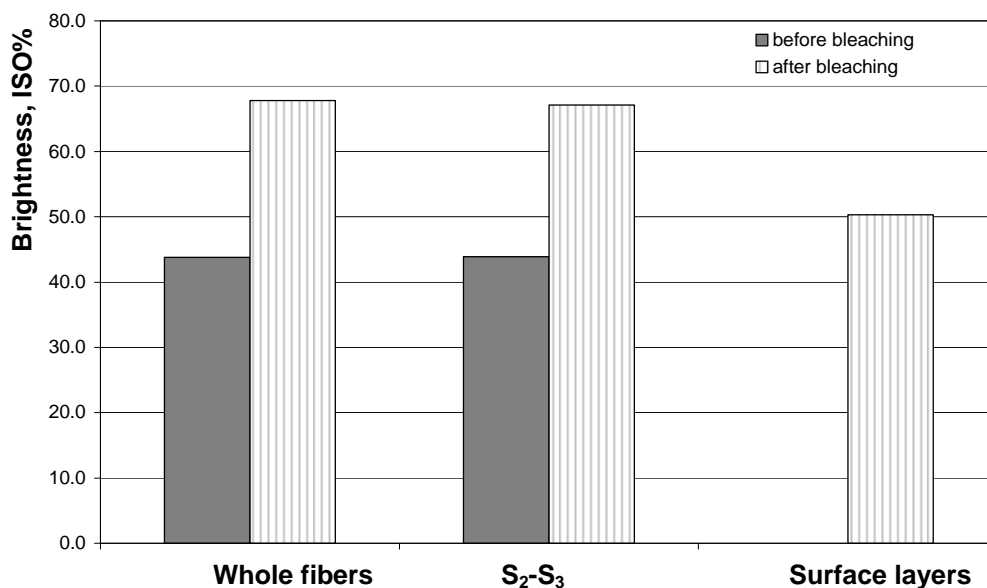
Fig. 6. Brightness values for eucalyptus kraft pulp fibers and separated fiber wall parts.

We suppose that the significant difference in the chemical composition of the eucalyptus kraft pulp fiber wall surface layers causes much lower bleachability as compared to the main part of the fiber walls. At the same time, in the experiments with eucalyptus kraft pulp fibers, the final brightness of whole fibers was not affected by the lower brightness of the very thin surface layers.

CONCLUSIONS

1. When bleaching is performed separately for the eucalyptus kraft and birch organosolv pulp fiber wall surface layers (P-S_1) and the main part of the fiber wall (S_2-S_3 layers), the determined brightness values are considerably lower for the surface layers.
2. These findings may be linked to the higher content of residual lignin as well as the higher concentration of heteroaromatic compounds and hexenuronic acids in the fiber wall surface layers, as established by chemical analysis and UV-spectra.
3. The hydromechanical peeling method can provide new opportunities in detailed studies of pulp fiber bleaching as well as other processes of chemical and biochemical conversion of lignocellulose fibers.

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