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The ultrastructure of spruce kraft pulps studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS)

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Abstract

Surface properties of spruce (*Picea abies*) kraft pulps cooked for different times and further $OD_0E_1D_1E_2D_2$-bleached were investigated with atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). A rough correlation between the increasing relative amount of the fibrillar surface structure in AFM images and increasing O/C atomic ratio in XPS-spectra was found with proceeding delignification. At the end of cooking (120 min) only about 1/3 of the fibre surface consisted of cellulose. The detailed analysis of the relative peak areas of the different C1s components in the XPS-spectra indicated that the granules at the beginning of cooking at 170 °C consisted mainly of lignin and extractives. The analysis also showed that different steps of the bleaching sequence were quite specific in removing structural components. Furthermore, the lignin removal was shown not to result automatically in increased fraction of exposed cellulose surface, but could also lead in increased relative amount of surface extractives. Evidence for the high surface content of hemicelluloses for the D2-stage sample was observed. Hemicelluloses with both fibrillar and amorphous morphology were found to be present.

Keywords: Atomic force microscopy; X-ray photoelectron spectroscopy; Spruce kraft pulp

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1. Introduction

Although surface analytical methods have been successfully used in pulp and paper research, specific knowledge and localisation of the surface components of a wood fibre needs further examination. For instance, the morphology and origin (native or re-precipitated) of lignin, hemicelluloses and extractives on the pulp surface is still quite unclear. Atomic force microscopy (AFM) together with X-ray photoelectron spectroscopy (XPS) has been applied increasingly to the surface characterisation of pulps and paper.

Dorris and Gray [1–3] published the first XPS investigations of the mechanical and chemical pulp fibres already in 1978. Since that, the oxygen-to-carbon atomic ratio (O/C) analysis and detailed interpretation of the deconvoluted binding states of the carbon C1s emission line have commonly been used to evaluate the surface content of extractives and/or lignin on pulp fibres [4–17]. The decreasing C1 component (C–C binding state) of the C1s emission line with increasing O/C atomic ratio correlates to decreasing lignin and/or extractive amount on the pulp surface. If the measurements are done both before and after the removal of extractives it becomes possible to distinguish between the relative amounts of extractives and lignin on the sample surface [10]. Also spectral background analysis has been applied for pulp samples. Johansson et al. [17] found similar backgrounds for different extracted pulp samples independent of the amount of surface lignin, but higher backgrounds for samples which were unextracted. The result indicated that lignin might be distributed in patches thicker than the XPS analysis depth whereas extractives might in some cases form a very thin layer on the pulp surface.

AFM (or SPM, scanning probe microscopy) has recently been applied to the structural studies of pulps and the main pulp components like cellulose, hemicelluloses, lignin and extractives [18–34]. Pereira [32] and Boeraas [24] have suggested lignin to appear as either irregular or regular patches on the fibre surface. Okamoto and Meshitsuka [21] have observed both fibrillar surface regions and regions where the fibres were covered by non-fibrillar material. The isolated lignin has been found to be granular, however, with

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irregular size and shape of the grains [28,30]. We have reported on a granular surface structure for samples from early stages of kraft pulping (after some minutes of cooking at 170 °C) of birch and pine [28]. The fraction of the granular surface was decreased for the pulp samples cooked for over 200 min, for the favour of a fibrillar surface. It was concluded that the granules mainly consisted of lignin but also some hemicellulose and extractives might have been embedded [28,30]. Maximova et al. [33] found similar globules on the cellulose surfaces in the studies of lignin adsorption, and Bessonoff et al. [34] on the paper and fibre surfaces of thermomechanical pulps (TMP). However, in the studies of Boeraas et al. [24,25] the amount of globular particles was found to decrease on the surface with decreasing amount of extractives, when the total lignin concentration was nearly constant throughout the sequence of mild treatments of chemithermomechanical pulp (CTMP) samples [24]. They suggested that the globular particles on the CTMP surface would represent extractives, which would locate over both lignin and carbohydrates on the fibre surface [25]. Several XPS and AFM studies have reported greatly higher lignin and extractive levels on the pulp surfaces compared with the bulk concentration [10,28,30]. Further, evidence of the hemicellulose–lignin complexes [35] have been reported and the role of the hemicelluloses has been discussed [36].

This study concentrates on the basic procedure of kraft cooking (with 5 time steps) and bleaching with $OD_0E_1D_1$-E_2D_2-sequence for spruce pulp, where samples from each process step were characterised with AFM and XPS. The last step of bleaching was further hemicellulose extracted. Besides morphology, the adhesion properties of the samples were studied by varying the measuring parameters (i.e. tapping amplitude, A_0 and (set-point/free-tapping-amplitude)-ratio, r_{sp}) in SPM phase contrast imaging of tapping mode.

2. Experimental

2.1. Materials and methods

Spruce (*Picea abies*) was cooked at a liquor-to-wood ratio of 4.5 (sample type A) or 3.5 (sample type B, supplied by KCL, Finland) and the effective alkali was 5 mol/kg (sample A and B) and the sulphidity was 30% (sample A) and 36.3% (sample B). The temperature was raised from 80 to 170 °C at 1 °C/min (sample A) or from 20 to 170 °C at 1.25 °C/min (sample B) and kept at 170 °C for 120 min (sample B) or 15, 30, 45, 105, 120 and 180 min (sample A). The kappa number of sample A was determined to be 76 (after 30 min of cooking), 58 (45 min), 25 (105 min), 23 (120 min) and 18 (180 min). The 15 min cooked sample was not fibrillar, and, thus, the kappa number was not defined. The kappa number of pulp sample B (marked as OR) was 21.6 and viscosity 1139 ml/g. Both the 120 min cooked samples A and B and the 180 min cooked sample A were further acetone extracted followed by rinsing several times with acetone and de-ionized water.

The kappa-number test is a standardized indirect method for determining the lignin content of pulps (ISO 302 standard). The viscosity was determined according to the ISO 5351/1 standard and brightness from split sheet surface ISO 2470. The total residual lignin content (TRLC) was evaluated from the kappa number according to TRLC = (kappa number)/6.546 [10,37].

The bleaching sequence $OD_0(E_1)D_1(E_2)D_2$ was carried out for sample B after acetone extraction (marked as EX). The O-stage was performed at a 10% consistency, an oxygen pressure of 8 bar and a NaOH concentration of 2.5%. In the D_0-stage the consistency was 10%, temperature 60 °C, the reaction time 60 min and the ClO_2 consumption 1.822% active chlorine (aCl). The E_1-stage was performed at a 8% consistency at 70 °C, 60 min. In D_1-stage the consistency was 9%, temperature 70 °C, the treatment time 180 min and the ClO_2 consumption 1.093% aCl. In the E_2 stage the consistency was 9%, the temperature 70 °C for 60 min and the NaOH concentration 0.8%. The D_2-stage was performed at a 9% consistency, 70 °C for 180 min and the ClO_2 consumption was 0.462% aCl. The brightness values of the pulps were 63 (E_1), 82.9 (D_1) and 89.1 (D_2) and the kappa number at the end of the process 0.65. For part of the completely delignified (D_2-stage) sample hemicelluloses were removed by acid methanolysis ($HCl + CH_3OH$) extraction. All the samples were measured as air-dried.

To avoid the contamination and risk of cutting the fibres as a result of pressing and sheet formation, samples were measured as fibres. However, prior to XPS analysis, pulp fibre samples were in small scale compressed smoothly with clean tools, dried at room temperature and mounted with screw-on clips to the sample holder (diameter of the hole of the clip was 1–3 mm). The samples were then allowed to outgas overnight in the turbo-pumped chamber in order to stabilise the water content in the sample matrix. The XPS-experiments were performed with a PHI Quantum 2000 Scanning spectrometer using monochromatized Al Kα (1486.6 eV) excitation and charge neutralisation by using electron filament and an electron gun. The photoelectrons were collected with a hemispherical analyser (diameter of the measuring area was 100 μm) having a constant pass energy of 117.10 eV for wide scans and 23.50 eV for narrow scans of C1s and O1s emission lines. The used power was 25 W. The base pressure was typically 1×10^{-9} Torr. During measurements, the pressure was not allowed to exceed 5×10^{-8} Torr. Measurements were carried out at three different spots. In order to avoid the risk of the chemical changes due to long X-ray radiation times, the radiation time of one spot did not exceed 30 min.

Using the curve-fitting programme (MultiPak v6.1A, Physical Electronics) supplied with the spectrometer, Gaussian curves were fitted for deconvolution of the carbon (C1s) and oxygen (O1s) emission lines. The chemical shifts relative to the C–C-component (referred to as C1 in the text) used in the deconvolution were 1.73 ± 0.02 eV for C–O (C2), 3.20 ± 0.10 eV for O–C–O or C=O (C3) and 4.40 ± 0.02 eV for the O=C–O-component (C4). The constant full-width-half-maximum (FWHM) values were used in the curve fitting of each spectrum. The surface coverage of extractives and lignin were calculated from the O/C atomic ratios by using the following equations described by Ström and Carlsson [10,16]

The surface coverage of extractives

$$= \frac{(\mathrm{O/C})_{\text{before-extraction}} - (\mathrm{O/C})_{\text{after-extraction}}}{(\mathrm{O/C})_{\text{extractives}} - (\mathrm{O/C})_{\text{after-extraction}}} \tag{1}$$

The surface coverage of lignin

$$= \frac{(\mathrm{O/C})_{\text{pulp-sample}_{\text{after-extraction}}} - (\mathrm{O/C})_{\text{pure-pulp}}}{(\mathrm{O/C})_{\text{lignin}} - (\mathrm{O/C})_{\text{pure-pulp}}} \tag{2}$$

where the values of 0.12 for $(\mathrm{O/C})_{\text{extractives}}$ and 0.33 for $(\mathrm{O/C})_{\text{lignin}}$ were used. The thickness of the regions, where extractives or lignin were located, was assumed to be greater than the XPS analysing depth (about 10 nm).

The AFM images were recorded with a Nanoscope IIIa microscope (Digital Instruments Inc., Santa Barbara, CA), equipped with the extender electronics module enabling phase imaging in tapping mode. Silicon cantilevers with a resonance frequency of 250–300 kHz were used. The radius of curvature of the used cantilever tips was 10–20 nm according to the manufacturer. The tip convolution effects [18] were not taken into consideration in dimensional analysis. Thus the real dimensions would be slightly smaller than measured. The trace and retrace signals were set identical before image capture. Unless otherwise mentioned the set-point amplitude/free tapping amplitude ratio (damping ratio: $A_{sp}/A_0 = r_{sp}$) was 0.6 and $A_0 = 80$ nm. A low tapping amplitude of 30 nm and damping ratio $r_{sp} \leq 0.4$ were used for the adhesion contrast studies. The principles of the analysis of the high and low tapping amplitude images have been described earlier [28,30 (with Refs. 15–23 therein)]. Prior to AFM imaging the pulp samples were dried on sample stubs covered by double-sided adhesive tape. All images were measured in air. Images were collected from 20–30 different fibres for each sample so that the main axis of the fibre was parallel to the slow scan axis of the AFM, with an accuracy of some degrees. Filtering was not used during scanning. The microscope was placed on an active vibration damping table (MOD-1, JAS Scientific Instruments) placed on a massive stone table to eliminate external vibration noise.

3. Results and discussion

3.1. XPS results

Fig. 1(a) shows a typical XPS (X-ray Photoelectron Spectroscopy) wide scan (0–1100 eV) spectrum for a spruce pulp sample. No other surface elements than oxygen (O) and carbon (C) were observed, except for small amounts of calcium (<0.38 at.%) in oxygen delignified sample and in cooked stages of spruce, chlorine (ca. 0.3 at.%) in D_0-delignified sample, and sodium (ca. 0.4 at.%) in E_1-delignified sample. Contamination was assumed to be small and constant within and between the sample types A and B. This can be seen, for instance, from similar O/C atomic ratios for the 120 min cooked sample type A (Fig. 2(a)) and B (Fig. 2(b)).

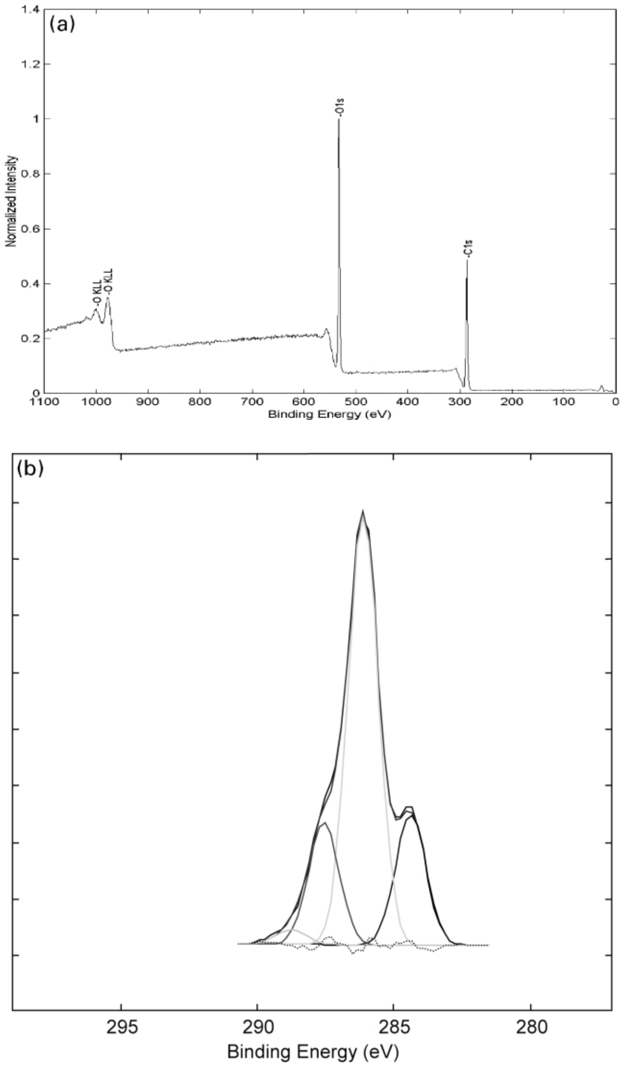

Fig. 1. (A) A typical XPS wide scan (0–1100 eV) spectrum of a spruce pulp sample. No other surface elements than oxygen (O1s, 531 eV) and carbon (C1s, 285 eV) were observed. (B). Deconvolution of the C1s emission line of D_1-delignificated sample B.

Fig. 1(b) represents a deconvolution of the carbon (C1s) emission line of D_1-delignified sample B. Indirect evidence for a successful neutralization of the samples was found from the symmetric form and realistically small FWHM value of the oxygen peak.

Fig. 2 shows how the O/C atomic ratio varied with the

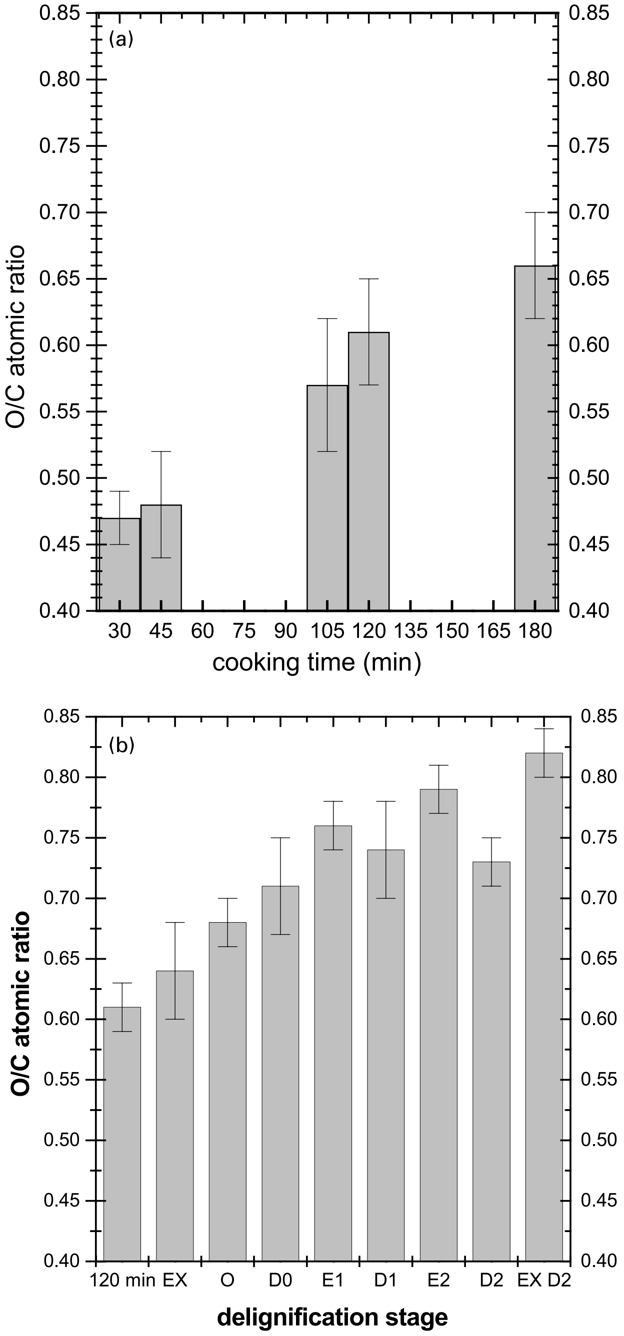

Fig. 2. The development of the XPS oxygen-to-carbon (O/C) atomic ratio during (a) cooking at 170 °C (sample A) and (b) $OD_0E_1D_1E_2D_2$-delignification (sample B) of spruce kraft pulp.

proceeding cooking (sample A, Fig. 2(a)) and delignification (sample B, Fig. 2(b)). When the measured O/C atomic ratios are compared with the known theoretical O/C ratios of cellulose (0.83 [10]), hemicelluloses such as arabionoglucuronoxylan (0.81 [10]), lignin (0.33 [10]) and extractives (from as low as 0.03 (calculated from chemical composition of, e.g. sitosterol) up to 0.11 [10]) the amount of lignin and extractives can be concluded to decrease with proceeding processing (Fig. 2(a) and (b)), with the D_1- and D_2-stages as exceptions.

The total (bulk) residual lignin content (TRLC) of the samples decreased as a function of cooking time as follows (compare with Fig. 2(a)): 11.4% (30 min), 8.7% (45 min), 3.7% (105 min), 3.5% (120 min) and 2.8% (180 min), respectively. The trend thus coincides with the changes in the surface properties, i.e. the increasing O/C atomic ratio, as a result of delignification. However, the amounts of surface lignin and surface extractives were found to be clearly higher than the corresponding bulk values. For example, for the 120 min cooked sample, the calculated values of the surface coverage of extractives (Eq. (1)) and lignin (Eq. (2)) were found to be 13 and 29%. In comparison, the bulk amount of extractives in spruce varies within 1–2% [38,39]. The observed high surface content of lignin and extractives agrees with the previous result for pine pulps [30,40].

In order to conclude more about the process-induced changes in the surface concentration of the various chemical components in the pulp fibre, a more detailed analysis of the C1s emission lines of the XPS-spectra was carried out. The relative peak areas of the C1–C4 components of the deconvoluted C1s peak, and their changes in comparison to the previous delignification stage and to the start sample, were calculated for each of the analyzed sample. The obtained values are plotted as a function of proceeding processing in Fig. 3(a). For comparison, the theoretical relative C1–C4 peak areas were calculated for each of the main chemical compounds of a wood fibre (Table 1). It is directly seen from Table 1 that each of the chemical compounds contributes to more than one component, but none of them to exactly the same carbon components of the C1s emission line. This enables one to draw several useful conclusions about the process-induced changes in relative surface fraction of the chemical components, as summarized in the following.

As a rule of thumb, the changes in C1 give the same information as the O/C atomic ratio: the decreasing relative amount of C1 with increasing O/C atomic ratio refers to decreasing amount of surface lignin and extractives (Fig. 3(b)). Analysis becomes even more simplified for extracted

Table 1
The theoretical O/C atomic ratios and the relative C1–C4 peak areas of the deconvoluted C1s emission line as calculated from the chemical composition of the compounds

	O/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)
Extractives					
Resin acids	0.11	94	–	–	6
Stearic acid	0.12	94	–	–	6
Oleic acid	0.12				
Sitosterol ester	0.04				
Lignin [10]	0.33	49	49	2	–
Hemicelluloses	0.80	–	83	17	–
Galaktoglucomannan	0.78	3	78	16	3
Arbinoglucuronoxylan [10]	0.83	–	78	19	3
Cellulose [10]	0.83	–	83	17	–

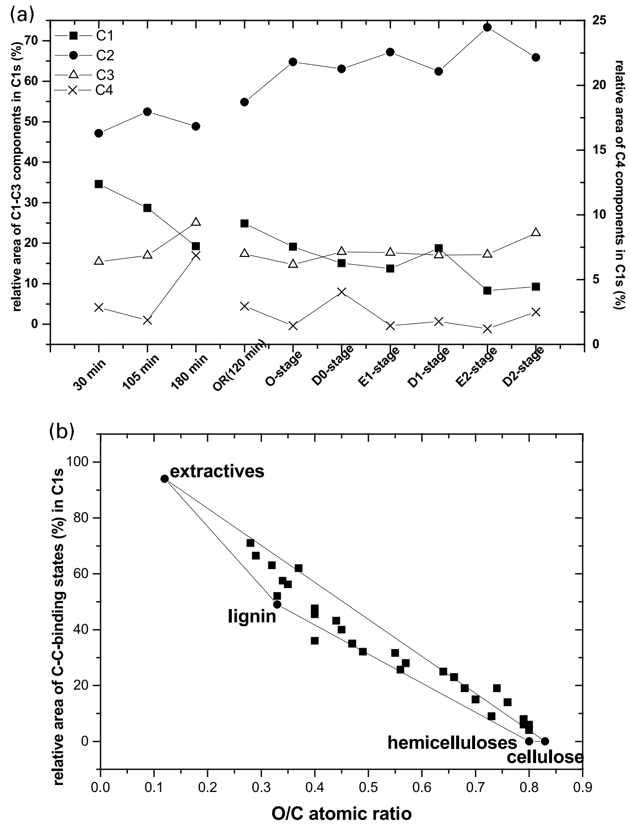

Fig. 3. (a) The development of the relative area of different carbons (C1–C4) of curve fitted C1s spectra during cooking at 170 °C and $OD_0E_1D_1E_2D_2$-delignification process (for 120 min cooked spruce kraft pulp sample B). (b) A plot of the dependence of O/C atomic ratio on the relative amount of C1 component in deconvoluted C1s emission line for wood pulp samples. Also theoretical points for extractives, lignin, hemicelluloses and cellulose are shown.

samples for which the changes in C1 directly correlate to changes in the amount of surface lignin [14].

The decreasing C1-values with proceeding delignification process are shown in Fig. 3(a), with, however, two exceptions, (as for O/C atomic ratios in Fig. 2(b)) to the rule: the process stages $E_1 \rightarrow D_1$ and $E_2 \rightarrow D_2$. It still seems that the amount of lignin decreases also during these stages, being motivated by the following conclusions. In the case of stage $E_1 \rightarrow D_1$ both C2 and C3 decrease meaning that the surface concentrations of cellulose and hemicelluloses decreases (Table 1). This was directly observed also from the decreasing O/C atomic ratio (when compared to the previous process stage). Simultaneously, however, the surface content of lignin cannot increase because in that case the decrease of the C2 component would be smaller in comparison to the decreasing of the C3 component. Therefore, the most interesting conclusion to be drawn is that the increase of C1 simultaneously with that of C4 indeed refers to increased surface content of extractives. The case of the $E_2 \rightarrow D_2$-stage is slightly different. Also here C2 decreases but now C3 increases, indicating either a decrease of lignin or increase of hemicellulose content. Since simultaneously C4 increases more than in the $E_1 \rightarrow D_1$-stage (Fig. 3(a)) the surface concentration of both extractives and hemicelluloses is suggested to increase, as a result of dissolved lignin. Similar behaviour was observed in the $O \rightarrow D_0$-stage (Fig. 3(a)), even if the decrease of C1 together with increasing C4 indicates that the fraction of exposed extractives was not as pronounced.

It was only during the first half of the cooking (30 → 105 min) at 170 °C when the relative surface concentration of lignin and extractives decreased simultaneously (Fig. 3(a)), i.e. both C1 and C4 decreased. Since C3 and C4 did not increase simultaneously the surface content of hemicellulose was concluded not to increase dessessively. Hence, the increase of C2 and C3 refers to an increased amount of exposed cellulose surface as a result of cooking-induced delignification. During the second half of the cooking (105 → 180 min) the amount of extractives and hemicellulose is suggested to increase on the sample surface due to the similar behaviour as in the $O \rightarrow D_0$ process stage (Fig. 3(a)).

The high amount of extractives at the D_0-, D_1- and D_2-stages in comparison to the E_1- and E_2-stages may explain the lower than expected O/C atomic ratio for the D1- and D2-stages in Fig. 2(b). In consistence with these results, Allen and Lapointe [40,41] have suggested that the content of extractives increases during acidic D-stages and decreases in alkaline E-stages due to the solubility properties of fatty and resin acids. When the D_2-stage was here further extracted (Fig. 2(b)) the O/C atomic ratio increased to close the theoretical O/C value of cellulose/hemicellulose (i.e. 0.82 ± 0.02 vs. 0.83). In addition, the clearly higher calculated coverage of extractives (13%; Eq. (1)) than of lignin (2%; Eq. (2)) in the D_2-stage was in consistence with the idea that the extractives, instead of lignin, are the main reason for decreasing O/C value in the D_1- and D_2-stages. The total residual lignin content (TRLC) of the samples decreased as a function of delignification (Fig. 2(b)): 3.24% (120 min, sample B), 1.37% (O-stage), 0.49% (E_1-stage), 0.10% (D_2-stage), respectively.

When the pH was stabilized, i.e. adjusted to 4.5 (by acidification with H_2SO_4) after E_1- and E_2-stages the O/C atomic ratio decreased from 0.76 ± 0.02 to 0.67 ± 0.04 for the E_1-stage and from 0.79 ± 0.02 to 0.75 ± 0.04 for the E_2-stage.

3.2. AFM results

A typical surface structure of 15–30 min at 170 °C cooked spruce pulp sample (Fig. 4(a)) was observed to be highly granular (over 90% of all the measured images). The diameter of the granules varied between 40 and 300 nm. Similar results have been found for pine and birch pulps [28], for which the diameter of the smallest granules was the same, but the size distribution clearly narrower than that of spruce. Combining the AFM data and XPS results, the granular phase may be interpreted to consist mainly of non-carbohydrates, i.e. lignin and extractives and only partly of

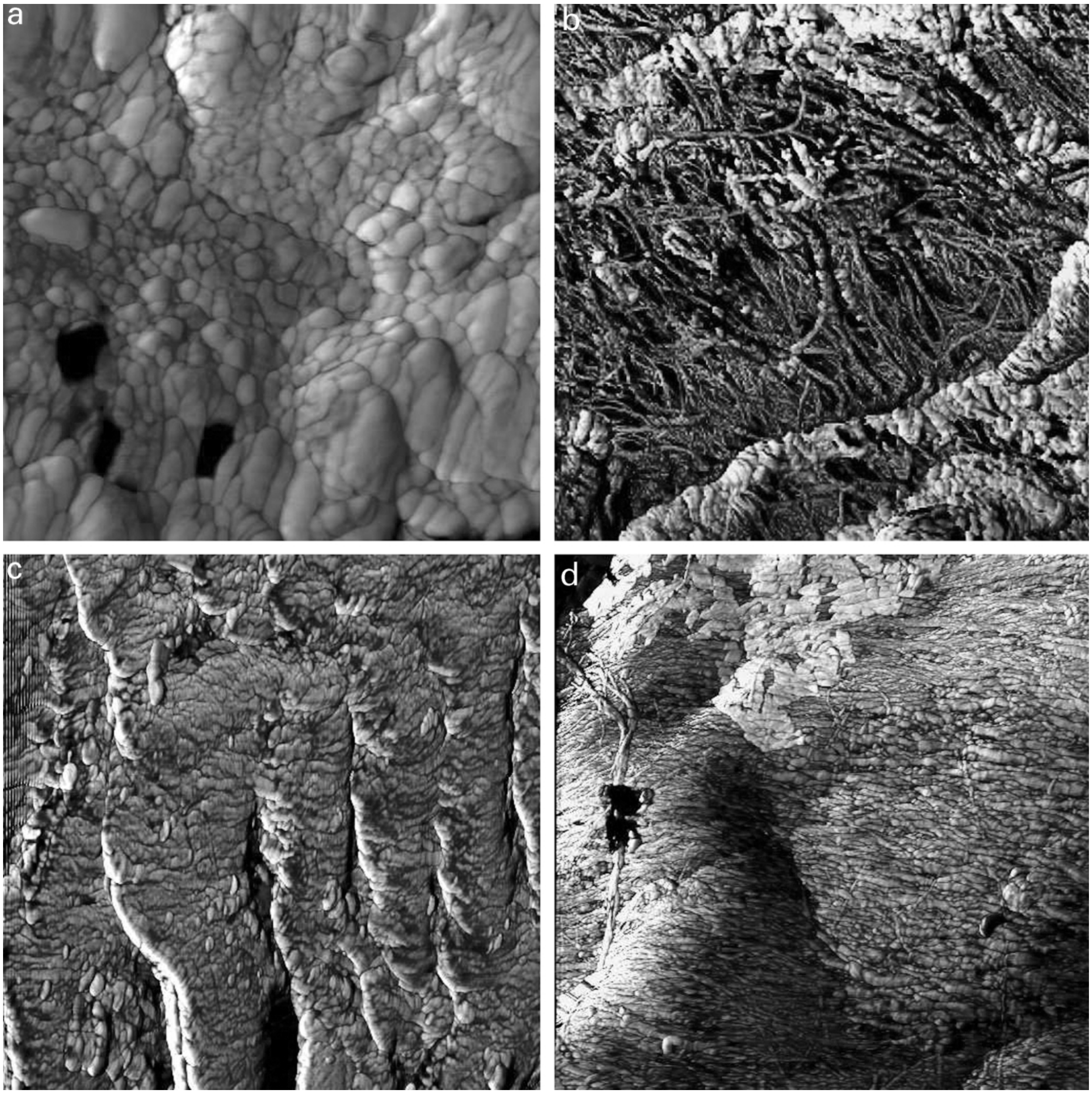

Fig. 4. AFM phase images of (a) 15 min, (b) 45 min and (c) 120 min at 170 °C cooked and (d) further acetone extracted spruce kraft pulp sample. Image size and z-scale (dark-light = low-high) are as follows: (a) 2 μm × 2 μm; 10 ° (b) 2.5 μm × 2.5 μm; 25 °, (c) 3 μm × 3 μm; 20 °, (d) 5 μm × 5 μm; 25 °.

carbohydrates. The O/C atomic ratio for the 30 min cooked sample was clearly lower than the theoretical values of carbohydrates ($0.47 \ll 0.80-0.83$), but, however, slightly higher than the theoretical O/C atomic ratios of the non-carbohydrates: lignin, 0.33 and extractives, 0.04–0.11. Thus, a minority of the granules in Fig. 4(a) may refer to other amorphous material than lignin/extractives. Indeed, in the phase contrast image of Fig. 4(a) certain granules appear much darker than the majority of the granules. Since the image has been measured using a low tapping amplitude of 30 nm and a r_{sp} value of ca. 0.3, the dark contrast refers to a large tip-sample adhesion, i.e. to a cantilever being trapped by the contamination layer on the sample surface [42]. The dark granules hence refer to a material being more hydrophilic than the surrounding light-appearing granules. Typically, carbohydrates can be considered more hydrophilic than lignin or extractives. Since the granular form speaks for an amorphous material rather than for a fibrillar crystalline matter, the dark granules are suggested to represent hemicellulose rather than cellulose. In consistence with this, Vikkula [43] has found that the re-precipitation of xylan–hemicelluloses begins immediately after the heating-up period, i.e. at the beginning of kraft cooking at 170 °C. Since the cooking liquor is not changed during the kraft cooking process the probability of re-precipitation of already dissolved components is high. In addition, Henriksson and Gatenholm [36] have shown that, by controlling the assembly process of xylans (hemicellulose), surfaces of cellulose fibres may be coated with regular micron-sized particles. The AFM and XPS results cannot exclude the possibility of hemicellulose–lignin complexes [35] on the surfaces. In general, the kraft pulping is a rather unselective delignification process and the loss of carbohydrates, mainly hemicelluloses, is about the same as the amount of removed lignin [43].

After cooking for 45 min the surface was still mainly granular with characteristics identical to that of Fig. 4(a). However, about 20% of the surface appeared fibrillar (Fig. 4(b)) with the diameter of the microfibrils being ca. 20 nm. The random cellulose microfibril orientation and the loose surface structure in Fig. 4(b) had characteristics of a primary cell wall (P). Because the amorphous material covering the microfibrils was observed to be most hydrophobic when measured with low tapping amplitude, these structures were concluded to consist preferably of extractives or lignin rather than of hydrophilic hemicelluloses. This conclusion is consistent with the fact that the middle lamella (ML) and the primary wall (P) of softwood tracheids consist mainly of lignin (65%), extractives such as pectic substances (15%) and cellulose (12%), and only in minority of hemicelluloses such as glucomannan (3%) and xylan (5%) [44]. The dark contrast, again, refers to the presence of a contamination layer, which is dominated by the surface moisture. The dark contrast appears strongest, as is logical, within the relatively hydrophilic cellulose microfibril region [42].

For the 120 min cooked sample still only 20–40% of the imaged area was fibrillar. The majority of the surface (i.e. 60–80%) consisted of non-fibrillar amorphous material, the typical structures being shown in Fig. 4(c). Since the surface coverage of lignin and extractives for this sample was found to be 42% in the XPS measurements (29% lignin and 13% extractives), the AFM results indicate, supporting the earlier conclusion, that at least part of the hemicelluloses contribute to the amorphous phase. It is worth noting that the amorphous structures of Fig. 4(a) and (c) clearly differ from each other, the grains and grain boundaries being much better resolved in the former case. Vikkula [43] has suggested that the more branched amorphous structures of carbohydrates exist primarily in the outer layers and the more rich in crystalline, ordered structures, in the inner layers of a wood fibre cell wall. For instance hemicelluloses exist mainly in amorphous form, but it has been demonstrated by polarised infrared spectroscopy that certain xylans exist in crystalline form in native wood slices [47]. Thus, the hemicelluloses may be present in both the amorphous and the fibrillar surface phase.

When the 120 min cooked sample was further extracted by acetone in order to remove extractives the fraction of fibrillar surface structures increased (Fig. 4(d)). This was in good agreement with the XPS results, where the O/C atomic ratio increased with extraction, indicating an increasing amount of carbohydrates. It is the broad width distribution of the microfibrils that strongly suggests that not all the fibrils represent cellulose. Most probably the thicker and by form also more irregular, but still clearly linear, fibrils represent hemicelluloses. That the hemicelluloses may appear both as an amorphous and a more crystalline phase becomes hence indirectly demonstrated.

One of the most interesting observations was that a thin layer (Fig. 4(d), upper left corner) locally covered the exposed surface. This layer was found to be quite hydrophobic, when imaged with low tapping amplitude, $A_0 = 30$ nm. The layer appeared to be so thin (about 5 nm) that the underlying fibril structure was clearly resolved. Both Laine and Stenius with XPS [10] and Pereira-Lorenzoni [45] with AFM have reported on a lignin layer with a thickness of about 10 nm on the fibres. Pereira-Lorenzoni [45] described a very thin coating of lignin that obscured the underlying microfibrils and appeared as smoother areas in the middle of the microfibrillar region. We cannot unambiguously conclude whether the observed thin layer represents lignin or extractives. Namely, complete extraction is very demanding and certain extractives may hence remain on the surface after extraction. An important difference between the two surface sensitive methods becomes, however, demonstrated: AFM probes the properties of the very surface but is also capable of resolving very thin structural layers. Such layers (in the thickness range under 10 nm) may be much more difficult to study or reveal at all by XPS because of the detection depth of typically 10 nm.

Fig. 5 shows typical surface structures of the $OD_0E_1D_1E_2D_2$-delignification stages of sample B. The amount of fibrillar surface structures suggested to represent carbohydrates was observed to be clearly higher for sample B (Fig. 5(a)–(c)) than for sample A. This result on morphology is in good agreement with the XPS results where the O/C ratios were clearly higher for sample B than for sample A, also indicating a higher surface content of carbohydrates for the sample B. The O/C atomic ratios increased from 0.61 of the 120 min cooked sample A to 0.68, 0.71, 0.77 and 0.74 for the samples representing the O-, D_0-, E_1- and D_1-stages, respectively.

Differences between the AFM images of delignification stages of $OD_0E_1D_1E_2D_2$ were in general small. Clearly microfibrillar cellulose structure such as that shown in Fig. 5(b) and (c) (diameter of microfibrils 10–40 nm) was observed regularly for samples from the E_1-, D_1-, E_2- and D_2-stages. This occurred thus at the delignification stages where the O/C atomic ratio was higher than 0.70 that indicates a high content of carbohydrates. In Fig. 5(b), even the characteristic features of the secondary cell wall such as the tightly parallel microfibrils are still recognisable. The locally observed amorphous structures, visible, e.g. in Fig. 5(a), resembled those of Fig. 4(c), i.e. only few clear grains were visible and the boundaries between the objects were quite diffuse.

The calculated surface coverage of lignin (Eq. (2), XPS-data) was found to be only 2% for the sample from the

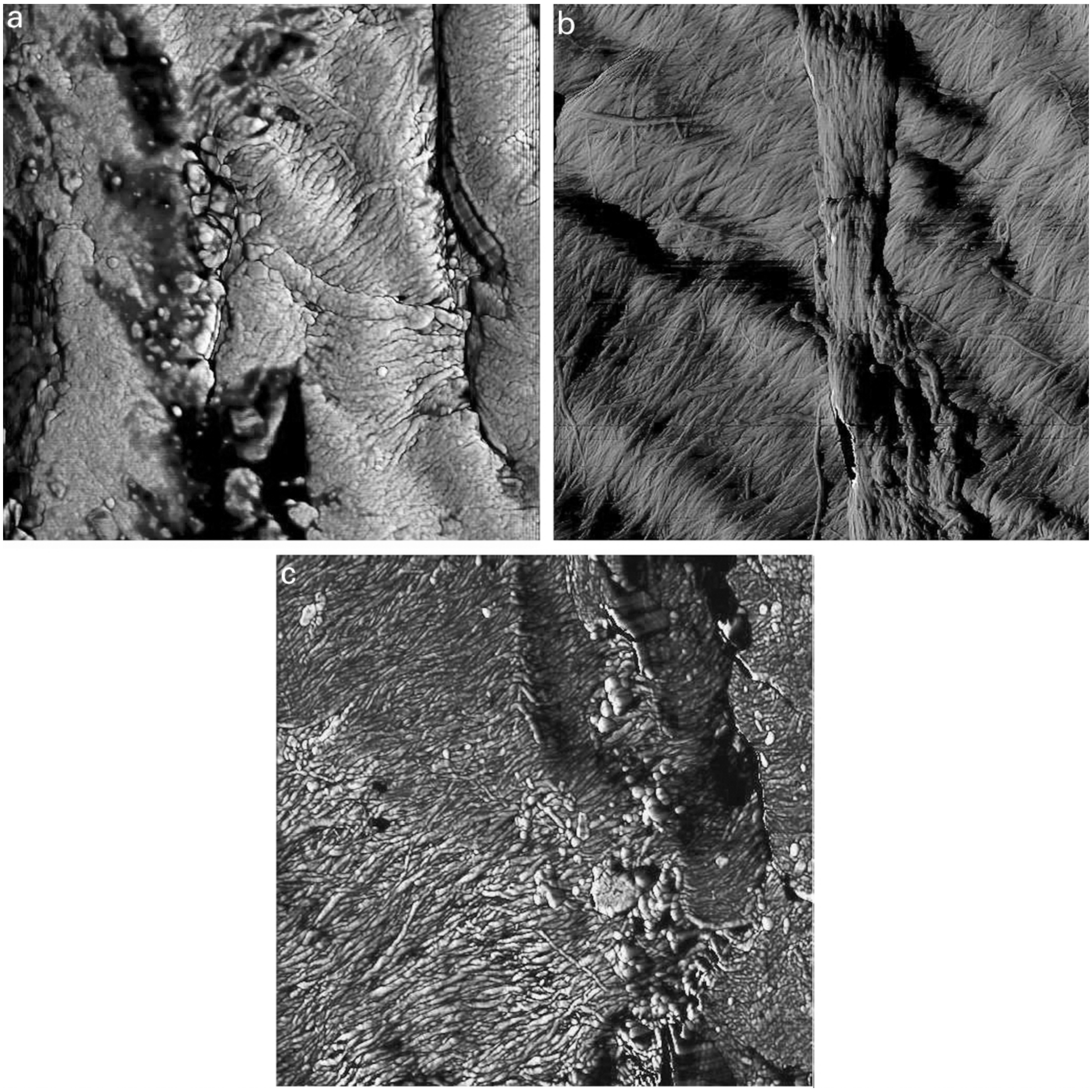

Fig. 5. AFM phase images of samples from the (a) O-stage, (b) E_1-stage and (c) D_1-stage of delignification. Before delignification the pulp was cooked 120 min at 170 °C and acetone extracted. Image sizes and *z*-scales are as follows: (a) 3 μm × 3 μm; 25 °, (b) 3 μm × 3 μm; 30 °, (c) 3 μm × 3 μm; 5 °.

D_2-stage. Thus, the amorphous structures in the respective AFM-images (Fig. 6(a)) most probably represent hemicelluloses and extractives rather than lignin. This result nicely supports the conclusions drawn from Fig. 3(a). According to the XPS results the extractives are in minority (13% surface coverage, Eq. (1)). Hemicellulose extraction ($HCl-CH_3OH$ treatment) of the D_2-delignified sample resulted in a surface with very peculiar short, randomly oriented, microfibril-like (diameter 20–25 nm) structures (Fig. 6(b)). As a first possibility, these well-reproducible structures might represent decomposed cellulose. As another alternative, structures surprisingly similar in form, size and orientation have been reported for glucomannans recrystallized from spruce wood after dissolution in KOH [39]. As a matter of fact, $HCl-CH_3OH$-treatment has been reported not to be very specific in dissolving deacetylated glucomannans, whereas it is clearly more effective in removing other hemicelluloses [46].

4. Conclusions

Scandinavian spruce kraft pulp samples were studied both with AFM and XPS as a function of cooking and $OD_0E_1D_1E_2D_2$-delignification. The AFM results were observed to correlate with the XPS results. In general,

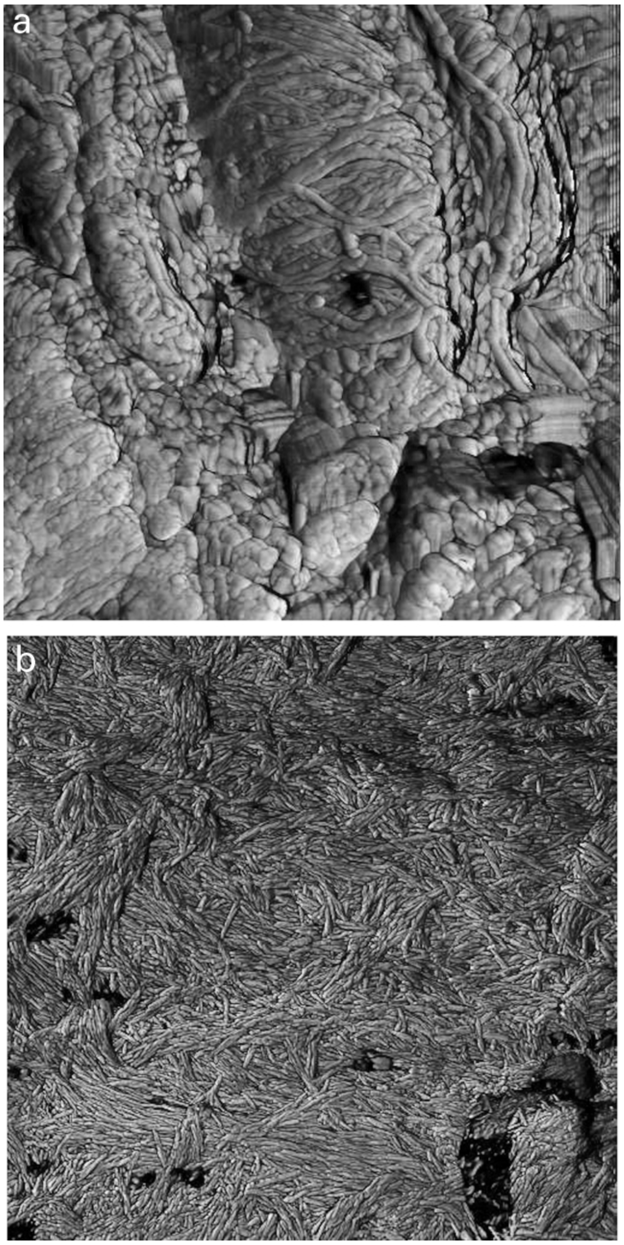

Fig. 6. AFM phase images of (a) a sample representing the D_2-stage of delignification and (b) further HCl + CH_3OH treated spruce kraft pulp sample. Image sizes and z-scales: (a) 3 μm × 3 μm; 25 °, (b) 3 μm × 3 μm; 60 °, respectively.

both the O/C atomic ratios and the amount of fibrillar surface structures increased as the delignification proceeded, indicating that these linear surface structures represented carbohydrates. The granules dominating the fibre surface at the beginning of cooking were suggested to consist mainly of extractives and lignin, due to the low O/C atomic ratios in the XPS-spectra. However, hemicelluloses were observed to contribute to both the amorphous (granular) and crystalline (fibrillar) surfaces phases. A question that remains partly unanswered is whether the hemicellulose extraction was complete or were the cellulose microfibrils destroyed as a result of this treatment. The two surface sensitive methods, AFM and XPS, were found to nicely complement each other in surface characterization. XPS gives the chemical composition of the surface and, therefore, helps one to interpret the morphological components observed in the AFM images. AFM, however, probes the very surface revealing not only the surface morphology and local adhesion properties but also very thin structural layers covering the fibre surface. Such layers (in the thickness range less than 10 nm) may be much more difficult to study by XPS.

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