

Surface characterization of unbleached kraft pulps by means of ESCA

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The effect of digestion conditions (amount of effective alkali, digestion time) on the surface compositions of unbleached softwood (*Pinus sylvestris*) kraft pulp has been investigated by electron spectroscopy for chemical analysis (ESCA). The quantities monitored were the angular dependence of the total O/C ratio, the relative amounts of carbons in different states of oxidation and the adsorption of Al and Ca ions to the carboxyl groups in the surface. Examination of the angular dependence of ESCA intensities shows that the concentration of alkyl carbon is high in a very thin surface layer and that it decreases linearly with decreasing kappa number. The concentration of alkyl carbon is decreased by extraction of the fibres with dichloromethane, but the amount remaining in the surface after extraction still decreases linearly with decreasing kappa number (i.e. it decreases with increasing digestion time). It is suggested that the observed enrichment of alkyl carbon in the outermost surface layers most probably is due to reprecipitation of lignin. In pulp that has not been extracted, there is also strong enrichment of extractives in the surface. This amount increases with increasing effective alkali but is relatively independent of digestion time. ESCA analysis of the Al and Ca bound to the carboxyl groups shows that the amount depends on digestion time; the results are consistent with the notion that the reprecipitated lignin contains carboxyl groups.

KEYWORDS: kraft pulp surface properties, ESCA, lignin, extractives, carboxyl groups

INTRODUCTION

The current development of new digestion, washing and bleaching procedures in the manufacturing of pulp has highlighted the need for a better understanding of how the fibre surface chemistry affects the properties of the final paper products. In the manufacture of pulp, the fibres undergo complex changes, and it is evident that a full description of the chemical composition and the electrical properties of their surface can be obtained only by combining several different thermodynamic and spectroscopic methods. Recently, we have initiated such a systematic study through a detailed investigation of the charge properties of unbleached kraft pulp in the pH range 2-8 (Laine *et al.*, 1994; Stenius and Laine, 1994). In this paper, we report on an

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investigation by electron spectroscopy for chemical analysis (ESCA) of how digestion parameters affect the surface chemical composition of the same pulps.

The use of ESCA (or X-ray photoelectron spectroscopy, XPS) to study cellulosic fibres was pioneered by Dorris and Gray (1978a). Since then, the ESCA technique has been used in many investigations of fibre surface chemistry, including the surface composition of mechanical pulps (Dorris and Gray, 1978b), the chemisorption of stearic acid on cellulosic fibres (Takeyama and Gray, 1982), the adsorption of polymer on fibres (Ödberg and Ström, 1983), the distribution of neutral size on fibre surfaces (Ström *et al.*, 1992), the functionality of chemically modified fibres (Sawatari and Nakamura, 1992), and the chemical composition of coated paper surfaces (Ström *et al.*, 1993).

The only atoms analysable by ESCA in pure cellulosic fibres are carbon and oxygen. The chemical shifts for carbon (C1s) in pulp fibres can usually be easily classified into four categories (Dorris and Gray, 1978a; Carlsson and Ström, 1991b): unoxidized carbon (C–C), carbon with one oxygen bond (C–O), carbon with two oxygen bonds (O–C–O or C=O) and carbon with three oxygen bonds (O=C–O). For lignin, it is also possible to observe the shake-up band of aromatic carbon. Detailed analysis of the oxygen (O1s) peak is generally less useful. Thus, quantitative data on the surface chemical composition can be obtained mainly from the O/C atomic ratio and the relative amount of each type of carbon (C1s). An additional possibility is offered by replacing exchangeable protons in the fibres (in the pH range 2–8 these are exclusively bound to carboxyl groups) by other ions that can be detected by ESCA.

Theoretical O/C ratios and relative amounts of carbons with different degrees of oxidation can be calculated for carbohydrates, lignin and extractives from their empirical carbon-oxygen formulae (Dorris and Gray, 1978b; Gray, 1978). The amount of alkyl (C–C) carbon in these pulp components decreases in the order: extractives > lignin > carbohydrates. Thus, it should be possible to monitor the amount of lignin in the surface by measuring the oxygen-carbon ratio and the relative amount of alkyl (C–C) carbon compared to a carbohydrate-rich surface. When extractives are present in the surface, the amount C–C carbon will increase further.

In the alkaline delignification process, the relative amounts of the different constituents of wood fibres, i.e. cellulose, hemicellulose, lignin and extractives, are changed radically. The total lignin content decreases from $\approx 27\%$ in wood to $\approx 3\%$ in low yield unbleached kraft pulp, and considerable degradation of polysaccharides takes place. Due to their amorphous state and their lower degree of polymerization (Sjöström, 1993), the yield of hemicelluloses decreases to a larger extent than that of cellulose. In addition, the extractive content decreases from $\approx 4\%$ in wood to $< 0.5\%$ in kraft pulp fibre.

While, thus, the 'bulk' composition of unbleached kraft fibres is fairly well known, the knowledge of how the chemical composition of their surface depends on yield and other pulping parameters is much less complete. The aim of this study is to evaluate by ESCA spectrometry how digestion time (level of residual lignin) and the used effective alkali affect the surface chemical composition of unbleached kraft fibres. The surface coverage of extractives and lignin was analysed using both untreated and dichloromethane (DCM)-extracted paper sheets. The chemical composition was studied with the help of ESCA spectra of model compounds. The effect of sampling depth was analysed by decreasing the angle of emission.

MATERIALS AND METHODS

Pulps

A series of unbleached kraft pulps (Scots pine, *Pinus sylvestris*) were prepared by digestion in a laboratory digester in the presence of three different levels (20, 22 and 26%) of effective alkali (sulphidity 30%). Digestion was carried to different degrees of delignification, producing pulps with kappa numbers in the range 18–57; the lignin content (L, %) in unbleached softwood kraft pulp can be evaluated from the kappa number according to $L = (\text{kappa number})/6.546$ (Kyrklund and Strandell, 1969). The temperature was increased from 20 °C to digestion temperature (173 °C) in 80 min. Duration of the treatment at the maximum temperature was varied depending on the used effective alkali and the target kappa number. The samples are summarized in Table 1. The kappa number was measured using the standard method SCAN-C 1:77. Laboratory sheets were made without any additives directly from the pulps according to the standard method SCAN-C 26:76. The paper sheets were drum-dried at 70 °C for 2 h. Part of each sheet was extracted with dichloromethane (DCM) to remove residual resin and fatty acids. The content of extractives in the pulps was analysed by extraction with DCM according to the standard method SCAN-C 7:62.

Pulps were converted to their calcium or aluminium form using a slightly modified version of the method described by Scallan and Grignon (1979). The method of modification of acidic groups is described in detail in Buchert *et al.*, 1993.

Model compounds

Analysis of the ESCA spectra of the pulps is based on the knowledge of spectra for model compounds. An extracted bleached softwood (*Pinus sylvestris*) kraft pulp was chosen as the model compound for carbohydrates. A typical hemicellulose (xylan) isolated from bleached kraft pulp was also analysed. Kraft lignin was isolated from the spent liquor from conventional kraft pulping of softwood (*Pinus sylvestris*). Model compounds for extractives were prepared as follows: after extraction of softwood pulp with DCM the solvent was evaporated and ≈ 0.5 ml acetone was added to the remaining material. The mixture (a concentrate of extractives) was shaken for approximately 30 min. A drop of the resulting acetone solution was placed in the sample pot of the spectrometer and analysed after evaporation of the acetone.

The DCM extracts were also roughly quantified by gas chromatography, using model

TABLE I. The choice of effective alkali and kappa number in the preparation of unbleached kraft pulp fibres

Sample	Effective alkali (%)	Kappa number
A	20	18
B	20	29
C	20	57
D	22	35
E	26	19
F	26	31
G	26	57

compounds for typical fatty and resin acids as reference. Per(trimethylsilylated) (TMS) samples were analysed in a Hewlett-Packard 5880A gas chromatograph equipped with a SE-54 fused-silica capillary column. The temperature programme was 2 min at 100 °C, 15 °C min⁻¹ to 260 °C and 10 min at 260 °C. The temperature of both the injection port and the flame ionization detector was 270 °C.

Apparatus

The ESCA measurements were carried out at the Institute of Surface Chemistry, Stockholm using an AXIS-HS spectrometer from Kratos Analytical. Monochromatized AlK_α radiation was used to excite the electrons. The effect of the sampling depth was analysed by changing the angle of emission, α , i.e. the angle between the paper sheet and analyser. The analysing depth then becomes reduced by the factor $\sin \alpha$ (Ström *et al.*, 1992). The angles of emissions 90°, 50°, 30° and 20° were used.

The surface of paper is rough and a complete analysis of the effect of changing the angle of emission should take the effect of roughness on the observed intensities into account. A theoretical analysis of the complex fibre structure formed in a paper sheet would be very difficult. We have therefore refrained from any roughness corrections. As support for this omission we note that (a) the method of preparation of the sheet is expected to result in randomly oriented fibres, (b) samples were taken from several locations in the same sheet, and (c) the method has been used in several other studies of paper (Ström *et al.*, 1992; 1993) and has been found to give results consistent with other observations.

Analyses were made on an area 800 × 500 μm, usually at three different locations in the paper for each sample. Using the curve-fitting programme supplied with the spectrometer, Gaussian curves were fitted for deconvolution of the carbon (C1s) peak. The chemical shifts relative to C–C used in the deconvolution were 1.7 ± 0.2 eV for C–O, 3.1 ± 0.3 eV for O–C–O or C=O and 4.4 ± 0.3 eV for O=C–O. For the lignin model compound, the shake-up band of aromatic carbon was located at approximately 6.5 eV (Ström *et al.*, 1993).

Strictly speaking, account should also be taken of the effect of carboxyl groups on neighbouring carbons by assuming that it gives rise to a peak at 0.6–1 eV (Pijpers and Donners, 1985). Since the effect is relatively weak and the carboxyl content of the cellulose surface is very low, we have not included this peak in our calculations.

Determination of surface chemical composition

The surface chemical composition was evaluated either using the C1s and O1s peaks by calculating the total O/C atomic ratio or the relative amounts of different carbons from the intensities of carbons with different chemical shifts of the C1s peak. The amounts of metal ions in pulps that had been transformed to their Ca and Al forms were analysed using the Ca2p and Al2p peaks recorded for these pulps.

The surface coverage of extractives, ϕ_{extr} , and lignin, ϕ_{lignin} , was calculated at different emission angles of the electrons from the O/C atomic ratios using the method described by Ström and Carlsson (1992). Assuming that the thickness of the patches of the extractives is greater than the deepest sampling depth (≈ 10 nm, $\alpha = 90^\circ$), ϕ_{extr} can be estimated from the O/C atomic ratios using the equation

$$\phi_{\text{extr}} = \frac{O/C_{(\text{before extraction})} - O/C_{(\text{after extraction})}}{O/C_{(\text{extractives})} - O/C_{(\text{after extraction})}} \quad (1)$$

where $O/C_{(\text{extractives})}$ is estimated from the spectrum of the model extractive compounds. Similarly, assuming that the thickness of the regions where lignin is located is greater than the ESCA analysing depth, the lignin surface coverage can be calculated from

$$\phi_{\text{lignin}} = \frac{O/C_{(\text{pulp sample})} - O/C_{(\text{pure pulp})}}{O/C_{(\text{lignin})} - O/C_{(\text{pure pulp})}} \quad (2)$$

where $O/C_{(\text{pulp sample})}$ is the O/C ratio of the analysed (kraft) pulp after extraction and $O/C_{(\text{lignin})}$ is the measured O/C value in the spectrum of the lignin model compound. Extracted bleached kraft pulp, which contains practically no lignin, was analysed to obtain a value for $O/C_{(\text{pure pulp})}$.

RESULTS

Model compounds

Figure 1 shows the ESCA C1s signal of kraft lignin and its deconvolution. The signal consists of five bands, in which C1–C4 originate from carbons at different oxidation levels and C5 is a 'shake-up' band due to the presence of aromatic rings in the lignin. The measured value of the O/C atomic ratio, 0.32, agrees well with the theoretical value for Freudenberg lignin (0.33) (Freudenberg and Neish, 1968). The relative amount of C1 in lignin was $\approx 50\%$ (Table 2), which makes it possible to roughly estimate the lignin coverage in extracted pulps using the C1 band. The presence of carboxyl groups in the lignin structure, i.e. a peak at the C4 position is obvious,

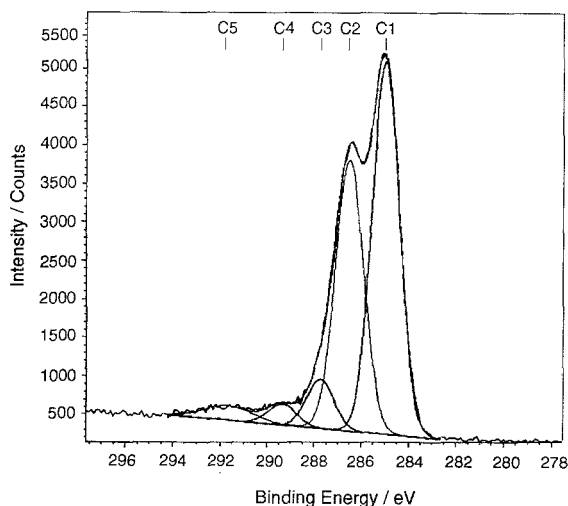


FIGURE 1. Curve-resolved ESCA C1s signal of kraft lignin. C1, unoxidized organic carbon (CH_x); C2, carbon with one bond to oxygen (C–O); C3, carbon with two bonds to oxygen (C=O or O–C–O); C4, carbon with three bonds to oxygen (O–C=O); C5, transitions in π -electrons of aromatic rings (shake-up satellite).

TABLE 2. The O/C atomic ratio and the relative amounts of different carbons (C1s) of the model compounds

<i>Model compound</i>	O/C	C1	C2	C3	C4
Cellulose (theoretical)	0.83	–	83	17	–
Bleached kraft pulp (this study)	0.80	6	75	18	1
Arabinoglucuronoxylan (theoretical)	0.81	–	78	19	3
Xylan (this study)	0.83	5	67	24	4
Lignin, theoretical (Freudenberg)	0.33	49	49	2	–
Kraft lignin (this study)	0.32	52	38	7	3
Oleic acid (theoretical)	0.11	94	–	–	6
Extractives (this study)	0.12	93	5	–	2

supports the notion that acidic groups bound to lignin are formed during alkaline pulping, as also suggested in Laine *et al.*, 1994 and Sarkanen and Ludwig, 1971.

The results for extracted bleached kraft pulp and for xylan agree fairly well with theoretical values for carbohydrates (Mjöberg, 1981) (Table 2). The main differences are the appearance of a small amount of alkyl carbon (C1) and a slight reduction in the O/C ratio of unbleached kraft fibre. The experimental O/C atomic ratio for extractives is somewhat higher than theoretical values for fatty and resin acids (0.08–0.10) (Dorris and Gray, 1978b; Ström and Carlsson, 1992), implying that a small amount of oxygen-rich material is removed from pulp during extraction.

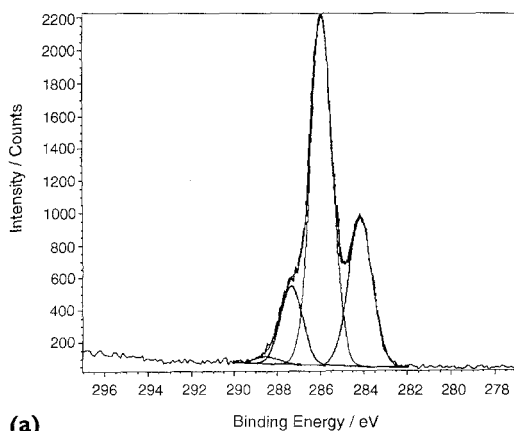
Unbleached kraft samples

Figs 2a and b compare the high resolution and curve-resolved ESCA spectra of the C1s peak for pulps prepared with the same effective alkali but digested to different kappa numbers. As expected for a surface containing cellulose, hemicellulose, lignin and extractives, four different types of carbons are observed (the amount of lignin is too small for the shake-up signal to be observed). The relative amount of alkyl (C1) carbon decreases strongly as the kappa number decreases, indicating that the amount of either extractives or lignin is decreased as delignification proceeds.

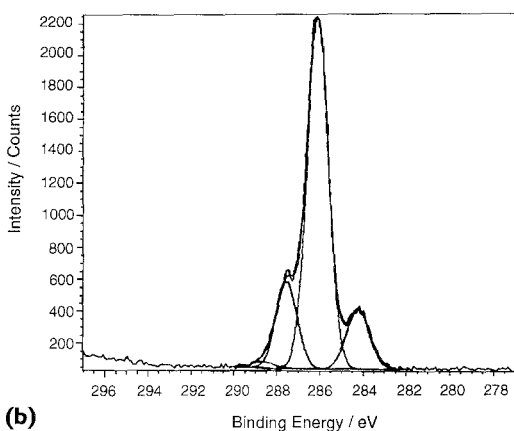
Extractives

In Fig. 3 the O/C atomic ratio and the amount of C1 are plotted as a function of the analysing depth, $\sin \alpha$, for an extracted kraft pulp. It should be noted that results can be presented as a variation either in C1 or in O/C because, without exception, a direct correlation between the amount of C1 carbon and the O/C atomic ratio was found. For this reason, only one type of presentation (relative amount of C1) is shown in the other figures of this paper.

The four different angles of emission were used to evaluate the depth profile of outermost surface layers of unextracted and extracted kraft pulps. Fig. 4a shows the variation in the relative amounts of alkyl carbon (C1) before and after extraction for one of the pulp samples as a function of $\sin \alpha$. The trend in the extracted pulp fibres indicates that some material, rich in aliphatic carbon that does not originate from



(a)



(b)

FIGURE 2. Curve-resolved spectrum of ESCA C1s peak of unbleached, unextracted kraft pulp. (a) sample C, (b) sample A.

extractives, is still present in the outermost surface of fibres. The clear difference in the level of the amount of C1 between extracted and unextracted pulps is due to a removal of hydrophobic fatty and resin acids (Carlsson, 1991).

Fig. 4b shows the amount of aliphatic carbon in extracted pulps digested to different kappa numbers as a function of the analysing depth. Similar results are obtained for all pulps.

Fig. 5 shows the surface coverage by extractives, ϕ_{extr} , calculated from Equation (1). ϕ_{extr} depends strongly on the amount of effective alkali. The surface content of extractives increases when the dosage of alkali increases. The difference between low and high alkali levels is larger in the outermost surface layer (angle of emission 20°). When wood fibres are digested at the same effective alkali level, variations in the kappa number do not significantly affect the fraction of the surface covered by extractives.

The total amount of DCM-extractable material in the fibres varies between 0.09 and 0.17 wt %. Gas chromatography analysis of the DCM extracts of unbleached kraft pulp fibres showed the presence of typical fatty acids, such as oleic, palmitic and stearic acid,

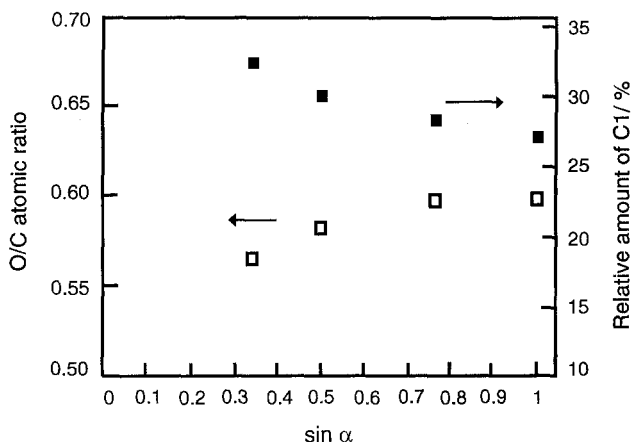


FIGURE 3. O/C atomic ratio and the relative amount of alkyl carbon (C1) as a function of $\sin \alpha$ (α = angle of emission of electrons) for unbleached, extracted kraft pulp fibre (sample C). □, O/C ratio; ■, relative amount of C1. Note that $\sin \alpha$ is proportional to the analysing depth.

as well as resin acids, such as pimaric acid. The predominating compound was oleic acid. The total and surface contents of extractives in different pulp samples are summarized in Table 3.

Lignin

Fig. 6 shows the coverage of the extracted fibre surfaces by lignin, ϕ_{lignin} , as a function of the total lignin content at two different emission angles. ϕ_{lignin} was calculated using Equation (2). Whether calculated from the emission at 90° (sampling depth 5–10 nm), or from a smaller analysing depth ($\alpha = 20^\circ$), ϕ_{lignin} increases with increasing kappa number, proving that the surface content of lignin also depends systematically on the duration of delignification. This rate of increase does not depend on the used dosage of alkali (Fig. 6). The surface coverage is quite high, i.e. enrichment of lignin, possibly due to reprecipitation, appears to occur in the outermost surface layers of the fibres.

Figure 7 compares the effect of extraction for pulps with different kappa numbers prepared by digestion with different amounts of effective alkali (20 and 26%). Extraction decreases the amount of C1 carbon considerably for both pulp series. However, after extraction, the relative amount of C1 carbon no longer depends on the amount of effective alkali used.

Carboxylic groups

As seen from Fig. 2, the carboxyl carbon band (C4) is rather small. Hence, the determination of the relative amount of carboxyl groups is relatively uncertain. In order to obtain more reliable values for the surface carboxyl group content, ESCA analysis was made of three pulps that had been changed to their calcium and aluminium form.

The amounts of calcium and aluminium (i.e. carboxyl group content) in the surface increase with increasing kappa number (Fig. 8). These results agree well with the trends

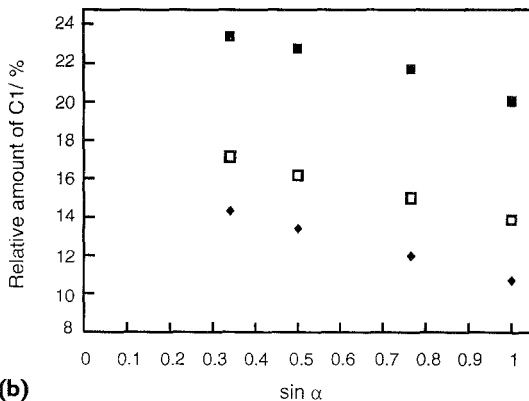
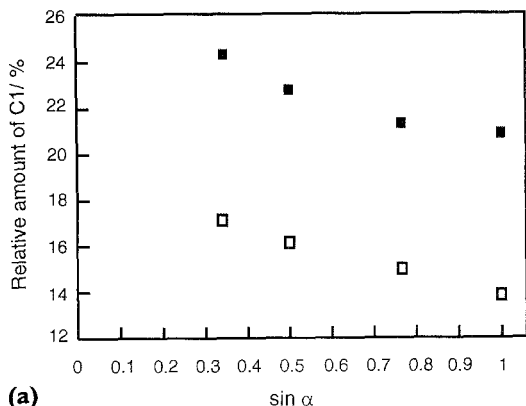


FIGURE 4. Relative amount of alkyl carbon (C1) of (a) untreated (■) and extracted (□) kraft pulp (sample B) and (b) extracted pulp samples (◆, sample A, kappa = 18; □, B, kappa = 29; ■, C, kappa = 57) as a function of $\sin \alpha$. Note that $\sin \alpha$ is proportional to the analysing depth.

determined by polyelectrolyte and potentiometric titration methods (Stenius and Laine, 1994).

The effect of sampling depth on the amount of carboxyl groups was also studied. Table 4 shows that the Al/C atomic ratio of pulps digested to three kappa numbers is independent of the emission angle of the electrons.

DISCUSSION

Analysis of model compounds

The analysis of model compounds demonstrates that significant chemical differences between carbohydrates, lignin and extractives are detected by the ESCA technique. The O/C values (Table 2) for model compounds are very useful in the evaluation of the surface content of extractives and lignin in the fibres (Figs 5 and 6).

The experimentally found amounts of different carbons and O/C ratios for model

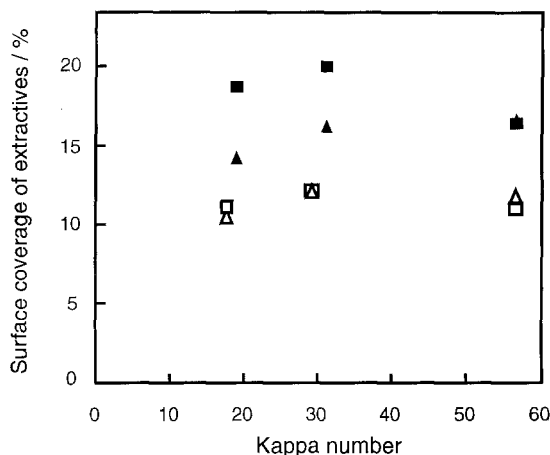


FIGURE 5. Surface coverage of extractives (Equation (1)) in unbleached kraft pulp fibres as a function of kappa number. ■, effective alkali (EA) 26%, emission angle (α) 20°; ▲, EA 26%, α 90°; □, EA 20%, α 20°; △, EA 20%, α 90°.

TABLE 3. Total amounts (determined by gas chromatography) and surface contents (determined by ESCA at angles of emission 90° and 20°) of extractives of different pulps

Sample	DCM-extract (%)	ϕ_{extr} (90°) (%)	ϕ_{extr} (20°) (%)
A	0.09	11	11
B	0.10	12	12
C	0.13	12	11
D	0.10	13	14
E	0.09	14	19
F	0.17	16	20
G	0.15	17	16

compounds agree fairly well with the theoretical values for carbohydrates, lignin and extractives (Dorris and Gray, 1978b; Freudenberg and Neish, 1968; Mjöberg, 1981). The appearance of alkyl carbon in the spectrum of bleached kraft pulp and xylan may be due to either a small amount of contamination of the material or a chemical change in the carbohydrate structure (Carlsson and Ström, 1991a; b). If the peak C1 is assumed to be due to a chemical change in the cellulose structure, the amount of C1 observed corresponds to the reduction of one carbon (C2) per three β -D-gluco-pyranose units to a methyl or methylene group. However, it seems most likely that the observed C1 on the extracted bleached kraft pulp is due to C1-containing material (e.g. a strongly adsorbed extractive) that is not removable by extraction.

Effect of effective alkali and digestion time on surface chemical composition

These effects are summarized in Fig. 7. Increasing digestion time (i.e. decreasing kappa number) results in a decreased amount of alkyl carbon (C1), irrespective of whether the

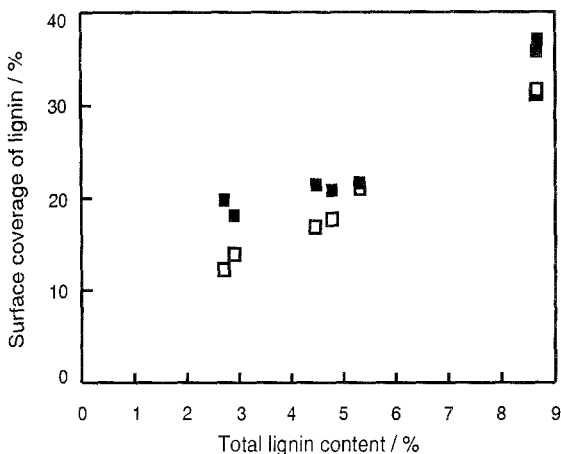


FIGURE 6. Surface coverage by lignin (Equation (2)) as a function of total lignin content in kraft pulps. ■, emission angle (α) 20°; □, α 90°.

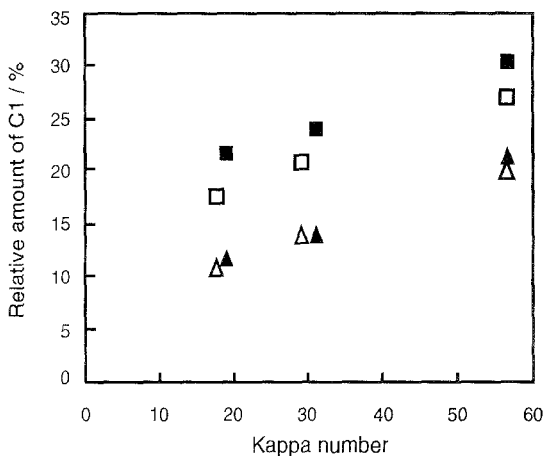


FIGURE 7. Relative amount of alkyl carbon (C1) of unextracted and extracted kraft pulps (samples A, B, C, E, F and G) as a function of kappa number. ■, effective alkali (EA) 26%, unextracted; □, EA 20%, unextracted; △, EA 20%, extracted; ▲, EA 26%, extracted.

pulp has been extracted or not (Figs 2, 4b and 7). The dependence of the amount of C1 (measured at a 90° angle of emission of the electrons) on the kappa number is almost linear. The obvious interpretation is that the surface content of hydrophobic material decreases when the total concentration of lignin decreases. A similar correlation between the alkyl carbon (C1) and the kappa number was also observed (for extracted pulps) by Carlsson (1991). The correlation did not depend on the manufacturing process of the pulp.

The absolute values of alkyl carbon (C1) depend on whether or not the pulp was extracted, but the variation with kappa number is independent of extraction. For

TABLE 4. The Al/C and O/C atomic ratios as a function of angle of emission of unextracted kraft pulps (samples C, D and E) in which the carboxyl groups were converted to aluminium form

Sample/angle of emission	Al/C $\times 10^2$ atomic ratio	O/C atomic ratio
E		
90°	1.0	0.64
50°	1.1	0.63
30°	1.1	0.62
20°	1.2	0.59
D		
90°	1.5	0.62
50°	1.4	0.61
30°	1.4	0.60
20°	1.5	0.58
C		
90°	1.6	0.60
50°	1.6	0.60
30°	1.4	0.58
20°	1.6	0.57

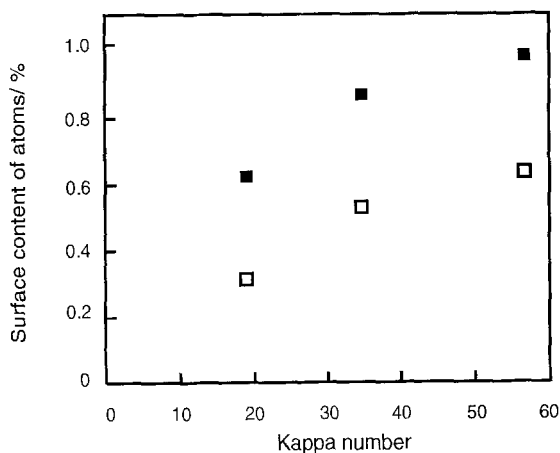


FIGURE 8. The surface content (at.%) of aluminium and calcium in fully ion-exchanged kraft pulps (samples C, D and E). □, calcium; ■, aluminium.

unextracted pulps digested to the same kappa number, higher effective alkali results in a higher amount of alkyl carbon (Fig. 7). Thus, fibre digested with higher concentration of excess alkali contains more DCM-extractable material in the surface. The GC analysis shows that this material mainly contains fatty and resin acids. In contrast, the surface composition of carbohydrates and lignin does not depend on the used alkali concentration (the data points for extracted pulp fibres in Fig. 7).

The calculation of surface coverage, ϕ , (Equations (1) and (2)) is based on the assumption that the layer of the material that covers the surface is thicker than the depth of analysis. If this is the case for all angles of emission, the same values of ϕ

should be obtained at 90° and 20°. Table 3 and Fig. 5 show that for extractives this is the case for all pulps except samples *E* and *F* for which the coverages are higher at 20°. This indicates that for these two samples, which represent high excess of alkali and low kappa number, the layers of extractives are thinner than the analysing depth at 90° (≈ 10 nm). For lignin, the calculated surface coverage at 20° is always larger than at 90°, i.e. the lignin-rich layer is probably always thinner than 10 nm.

Effect of lignin in the fibre surface

Although the total amount of lignin in the fibres is small, the surface layer contains substantial amounts of carbon that cannot possibly be chemically bound in cellulose or hemicellulose. As is evident from the above discussion, it may be assumed that all the C1 carbon that remains in the fibre surface after extraction is lignin. Using Equation (2), it is found that the calculated surface coverage of lignin is much higher than the average content of lignin in fibres (Fig. 6), i.e. there is a strong enrichment of lignin in the surface of unbleached kraft pulp fibres. This enrichment is localized to the outermost surface layers, as is clearly seen from the angular dependence of the amount of C1 carbon (Fig. 4). As noted above, the angular dependence of the calculated degree of coverage suggests that the lignin-rich layer in the surface is very thin.

Clearly, one would expect the extraction process taking place in the digestion of fibres to result in a *decreasing* lignin concentration towards the surface of the fibres. We therefore suggest that the observed *enrichment* in the outermost surface layers is due to lignin resorption. That the lignin-rich layer is apparently always very thin supports this idea. Indeed, it has been shown in flow-through experiments that lignin is resorbed onto the fibre surface during kraft pulping (Janson *et al.*, 1975) and, hence, it was suggested that after the digestion and washing processes unbleached chemical pulp fibres contain several forms of residual lignin, viz., crosslinked lignin, lignin chemically bound to polysaccharides and also lignin resorbed into the fibres during the digestion process (Sundquist, 1985).

Effect of extractives in the fibre surface

While the alkali dosage has little effect on the lignin content in the fibre surface, it strongly affects the surface concentration of extractives. The digestion time is less important (Fig. 5). Fig. 5 also shows that the resin and fatty acid content is independent of analysing depth ($\approx 11\%$, 90° and 20°) in the case of the lower effective alkali level (20%). At the higher effective alkali level (26%) the surface concentration of extractives is higher and, for the lower kappa numbers, the layer of extractives becomes very thin (as shown by the angular dependence of the calculated degrees of coverage).

The poor correlation between the total and the surface content of extractives (Table 3) indicates that the enrichment of fatty and resin acids is mainly due to reprecipitation of extractives during digestion or washing. It has been shown (Björklund Jansson *et al.*, 1985; Ström *et al.*, 1990) that the quantity of extractives is strongly enriched in the surface layers of washed kraft fibres. During the washing process the concentration of fatty and resin soaps in the washing liquor may decrease below their critical micelle concentration (c.m.c). As a result, solubilized extractives may resorb onto the fibre surface.

Carboxylic groups

In a previous publication (Stenius and Laine, 1994), we have shown that the combination of titration data and ESCA analysis is able to yield a very detailed picture of the effect of digestion conditions on the amount of carboxyl groups in the fibre surface. Fig. 8 corroborates the earlier findings that the ionizable group content increases, i.e. both the aluminium and the calcium content of the surfaces increase with increasing kappa number. As argued in Laine *et al.*, 1994 and Stenius and Laine, 1994, this is very probably due to the presence of carboxyl groups chemically bound to hemicellulose and lignin. It should be noted that the analysis of Al and Ca was done on pulps that had not been extracted with DCM. The surface carboxyl group content of unextracted fibres depends on the quantity of extractives in the surface layer. However, as discussed above, this amount is fairly independent of the kappa number.

The surface content (at. %) of inorganic material is higher for the cation of higher valency (Al). A similar trend has been observed for the total equivalents of metal ions in pulps (Scallan and Grignon, 1979; Buchert *et al.*, 1993). However, one should not expect stoichiometric equivalence between the adsorption of calcium and aluminium, because in the pH range at which ion exchange is performed, aluminium forms polynuclear complexes that may be strongly adsorbed.

The angle of emission did not significantly affect the Al/C atomic ratio (Table 4). However, the amount of C1 carbon increases in the outermost layers (Table 4, $\alpha = 20^\circ$). Thus, the carboxyl group content in the outermost layer (which contains a large amount of lignin) does not decrease. This is consistent with the spectrum of the lignin model compound (Fig. 1) which contains a significant amount of carboxyl carbon (C4).

CONCLUSIONS

1. There is an enrichment of lignin and extractives on the surface of unbleached kraft pulp fibres.
2. The surface content of extractives increases when the alkali dosage used in the digestion increases, while the amount is relatively independent of digestion time.
3. Analysis of the angular dependence of the calculated degree of coverage shows that the lignin-rich layer in the surface is very thin. It is concluded that this alkali-independent enrichment of lignin in the outermost layers is very probably reprecipitated.
4. The carboxyl group content in the surface decreases with decreasing kappa number.

ACKNOWLEDGEMENTS

The authors thank MSc. Ursula Klemetti for preparation of pulp samples and Ms. Aila Siltala for excellent laboratory assistance. This work was funded by grants from the Finnish Technology Development Centre (TEKES) and the industrial group supporting the programme 'Uudistuva paperi' ('New generation paper technology') run by TEKES.

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