

Kleen, M., Kangas, H. and Laine, C. (2003). Chemical characterization of mechanical pulp fines and fiber surface layers. *Nordic Pulp and Paper Research Journal* 18 (4): 361-368.

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Chemical characterization of mechanical pulp fines and fiber surface layers

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KEYWORDS: Surface chemistry, Peeling, Thermomechanical pulp, Fiber, Fines, ESCA, TOF-SIMS, Lignin, Extractive, Hemicellulose, Pectin, Chemical composition, *Picea abies*

SUMMARY: The chemical compositions of TMP fines and material isolated from the surface layers of TMP long fibers were compared with that of the inner layers (i.e. bulk) of the long fibers. Both fines and fiber surface layers contained more extractives, lignin and pectins than the bulk fibers. The fiber surface layer material consisted mainly of fibrils, which were concluded to originate from the primary cell wall layer. These fibrils contained more cellulose and mannan and less xylan than the ray cell-rich fines fraction. The frequency of methylglucuronic acid groups in the primary wall fibril xylan was found to be about 30% lower than in the bulk fiber xylan.

The outermost surfaces of the primary wall fibrils were very rich in extractives, lignin and protein. The lignin on the bulk fiber surfaces contained about 50% more guaiacyl units than lignin on the surface of the primary wall fibrils or of fines. The composition of extractives on the surface of bulk fibers was also different from that on the surface of fines and the primary wall fibrils. Both the fines and the primary wall fibrils were found to possess greater ability to contribute to surface charge, if treated with alkali, compared with the bulk fibers. Surface extractives as well as lignin were found as small patches all over the surfaces of TMP fibers and fines. Thus, the results showed differences in the distribution, structure and composition of protein, lignin, polysaccharides and wood extractives across the fiber wall.

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Due to the rather harsh process conditions employed, mechanical pulps contain different types of fine material (fines) in addition to fibers with varying degrees of intactness. The proportion of fines in mechanical pulps is high, normally 10-40% of the total pulp. Fines are usually defined as the fraction of the pulp passing through a round hole 76 μm in diameter or through a nominally 200 mesh screen (Fines fraction of paper stock by wet screening, Tappi Testing method T 261 pm-80).

Fines consist of various types of particles, such as broken fibers, cell wall fragments, middle lamella fragments, ribbons, fibrils, fibril bundles, bordered pits as well as ray cells or pieces of these. These particles have different properties. Thus, the properties of a certain mechanical pulp depend on both the nature and quantity of the different fines types.

Cellulose-rich fibrillar fines have been reported to give good bonding ability (Brecht, Klemm 1953; Kallmes 1960; Marton 1964) and to improve paper strength

(Kallmes 1960; Luukko, Paulapuro 1999), while ray cells have been found to give very poor bonding ability (Westermarck, Capretti 1988; Wood et al. 2000) and thus may cause linting problems in printing processes. Flake-like particles from the fiber cell wall and middle lamella have poor bonding ability, but they improve other paper properties such as light-scattering and thereby the opacity (Luukko, Paulapuro 1999).

Different types of fines differ not only in their physical characteristics but also in their chemical properties. The lignin content of ray cells has been found to be higher than that of fibers (Hardell et al. 1980). The middle lamella has been reported to contain more lignin (Boutelje, Eriksson 1984) and rhamnose, arabinose, xylose and galactose, but less mannose and glucose than the secondary wall (Sorvari et al. 1986). While the bulk chemical compositions of both fines and fibers have been carefully studied, less is known about their surface chemistry (Luukko et al. 1999; Kleen et al. 2001).

Physical characteristics and surface chemistry are both of great importance for the behavior of fibers and fines in papermaking and for the properties of the final paper products. The surface composition of mechanical pulp fibers and fines can affect fiber bonding properties, i.e. paper strength, as well as the sorption and spreading of water, adhesion between fibers and coating materials, and the penetration and setting of printing ink.

Previously, mechanical pulp surfaces have been characterized by ESCA (Electron spectroscopy for chemical analysis) (Koljonen et al. 1997; Mustranta et al. 1998), a technique that allows determination of the surface coverage by extractives and lignin. The presence of some metal ions (Al, Ca, Si) on PGW pulp surfaces has been investigated by dynamic SIMS (Secondary ion mass spectrometry) (Saastamoinen et al. 1994), but very little attention has been given to the potential of static TOF-SIMS (Time-of-flight secondary ion mass spectrometry) as an analytical tool for studying wood components on mechanical pulp fiber surfaces (Kleen et al. 2001). On the other hand, TOF-SIMS has been shown to give structural information about the lignin and extractives on softwood kraft pulp surfaces (Kleen 2000a and 2000b). TOF-SIMS is very surface-specific and particularly useful for investigating the elements and organic compounds present in the outermost monolayer of the sample.

The aim of the present work was to gain fundamental information about differences in the chemical characteristics of the TMP fines, fiber surface material and bulk (i.e. peeled or inner layers) fibers, using TOF-SIMS and ESCA as the main tools for investigation.

Experimental

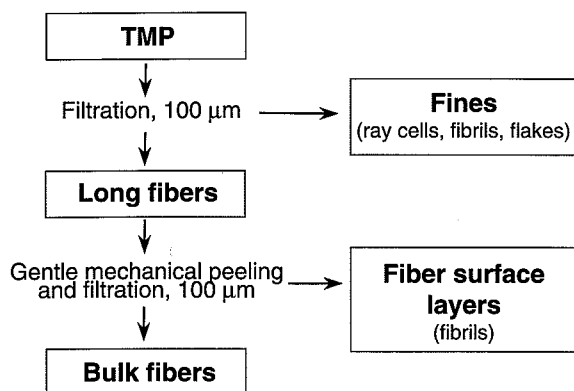


Fig. 1. Scheme for isolation of fines, fiber surface layers and bulk fibers from TMP.

Unbleached 2nd stage spruce (*Picea abies*) TMP (CSF 150 ml) was fractionated into fines, fiber surface material and peeled fibers. The fiber surface material represents material from the outer layers of the TMP long fibers and is denoted as fiber surface layers, whereas the peeled long fibers represent the inner fiber layers and are denoted as bulk fibers.

The fractionation was based on the principle described by Kallmes (1960), but modified according to the procedure published by Heijnsson et al. (1995a). The fractionation scheme is shown in Fig. 1. TMP was diluted to 2% consistency and the fines fraction was obtained by filtration of the pulp suspension through a nylon cloth with a pore size of 100 μm (corresponding to about 200 mesh). The fiber surface layers were released using gentle mechanical peeling (approximately 20 000 revolutions) of the long fibers in a British standard disintegrator at 4.5% consistency. The material released was removed by filtration through a nylon cloth filter with a pore size of 100 μm . In this way, peeled long fibers (i.e. bulk fibers) were obtained.

All the isolated fractions were freeze-dried. For surface analysis, small sheets were made of fibers and fines. For total chemical analysis, the samples were ground to a fine powder using a ball milling apparatus from Retsch specially designed for gentle milling of small amounts of sample.

Materials

Conventional analysis methods

The total content of extractives in the powdered samples was determined by acetone extraction (SCAN-CM 49:93). The lignin content was determined as Klason and acid-soluble lignin after acid hydrolysis (Browning 1967). The cellulose content was determined using acid hydrolysis and HPLC/PAD (Hausalo 1995).

Acid methanolysis

The chemical compositions of hemicelluloses and pectins were determined by subjecting the powdered samples to

acid methanolysis as described by Sundberg et al. (1996). The reaction time was 3 h. The resulting samples were silylated and analyzed using GC/MS (Laine et al. 1999). Acid methanolysis was chosen for its ability to determine uronic acids simultaneously with neutral sugars.

The amount of hemicelluloses and pectins (i.e. galacturonans, arabinogalactans and arabinans) was calculated from the sugar units obtained by methanolysis. Glucomannan was determined as Ac:Gal:Glc:Man 1:0.5:1:4 and converted to polysaccharide using the factor 0.9, while xylan was determined as Ara:4-O-MeGlcA:Xyl 1.3:2:10 and converted to polysaccharide using the factor 0.88 (Sjöström 1981a). Arabinogalactan was determined as GlcA:Ara:Gal 0.8:1:3.6 (Willför et al. 2002) and converted to polysaccharide using the factor 0.9. The residual arabinose was calculated as arabinan using the factor 0.88. Rhamnogalacturonan was calculated using the factor 0.9.

ESCA analysis

ESCA measurements were recorded with an AXIS 165 high-resolution electron spectrometer (Kratos Analytical), using monochromatic Al K α irradiation of sample sheets before and after acetone extraction. Both survey scans (1 eV step, 80 eV analyzer pass energy) and high-resolution spectra of C 1s and O 1s regions (0.1 eV step, 20 eV pass energy) were acquired at three different locations for each sample. The surface coverage by lignin and extractives was calculated from the averaged C-C percentages as reported earlier (Kleen et al. 2002a).

TOF-SIMS analysis

The instrument used was a PHI TRIFT II time-of-flight secondary ion mass spectrometer at Top Analytica Ltd., Turku, Finland. High mass resolution spectra and images in positive and negative ion modes were acquired using a $^{69}\text{Ga}^+$ liquid metal ion gun with 15 keV primary ions in bunched mode (mass spectra) and with 25 keV primary ions in unbunched mode (images) over the mass range 2-2000 m/z. The primary ion current was 600 pA and the time per channel 0.138 ns. The pulse width was 19 ns for spectra and 40 ns for images. The analysis area was 100x100 μm^2 and the acquisition time 5 minutes for spectra and 250x250 μm^2 and 10 minutes for images. Analytical charge compensation was used for insulating pulp samples. Three replicate runs were made for each sample. To be able to compare the surface content of extractives and lignin with those analyzed by ESCA, extractives were analyzed on the original samples and lignin on the extracted samples. Selected peak areas were integrated from TOF-SIMS spectra and images reconstructed from raw data files using off-line WinCadence software.

Results and discussion

With the fractionation procedure employed, 19% fines were isolated from the TMP. A further 10% fine material was obtained after gentle mechanical peeling of the TMP

fiber surfaces. Thus, about 71% of the original TMP were collected after peeling; this consisted of the inner layers of fibers, denoted here as bulk fibers.

The type of material present in the different fractions was studied by light microscopy. It was found that ray cells were enriched in the fines fraction, which also contained parts of flake-like material (e.g. parts of middle lamella), fibrils and ring pores. Material isolated from the fiber surfaces was fine material consisting mainly of fibrils. The peeled fiber surfaces of the bulk fibers were clearly less fibrillated than the long fibers before mechanical peeling, though some attached fibrils could still be seen on the peeled fiber surfaces.

It should be pointed out that the isolation method employed in this study uses much less water than the Bauer McNett fractionation procedure, and thus the fractions isolated should have undergone less washing.

Table 1. Contents of saccharides, lignin and extractives (mg/100 mg) in the unfractionated TMP and in the isolated TMP fractions. Glucose was determined by acid hydrolysis and the other saccharides by methanolysis. Ara=arabinose, Xyl=xylose, Gal=galactose, Man=mannose, Glc=glucose, Rha=rhamnose, MeGlcA=methylglucuronic acid, GlcA=glucuronic acid, GalA=galacturonic acid.

	TMP	Fines	Fiber surface layers	Bulk fibers
Ara	1.5	2.7	2.8	1.2
Xyl	7.4	7.1	6.7	6.5
Gal	3.2	5.6	5.5	3.1
Man	11.8	7.1	7.9	11.5
Glc	44.3	27.7	30.8	44.7
Rha	+	0.1	0.1	+
4-O-MeGlcA	1.4	1.4	1.1	1.5
GlcA	0.1	0.2	0.2	0.1
GalA	2.1	6.7	6.2	2.1
Lignin	26.4	38.5	39.8	24.7
Extractives	1.5	4.8	5.0	0.8

Gross chemical composition of fines, fiber surface layers and bulk fibers

Table 2. Percentages of polysaccharides in the unfractionated TMP and in the isolated TMP fractions. Corresponding data for spruce wood are also given (Sjöström 1981b). The contents of polysaccharides (mg/100 mg sample) are given in brackets.

	TMP	Fines	Fiber surface layers	Bulk fibers	Spruce wood
Cellulose	57.2 (37.2)	44.1 (23.3)	46.6 (25.9)	58.9 (37.6)	59.6
Arabinoglucuronoxylan	13.3 (8.7)	15.4 (8.1)	14.1 (7.8)	11.9 (7.6)	12.3
Glucomannan	23.2 (15.1)	17.2 (9.1)	18.2 (10.1)	23.1 (14.7)	23.3
Arabinogalactan	3.3 (2.1)	11.0 (5.8)	10.0 (5.6)	3.2 (2.1)	4.8*
Arabinan	0.1 (0.1)	0.8 (0.4)	1.1 (0.6)	0 (0)	
Galacturonan	2.9 (1.9)	11.5 (6.1)	10.1 (5.6)	3.0 (1.9)	

* other polysaccharides than cellulose, xylan and mannan

The contents of saccharides, lignin and extractives in the studied fractions are shown in Table 1. Based on the content of saccharides, the contents of polysaccharides, i.e. cellulose, hemicelluloses and pectins, were calculated (Table 2). Table 2 shows that the present TMP results are in good agreement with those reported for spruce wood (Sjöström 1981b). The compositions of TMP, fines, fiber

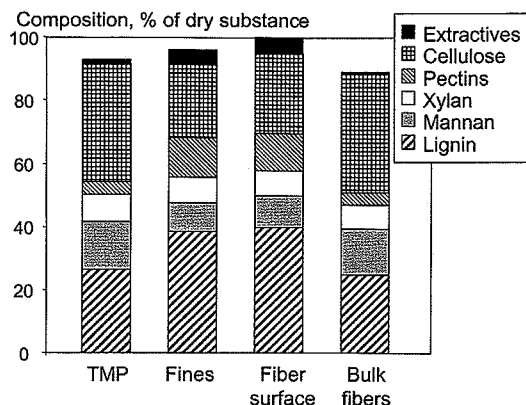


Fig. 2. Composition of cellulose, layers, hemicelluloses, lignin and extractives in unfractionated TMP and the isolated TMP fractions. Glucose in hemicelluloses was excluded from calculation of cellulose. Pectins represent galacturonans, arabinogalactans and arabinans.

surface layers and bulk fibers are given in Fig. 2. Table 2 and Fig. 2 show that the composition of both fines and fiber surface layer material differed significantly from that of the bulk fibers. Both the fines and the fiber surface layers contained about 6 times more extractives than the bulk fibers. The bulk fibers had higher contents of cellulose and mannan (38 and 15%) and lower contents of lignin (25%) and pectin (4%) than the fines and fiber surface layers. The results thus showed that the bulk fiber fraction mainly consisted of secondary cell wall (S₂) layers.

The fiber surface layers contained less cellulose (26%) and mannan (10%) than the bulk fibers, but were rich in pectins (i.e. galacturonans, arabinans and arabinogalactans, totally 12%). Since only small amounts of pectin are found in S₂ layers (Hafren 1999; Alen 2000), our results suggest that the fibrils in the fiber surface layer material do not originate from S₂ layers, but from the primary wall (P) or the outer secondary wall (S₁) layers. In addition, it has been shown that the S₁ layer in spruce wood is very poor in arabinan and galactan, but rich in cellulose and mannan, while the opposite is true for the middle lamella (ML) and P layer (Meier 1964). This suggests that the fiber surface layer fibrils originate from the primary cell wall layer. It was further found that the primary wall fibrils were rich in lignin, as they contained 40% lignin, which is 60% more than in the bulk fibers.

The fines contained the least cellulose (23%) and mannan (9%), but were rich in galactan (6%), arabinan (0.4%), galacturonan (6%) and lignin (39%). The fines also had a higher content of xylan than the other fractions. Large amounts of galactan and arabinan and less cellulose and mannan have been found in the ML and P layer (Meier 1964; Westermark et al. 1986; Sorvari et al. 1986). The lignin content of ML fractions has been reported to be high (Sorvari et al. 1986). High pectin contents in the ML and P was reported by Meier (1964) and in the ML, ray cell walls and pit membranes by Hafren and Westermark (2001). High contents of xylan (Meier 1964) and lignin (Westermark, Capretti 1988) have been reported for ray cells. Thus, the gross chemical results obtained for the fines fraction support the results of microscopy, showing that the TMP fines fraction con-

sisted of ray cells, pieces of ML, ring pores and outer fiber wall fibrils.

According to the results in *Table 1*, the molar ratios of 4-O-methylglucuronic acid groups/10 xylose units were 1.4, 1.2 and 1.7 for fines, fiber surface layer fibrils and bulk fibers, respectively. This suggests that 4-O-MeGcIA groups appear less frequent in the primary wall fibril xylan than in the bulk fiber xylan, though the content of xylan is similar in these fractions. The numbers thus would indicate that there are about 30% less uronic acid groups in the primary wall xylan than in the bulk fiber xylan.

Some of the xylose units in the fines or fiber surface layer could be suspected to originate from xyloglucan, known as a component in primary cell walls of e.g. Sycamore cells (*Acer pseudoplatanus*) (Stephen 1983). This would reduce the amount of xylose that could be assigned to xylan and thus change the uronic acid/xylan ratio. However, a study on ray cells (Hoffmann, Timell 1972) reported that only 1% of the content of ray cells of red pine (*Pinus resinosa*) were other polysaccharides than cellulose, pure 1,3-linked β -glucan, galactoglucomannan, arabino-4-O-methylglucuronoxylan or pectin. In addition, the xylose extracted using aqueous barium hydroxide was shown to be arabinoxylan. Generally, xyloglucan is reported as a minor component in softwoods (Sjöström, Westermark 1998). Based on the referred literature, the presence of significant amounts of xyloglucan was excluded.

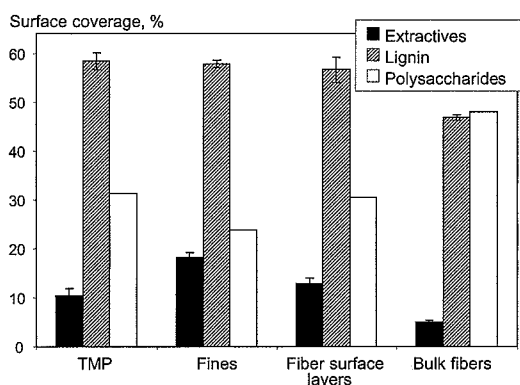


Fig. 3. Surface coverage by extractives, lignin and polysaccharides on unfractionated TMP, TMP fines, fiber surface layers and bulk (peeled) fibers as determined by ESCA.

Since practically no xylan dissolves during the TMP process (Kleen, Lindström 1994), it is suggested that the xylan in the primary wall layer in spruce wood fiber cell wall also has about 30% less uronic acid groups than the bulk fiber xylan.

Characterization of surface chemistry by ESCA

Fig. 3 shows the surface coverage by extractives, lignin and polysaccharides on the unfractionated TMP, TMP fines, fiber surface layers and bulk (peeled) fibers. The surface coverage by polysaccharides was calculated as the difference between the total surface area and the area covered by extractives and lignin. The surface coverage by extractives on the unfractionated TMP was found to be

within the range reported in the literature for mechanical pulps (8-30%), while the surface coverage by lignin was slightly higher than the figures reported (33 to 54%) (Koljonen et al. 1997; Mustranta et al. 1998; Luukko et al. 1999; Koljonen et al. 2001). The high surface lignin concentration in the pulp studied here is thought to be due to the actual pulp properties rather than to the analytical conditions. In any case, the sample fractions are readily comparable with each other.

Both the fines and the fibrils isolated from the fiber surface layers (i.e. the primary wall layer) had a greater coverage by extractives and lignin than the bulk fiber surfaces. The difference in coverage was greater for extractives than for lignin. The fines and the primary wall fibrils had 3.7 and 2.5 times more extractives, respectively, covering their surfaces and over 20% more lignin than the bulk fiber surface. The higher surface coverage by extractives on the TMP fines compared to that on the primary wall fibrils suggests that more extractives are originally bound to or sorbed on the flake-like fines (i.e. ray cells and ML pieces) than on the fibrillar fines. Only 5% of the bulk fiber surface was covered by extractives and 47% by lignin, thus exposing polysaccharides on about half of the surface. The high surface coverage by extractives and the hydrophobic nature of these compounds suggests that the surfaces of TMP fines and also primary wall fibrils are more hydrophobic than those of the bulk fibers.

It was also noted that the ratio between the concentration of surface and total extractives was lowest for fiber surface layer fibrils (about 3) and highest for bulk fibers (about 7). This indicates that the extractives in the bulk fibers are more enriched on the surface than those in the isolated fibrils. This is probably due to a lower sorption capacity of the fibers compared to the fibrils.

Using ESCA, it was further found that the fines and fiber surface layers contained 3 times more nitrogen-containing compounds on their surface (both 0.3%) than the bulk fiber surfaces (0.1%). The nitrogen peaks probably originate from the proteins, since it has been reported that proteins are highly enriched in the P wall fibrils and somewhat concentrated also in the ML fraction in spruce wood (Westermark et al. 1986). After removal of extractives from the surface, the difference became even more pronounced. The fines and fiber surface layer fibrils had 4 and 5 times more nitrogen compounds, respectively, than the bulk fiber surfaces. These results further confirm the earlier conclusion that the fiber surface layer fibrils originate from the P wall.

The total number of free and esterified carboxylic groups (O-C=O) on the surface of the sample fractions was measured by ESCA and is expressed as percentage of total carbon (i.e. % of the C 1s peak) before (total COO) and after (COO in uronic acids) extraction (Fig. 4). It was found that fines and fiber surface layer fibrils were richer in carboxylic groups than the bulk fibers. The main source of carboxylic groups obviously is uronic acid groups, i.e. mainly galacturonic acid groups in pectins and, to some extent, methylglucuronic acid groups in xylan. Although the contents of carboxylic groups on the

surface of TMP fines and primary wall fibrils are similar, there are more uronic acids on the surface of TMP fines. This indicates that there are more uronic acids on the ray cell and ML surfaces compared to the fibril surfaces. This is in good agreement with the result found in gross chemical analysis, which shows that the content of galacturonan and methylglucuronic acid in TMP fines is higher than in the fiber surface layer fibrils. The largest amount of extractable carboxylic groups (i.e. free or esterified fatty acids and resin acids) was found on the surfa-

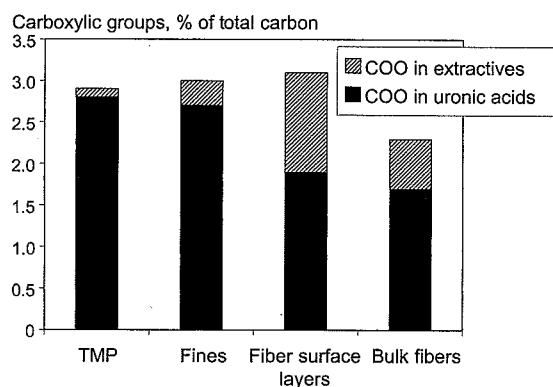


Fig. 4. Content of carboxylic groups (calculated as a percentage of total carbon, i.e. C 1s in ESCA) and their probable origin measured on the surface of unfractionated TMP, TMP fines, fiber surface layers and bulk (peeled) fibers.

ce of primary wall fibrils, while only a very small amount was found on the surface of the other types of fines particles or the bulk fibers.

Since most of the carboxylic groups in an unbleached mechanical pulp consist of methyl-esterified galacturonic acids (Hafren, Westermarck 2001) and esterified fatty acids (Ekman et al. 1990), the number of carboxylic groups on the surface can be used to indicate the number of groups able to contribute to surface charge in a subsequent alkaline treatment, for example in bleaching with hydrogen peroxide. The results in Fig. 4 suggest that such treatment may result in a higher increase in the surface charge of fines particles, i.e. fibrils, ray cells, middle lamella fragments and pores, than in the surface charge of the bulk fibers. The reason for this is apparently the higher content of uronic acids or surface extractives, or possibly the type of surface extractives.

Table 3. Secondary ions in TOF-SIMS spectra used as markers for lignin and polysaccharides.

m/z	Origin	Secondary ion
31	methoxyl groups	$[CH_3O]^+$
77	aromatic units	$[C_6H_5]^+$
127	hexosaccharides ¹⁾	$[C_6H_7O_3]^+$
137	guaiacyl units	$[C_8H_9O_2]^+$
151	guaiacyl units	$[C_8H_7O_3]^+$

1) mainly from cellulose, but also from mannans and galactans.

Characterization of surface chemistry by TOF-SIMS

TOF-SIMS yields high-resolution mass spectra from

which different organic materials can be characterized simultaneously with the determination of metal ions (Kleen 2000a,b). In the present work, TOF-SIMS was used to reveal information from the chemical nature of the surface lignin and extractives.

Surface lignin on TMP fines, outer fiber layers and bulk fibers

The secondary ion mass spectrum obtained for mechanical pulp contains information on the chemical structure of the surface lignin. Table 3 gives the identified structures, which were chosen to describe the relative amount and some structural features of the surface lignins.

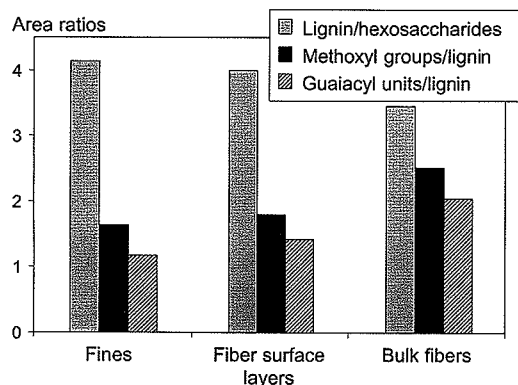


Fig. 5. Relative amount of surface lignin and its structure on the extracted TMP fines, outer fiber layer fibrils and bulk (i.e. peeled) fibers as analyzed by TOF-SIMS.

Fragment ions were chosen based on model lignin analyses by TOF-SIMS (Kleen 2000a, 2000b; Fukushima et al. 2001).

The relative surface content of lignin (Fig. 5) is described by the area ratio of aromatic units and hexosaccharides (77/127) and is calculated as an average of three analyses. Fig. 5 shows that there is more lignin on the outermost surface of fines and fiber surface layer fibrils than on the surface of the bulk fibers. Thus, TOF-SIMS results support those obtained by ESCA (Fig. 3). In addition, TOF-SIMS results indicate that the bulk fiber surface lignin contains about 50% more guaiacyl units (measured as $(137+151)/77$) than the lignin on the surface of fines or primary wall fibrils. This result is also supported by the higher amount of methoxyl groups in the bulk fiber lignin (Fig. 5). These surface analysis results are in good agreement with the gross analysis results reported for S₂ and ML fractions isolated from spruce wood, where it was found that the S₂ fraction lignin contained more methoxyl groups than the ML fraction lignin (Sorvari et al. 1986).

Surface extractives on TMP fines, outer fiber layers and bulk fibers

Using model compounds, we have found that positive ion mass spectra from TOF-SIMS give chemical information on neutral extractives (e.g. sterols, triterpenes and triglycerides) and fatty acid salts. On the other hand, negative ion mass spectra are useful for describing free fatty and resin acids (Kleen, Nilvebrant 2001; Kangas et al. 2002; Kleen et al. 2002b).

Table 4. Normalized intensities (specific ion intensity/total ion intensity, $\times 10^{-6}$) of identified fatty and resin acids (negative ions) and sterols, steryl esters and glycerides (positive ions) in TOF-SIMS spectra.

m/z	Origin	Mw	Secondary ion	TMP	Fines	Fiber surface layers	Bulk fibers
255	palmitic acid	C16:0	256	[M-H] ⁻	4	14	13
269	anteisoheptadecanoic acid	C17:0	270	[M-H] ⁻	4	14	11
277	pinolenic and/or linolenic acid	C18:3	278	[M-H] ⁻	1	1	1
279	linoleic acid	C18:2	280	[M-H] ⁻	1	2	1
281	oleic acid	C18:1	282	[M-H] ⁻	1	15	17
283	stearic acid	C18:0	284	[M-H] ⁻	2	6	5
299	dehydroabietic acid	300	[M-H] ⁻	5	6	5	4
301	abietic acid and isomers	302	[M-H] ⁻	3	3	2	3
383	campesterol	400	[M-OH] ⁺	13	20	19	53
397	sitosterol	414	[M-OH] ⁺				
	and/or steryl esters		[M+H-RCOO] ⁺	55	90	83	32
411	steryl esters		[M+H-RCOO] ⁺	86	153	117	50
429	oxo-sitosterol (tentative)		[M-H+O] ⁺	143	59	44	37
1)	glycerides			42	42	37	51
sum				360	425	357	256

1) glyceridic fragment ions at 335, 337, 339 and 341 m/z probably mainly originate from triglycerides, but di- and monoglycerides can also contribute if present. E.g. the ion at 341 m/z is assigned to [C21H41O3]⁺ and is formed from tristearin after loss of two stearic acid side chains.

All samples in the present work showed dominant ions at 383, 397, 411 and 429 m/z in their positive ion mass

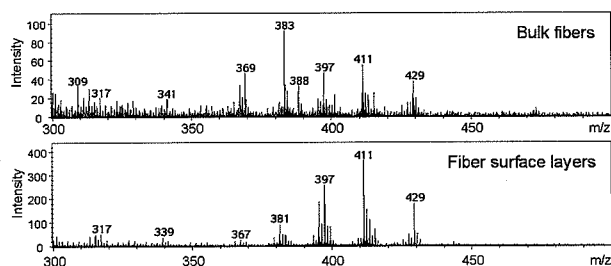


Fig. 6. Part of positive TOF-SIMS spectra recorded on the surface of the bulk fibers (upper) and of the fibrils isolated from the outer surface layers of TMP fibers (lower). Compound identification is given in Table 4.

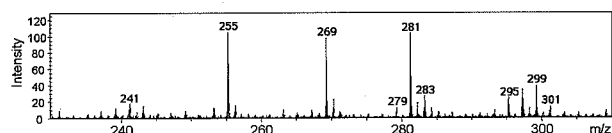


Fig. 7. Part of negative TOF-SIMS spectrum recorded on fibrils isolated from the outer surface layers of TMP fibers. Compound identification is given in Table 4.

spectra. These ions originate from sterols and steryl esters (Table 4). However, the intensities of these ions varied for different samples. Fig. 6 shows the result obtained

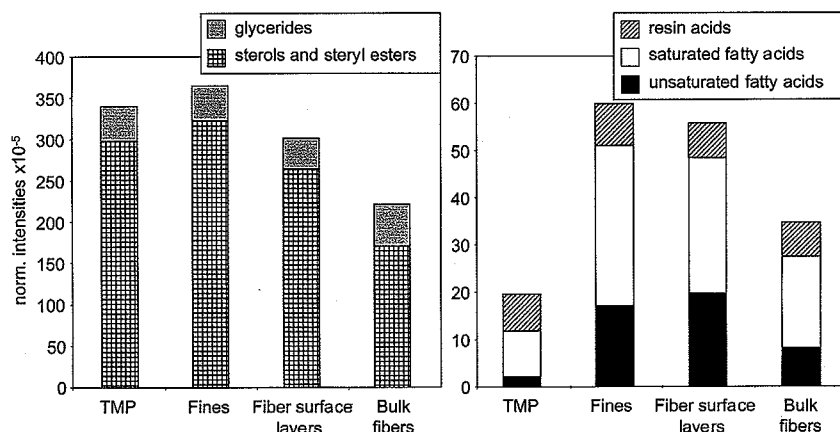


Fig. 8. Relative composition of extractives groups on the surfaces of samples as analyzed by TOF-SIMS. Calculations are based on values in Table 4.

ned for the bulk fibers and the fibrils isolated from the fiber surface layers. The fatty and resin acids present on the all sample surfaces are shown in Fig. 7 for the primary wall fibrils. Secondary ions originating from palmitic, anteisoheptadecanoic, pinolenic, linoleic, oleic and stearic acids are observed together with ions assigned to dehydroabietic acid and abietic acid or its isomers. Abietic acid isomers may include the most abundant levopimaric, palustric, isopimaric, neoabietic, sanderacopimaric and pimaric acids. It was also noted that secondary ions [M-H]⁻ could originate from free as well as from esterified fatty acids.

Most of the wood extractives found on the bulk fiber surface were also found on the surface of the fines and fiber surface layer fibrils, but their composition was different. This indicates that the extractives composition varies between samples. The normalized intensities (specific ion intensity divided by the total intensity of the spectrum) of the ions identified can be used to compare samples, though they cannot be regarded as fully quantitative (Table 4). In Fig. 8, the values from Table 4 are presented as groups of unsaturated and saturated fatty acids, resin acids, sterols or steryl esters and glycerides. The relatively low concentration of resin acids compared to fatty acids on the surfaces of the different fractions is probably due to more extensive washing of resin acids from the sample surfaces during fractionation and/or the fact that a part of secondary ions identified as fatty acids originates from the fatty acid chains in triglycerides.

By comparing the results from TOF-SIMS (Fig. 8) and ESCA (Fig. 3), it was concluded that semiquantitative information on the surface coverage by extractives can be obtained by TOF-SIMS. In addition, the TOF-SIMS results suggest that more both neutral (i.e. sterols, steryl esters and glycerides) and acidic extractives cover the surface of the fines and fibrils than of the bulk fibers. However, the amount of campesterol was highest on the surface of the bulk fibers. The surface of the outer fiber layer fibrils seems to contain the highest relative amount of unsaturated fatty acids.

The most common surface fatty acids seem to be the saturated palmitic and anteisoheptadecanoic acids and the unsaturated oleic acid (Fig. 7 and Table 4). Thus the results show that the main saturated fatty acids on the sample surfaces are the same as have been found in a dichloromethane (DCM) extract from TMP (Ekman et al. 1990). On the other hand, the unsaturated fatty acids show different distribution on the surface and in a DCM-extract. The most common unsaturated surface fatty acid seems to be oleic acid, whereas more linoleic and pinolenic acids than oleic acid have been reported in a DCM-extract (Ekman et al. 1990). This indicates that the more unsaturated

fatty acids are more easily removed from the surfaces, e.g. by washing. In addition, the results suggest enrichment of *anteisoheptadecanoic acid* and *oleic acid* on the surface of primary wall fibrils compared to the surface of the bulk fibers.



Fig. 9. Total ion image (left) and distribution of lignin (middle) and extractives (right) on the surface of TMP bulk fibers. The images were obtained by positive ion TOF-SIMS imaging. Scale: 100 μm .

Lateral distribution of surface lignin and extractives

The lateral distribution of surface compounds was studied using imaging TOF-SIMS. Fig. 9 shows as an example the result on the TMP bulk fibers. In addition to the total ion image, images describing the distribution of lignin and extractives were obtained by mapping corresponding specific secondary ions (Tables 3 and 4). It is evident that lignin and extractives were distributed as small patches all over the surfaces of TMP bulk fibers. The patch-like distribution of wood resin in groundwood (GW) pulp has earlier been suggested by Allen (1975). He found that most of the colloidal pitch particles on the surface of GW pulp were slightly smaller than 1 μm in diameter. In our work, the sizes of the lignin and extractives patches vary, but seem to be mostly about 1-5 μm . Since the lateral resolution of the TOF-SIMS instrument is roughly 1 μm , smaller patches cannot be observed. All the studied sample fractions showed similar patch-like distributions of lignin and extractives over their surfaces.

Recently published AFM (atomic force microscopy) phase contrast images reveal that the surface of TMP is very heterogeneous, i.e. partly covered by granules and partly by cellulose fibrils (Koljonen et al. 2001; Kangas et al. 2002). The granules are interpreted as being lignin. These AFM results and the finding that lignin does not fully cover the fiber surfaces as seen by ESCA (Fig. 3) support the conclusion based on imaging TOF-SIMS that the surface lignin on TMP fibers is distributed as small patches over the surfaces.

Conclusions

TMP *finer*, composed of ray cells, parts of middle lamella, ring pores and fibrils, contain high amounts of lignin and extractives both on their surface and in the bulk. In spite of the high surface coverage by extractives, the surface extractives are low in carboxylic groups (as determined by ESCA), indicating more sterols and/or triterpenes on the fines surface. This was confirmed by TOF-SIMS. Only about 23% of the fines surface is covered by polysaccharides, but these surface polysaccharides are rich in carboxylic groups, mainly due to pectins, but also to the methylglucuronic acid groups in xylan.

The **fiber surface layer** material consisted mainly of fibrils and contained more lignin and pectins and less cellulose and mannan than the bulk fibers. Based on the comparison of our results to literature data, it is concluded that the fiber surface layer fibrils originate from the primary wall layer. These fibrils also have lignin-, extractive- and protein-rich surfaces. The chemical structure of the surface lignin on the primary wall fibrils differs from that on the bulk fibers in that the fibril surface lignin contains less guaiacyl groups.

The results indicated that the frequency of uronic acid groups in the TMP primary wall fibril xylan is about 30% lower than that in the bulk fiber xylan. Since practically no xylan dissolves during the TMP process, it is suggested that this difference can also be found in the spruce wood fiber cell wall.

The **bulk fibers** (i.e. the inner layers of the fibers, sometimes also called peeled fibers) contain most cellulose and mannan. The bulk fiber xylan seems to be richer in uronic acids than the primary wall fibril xylan. The bulk fibers have lower extractives content and less extractives covering the surface than the fines and fibrils. Carboxylic groups on the surface of the bulk fibers originate mainly from methylglucuronic acid groups in xylan.

In general, the results confirm known differences in the distribution and structure or composition of protein, lignin and polysaccharides across the spruce wood fiber wall. In addition, the results suggest that the bulk fibers differ from the fines and primary wall fibrils not only in the amount of surface extractives and lignin, but also in the composition of surface extractives and in the structure of surface lignin and xylan. The results suggest that bulk fiber surfaces and fines surfaces in mechanical pulp have different affinities for wood extractives. Due to the high surface coverage by extractives and the hydrophobic nature of these compounds, it is suggested that the ray cells, parts of the middle lamella and also the primary wall fibrils have a hydrophobic surface. Further, the extractives and lignin are found as small patches all over the surfaces of TMP fibers and fines.

As TOF-SIMS gives structural information about surface lignin and extractives, it is a good complement to the frequently used ESCA technique, which quantifies surface coverage by lignin and extractives, but gives much less structural information.

Acknowledgements

The authors wish to thank Dr. Leena-Sisko Johansson at Helsinki University of Technology, Center for Chemical Analysis, for running the ESCA experiments.

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*Manuscript received January 22, 2003
Accepted September 2003*