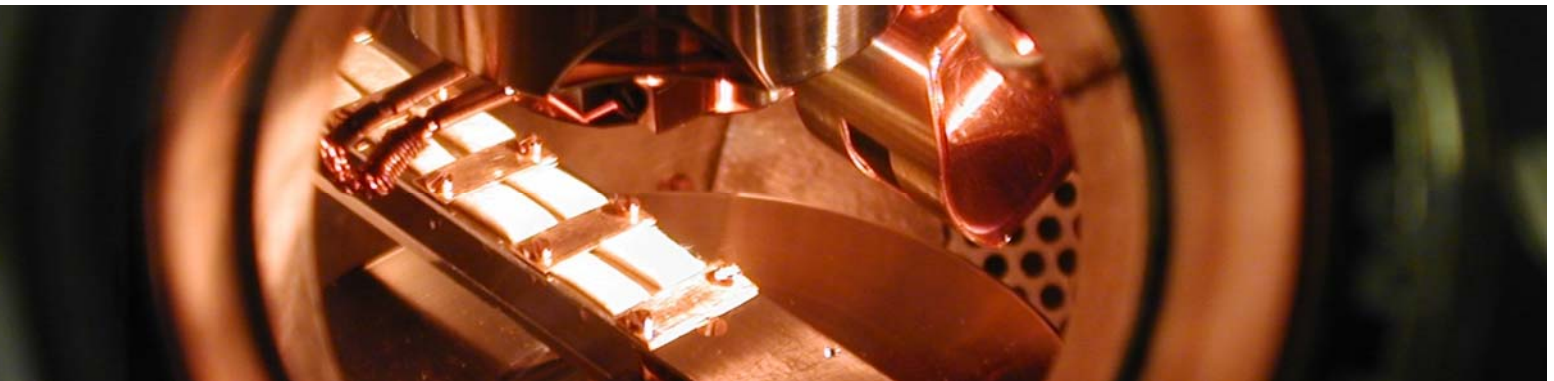


EFFECT OF SURFACE PROPERTIES OF FIBRES ON SOME PAPER PROPERTIES OF MECHANICAL AND CHEMICAL PULP

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Krista Koljonen

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To Timo

PREFACE

The work for this thesis was carried out at the Laboratory of Forest Products Chemistry, Helsinki University of Technology, during the years 1997-2003. The work was accomplished during several technology programs:

- (1) “The effect of surface chemistry on paper properties made of mechanical pulps (MEKKA)” by TEKES (1996-1999),
- (2) “Fibre engineering: The surface properties of wood and cellulose fibres and their adsorption properties (FINE), Forest Cluster Research Programme WOOD WISDOM” by TEKES (1998-2001),
- (3) “Characterisation of fibre surfaces from TCF bleached softwood and hardwood kraft pulps: Keys to closing the bleaching loops (NI)” by Nordic Industrial Fund (1998-2000) and
- (4) “Utilisation of the unique properties of wood and fibres from Finnish forests (UniFiber), Forest Cluster Research Programme WOOD WISDOM” by Academy of Finland (1998-2001).

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Espoo, 29.4.2004



Krista Koljonen

LIST OF PUBLICATIONS

The thesis consists of this summary and the following publications, referred to herein by their Roman numbers. Additional data are also presented.

- I Koljonen, K. and Stenius, P. (2004). Surface characterisation of single mechanical fibres by contact angle measurement. Submitted to *Nordic Pulp and Paper Research Journal*, published in 2005.
- II Koljonen, K., Mustranta, A. and Stenius, P. (2004). Surface characterisation of mechanical pulps by polyelectrolyte adsorption. *Nordic Pulp and Paper Research Journal* **19**(4).
- III Koljonen, K., Österberg, M., Kleen, M., Fuhrmann, A. and Stenius, P. (2004). Precipitation of lignin and extractives on pulp fibres: Effect on surface chemistry, surface morphology and paper strength. *Cellulose* **11**(2), pp. 209-224.
- IV Koljonen, K., Österberg, M., Johansson, L.-S. and Stenius, P. (2003). Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **228**(1-3), pp.143-158.
- V Maximova, N., Österberg, M., Koljonen, K. and Stenius, P. (2001). Lignin adsorption on cellulose fibre surfaces: effect on surface chemistry, surface morphology and paper strength. *Cellulose* **8**(2), pp. 113-125.
- VI Johansson, L.-S., Campbell, J.M., Koljonen, K. and Stenius, P (1999). Evaluation of surface lignin on cellulose fibers with XPS. *Applied Surface Science* **144-145**, pp. 92-95.

AUTHOR'S CONTRIBUTION

- I all experiments, analysis, first version of the manuscript
- II all experiments, analysis, first version of the manuscript
- III experiments in part, analysis, first version of the manuscript
- IV experiments in part, analysis, first version of the manuscript
- V experiments in part, analysis, manuscript in part
- VI experiments in part, analysis, manuscript in part

OTHER RELATED PUBLICATIONS

Koljonen, K., Stenius, P. and Buchert, J. (1997). The surface chemistry of PGW fibre fractions. 1997 International Mechanical Pulping Conference: Tomorrow's challenges for mechanical pulps, 9-13 June 1997, Stockholm, Sweden, pp. 407-411.

Koljonen, K., Österberg, M. and Stenius, P. (2000). The effect of closure of bleaching loops on the surface properties of kraft pulp fibres. Sixth European Workshop on Lignocellulosics and pulp (EWLP 2000): Advances in lignocellulosics chemistry towards high quality processes and products, 3-6 September 2000, Bordeaux, France, pp. 399-403.

Koljonen, K., Österberg, M. and Stenius, P. (2001). Surface chemistry and morphology of mechanical pulp fibres. 2001 International Mechanical Pulping Conference: Mechanical pulps- added value for paper and board, 4-8 June 2001, Helsinki, Finland, pp. 305-314.

Koljonen, K., Österberg, M., Kleen, M., Fuhrmann, A. and Stenius, P. (2001). Precipitation of lignin and extractives on pulp fibres: effect on surface chemistry and surface morphology. The 3rd Biennial Johan Gullichsen Colloquium: Fiber raw materials, their characterization and relationship with product quality, 13-14 September 2001, Espoo, Finland, pp. 21-30.

Yu, Y., Koljonen, K. and Paulapuro, H. (2002). Surface chemical composition of some nonwood pulps. *Industrial Crops and Products* **15**(2), pp. 123-130.

Kleen, M., Sjöberg, J., Dahlman, O., Johansson, L.-S., Koljonen, K. and Stenius, P. (2002). The effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces. *Nordic Pulp and Paper Research Journal* **17**(3), pp. 357-363.

Johansson, L.-S., Campbell, J., Koljonen, K., Kleen, M. and Buchert, J. (2004). On surface distribution in natural cellulosic fibres. *Surface and Interface Analysis* **36**(8), pp. 706-710.

LIST OF SYMBOLS AND ABBREVIATIONS

$\gamma_L, \gamma^{LW}, \gamma^+, \gamma^-$	surface tension of liquid, Lifshitz- van der Waals, acid parameter, base parameter, respectively
$\gamma_S, \gamma_S^{LW}, \gamma_S^+, \gamma_S^-$	surface tension of solid, Lifshitz- van der Waals, acid parameter, base parameter, respectively
ρ_l, ρ_v	liquid and vapour densities, respectively
σ	amount of elementary charge ($\mu\text{mol/g}$ or mmol/kg) in pulp
$\theta, \theta_A, \theta_R$	contact angle between fibre and wetting liquid, advancing, receding, respectively
c_{eq}	equilibrium concentration of cationic polyelectrolyte in filtrate
C1, C2, C3, C4	relative amount of C-C, C-O, O-C-O, O-C=O component in deconvoluted high-resolution C1s spectrum, respectively
C1s	carbon spectrum from wide-spectrum
d.w.	dry weight
E	alkaline treated mechanical pulp
F, F _A , F _R	force acting on fibre, average advancing, average receding, respectively
m	mass of single fibre
m _{poly} , m _{pulp}	dry weights of polyelectrolyte and pulp sample, respectively
O1s	oxygen spectrum from wide-spectrum
O/C	oxygen-to-carbon ratio (O1s/C1s)
O.D.	oven-dried pulp
p	wetted perimeter of single fibre
P	peroxide bleached mechanical pulp
r _{sp}	set-point ratio in AFM
uw	unwashed pulp
V	submerged volume
V _{bt} , V _{tit}	PES-Na consumption at point of equivalence of blank test and sample, respectively
V _{tot}	total volume of filtrate
w	water washed mechanical pulp
W _a , W _a ^{LW} , W _a ^{AB}	work of adhesion, contribution of Lifshitz- van der Waals and Lewis acid-base, respectively
Y	dithionite bleached mechanical pulp
Z	ozone treated mechanical pulp
AFM	atomic force microscope
CD _{poly}	charge density of polyelectrolyte
CSF	Canadian standard freeness
CTMP	chemithermomechanical pulp
cmc	critical micelle concentration
DCM	dichloromethane
DCS	dissolved and colloidal substances
ECF	elemental chlorine free
ESCA	electron spectroscopy for chemical analysis
FTIR-PAS	fourier transform infrared spectrometer equipped with a photoacoustic (PA) detector
FWHM	full width at half maximum

GalA	D-galacturonic acids in pectin
GC	gas chromatography
GlcA	D-glucuronic acids in arabinogalactan
HexA	hexenuronic acids in xylan
HPLC	high-performance liquid chromatography
ISO-%	diffuse blue reflectance factor (ISO brightness) of pulp
M _w	molecular weight
MeGluA	4- <i>O</i> -methyl-D-glucuronic acids in xylan
ML	middle lamella in fibre wall
ML+P	compound middle lamella includes middle lamella and primary wall
NaAb	sodium abietate, a model substance of resin acids
NaOl	sodium oleate, a model substance of fatty acids
PCD	particle charge detector
PDADMAC	poly-(dimethyldiallylammonium)chloride
PES-Na	sodium polyethensulphonate
PGW	pressure groundwood
Polybrene	poly(1.5-dimethyl-1.5-diazaundecamethylene)bromide
RBA	relative bonded area
SBS	specific bond strength
SPM	scanning probe microscope
TMP	thermomechanical pulp
ToF-SIMS	time-of-flight secondary ion mass spectroscopy
XPS	x-ray photoelectron spectroscopy

CONTENTS

Page

PREFACE	
LIST OF PUBLICATIONS AND AUTHOR'S CONTRIBUTION	
OTHER RELATED PUBLICATIONS	
LIST OF SYMBOLS AND ABBREVIATIONS	
1 INTRODUCTION.....	1
2 OBJECTIVES AND OUTLINE OF THIS STUDY.....	3
3 BACKGROUND.....	7
3.1 Wood fibre structure.....	7
3.2 Mechanical pulp surface and its characterisation.....	9
3.3 Kraft pulp surface and its characterisation.....	12
3.4 Effect of wood components on strength properties of paper.....	12
4 EXPERIMENTAL.....	15
4.1 Mechanical pulps.....	15
4.2 Chemical pulps.....	17
4.3 Adsorption experiments with chemical pulps.....	18
4.4 Methods to investigate surface properties.....	19
4.4.1 ESCA/XPS.....	19
4.4.2 Wilhelmy balance.....	22
4.4.3 Polyelectrolyte titration.....	23
4.4.4 ToF-SIMS.....	25
4.4.5 AFM/SPM.....	26
4.5 Other analyses and accuracy of measurements.....	27
4.5.1 Paper properties.....	27
4.5.2 Other analysis (HPLC, HexA, FTIR-PAS, etc.).....	27
4.5.3 Accuracy of measurements.....	29
5 RESULTS.....	30
5.1 Surface lignin.....	30
5.1.1 Mechanical pulps.....	30
5.1.2 Adsorbed kraft lignin on chemical pulps.....	33
5.2 Surface extractives.....	35
5.2.1 Mechanical pulps.....	35
5.2.2 Adsorbed components on chemical pulps.....	37
5.3 Pulp charge.....	40
5.4 Surface energy of single fibres.....	44
5.5 Effect of surface properties of fibres on strength properties of paper.....	46
5.5.1 Mechanical pulps.....	46
5.5.2 Adsorbed material on chemical pulps.....	50
6 DISCUSSION.....	53
7 CONCLUSIONS.....	63
RECOMMENDATIONS FOR FUTURE WORK.....	66
REFERENCES.....	67
APPENDICES	

1 INTRODUCTION

Wood fibres are made suitable for papermaking with desired paper properties by liberating them from the wood (Sundholm 1999). Mechanical pulps have a broader distribution of fibre length, higher yield and higher opacity but lower strength and brightness properties than kraft pulps. Depending on the paper grade, the strength of paper made from mechanical pulp is usually improved by adding reinforcement (kraft) pulp to the fibre furnish. Improved surface smoothness, opacity, bonding and strength properties of mechanical pulps reduce the need for chemical pulp.

In mechanical pulping, the middle lamella and primary wall in the outermost part of the cell wall are softened using heat and moisture, allowing fibres to be separated more or less intact (Salmén et al. 1999). Ideally, the lignin should be so soft but still so tough that the separation occurs partly in the fibre wall where hemicellulose and cellulose surfaces increase the bonding ability between fibres. In chemical pulping, goal is to remove lignin by bleaching chemicals without any extensive loss of hemicelluloses (Roberts 1996). However, a greater degree of closing of process water loops may cause more material to be adsorbed on the fibre surface. The adsorbed material may interfere with the fibre-to-fibre, fibre-to-fines and additives-to- fibre/fines interactions.

Correlations between strength properties and surface properties of fibres have been comprehensively studied with kraft pulps but less with mechanical pulps. The number of charged groups is known to improve the strength properties of paper indirectly (Laine 1996). The more charged groups that are attached to the fibres, the more they swell, thus increasing the flexibility and conformability of the fibres. An increased amount of xylan on the surface strengthens the paper (Molin 2002), whereas kraft lignin (Lindström et al. 1977) and lipophilic extractives (Zhang et al. 1999, Sundberg et al. 2000) are known to impair the strength properties of paper.

Anionic wood components may also interact with the compounds found in process waters. For example, anionic compounds can form complexes with cationic compounds (Ström et al. 1985), and dissolved neutral components can sterically stabilise colloidal anionic material (Sundberg 1995). The complexity of nature-designed fibres and the numerous wood-based

components and additives circulating in the liquors during pulping and bleaching make this subject even more intricate.

The general objective of this study was to gain knowledge of different pulps and their surface properties, and a better understanding of the behaviour of adsorbed material on the fibre surface. Moreover, an attempt was made to find relevant surface properties of pulps which contribute to their strength properties. Particular attention was paid to *mechanical pulps*. Adsorption experiments were made with *kraft pulps* using various model substances of extractives, pitch and kraft lignin. Adsorption of these substances may occur especially during cooking/refining, pulp washing and recirculation of mill filtrates. Keeping these aspects in mind, the surface properties of kraft pulps from highly closed mills were compared to pulps treated and washed in the laboratory. The objectives of this study are discussed in more detail in Chapter 2.

2 OBJECTIVES AND OUTLINE OF THIS STUDY

In this work, special emphasis was given to the naturally complex-structured mechanical pulp surfaces and the effect of different treatments on these (Papers I, II, IV). The effects of water washing, alkaline treatment, peroxide bleaching, dithionite bleaching and ozone treatment on the surface chemical composition and topography of mechanical pulp fibres were studied in particular. Mixtures of mechanical and chemical pulps were not examined.

To gain a deeper understanding of the behaviour of material adsorbed on the fibre surface, experiments were also performed with kraft pulps. Model extractives (fatty and resin acids) (additional results, p. 18, 27, 37 and 38), pitch (additional results, p. 18, 38 and 39) and kraft lignin (Paper V) were used in the experiments. It is known that these substances are adsorbed mainly during kraft pulping and pulp washing. Extractives may also cause problems in mechanical pulping. The idea of these experiments was to determine the effects of these single wood components on the strength properties of paper. These experiments were also found to be important for mill closure experiments.

The effects of mill closure and lowering the pH were clarified. First, numerous samples were collected from different bleaching stages in highly closed softwood and hardwood kraft pulp mills and compared with laboratory-washed samples (Fuhrmann et al. 2000, Koljonen et al. 2000). Second, dissolved material was adsorbed on the pulp by lowering the pH of the slurry containing fibres and process water taken after the oxygen delignification stage (Paper III, Fuhrmann et al. 2002). The slurry was acidified with sulphuric acid alone or with both Z filtrate and sulphuric acid.

One general goal of the thesis work was to acquire a better understanding of the nature of precipitates that are formed on pulp surfaces under different process conditions and of their effect on sheet properties. The effects of the precipitates on strength properties are discussed. ESCA was used extensively for analysing fibre surface compositions, and the work therefore also includes an assessment of the usability of the ESCA spectrometer for pulp samples (Paper VI).

Chapter 3 describes today's knowledge of mechanical and kraft pulp surfaces, and examines the effect of wood components on the strength properties of paper as a part of the background for this work. In the past decade, techniques for analysing the surfaces of fibres and paper have improved greatly, providing new valuable information on the chemistry and morphology of fibre surfaces.

The experimental methods used in the study are described in Chapter 4. Sample material, chemicals, surface analysis methods used and the reliability of the measurements are described. Further details are found in Papers I-VI. The approximate analysis depths of the methods used are discussed in section 4.4. The difference between acetone and dichloromethane as an extraction solvent is discussed in Chapter 4.4.1. In addition, the difference between the dye indicator and particle charge detector used in polyelectrolyte titration is briefly described in Chapter 4.4.3.

The results of the work are presented in Chapter 5. First, in Chapters 5.1 and 5.2, the effect of treatments on the surface lignin and extractives of mechanical and chemical pulps are evaluated. The charge of the pulps and surface energy of single fibres are estimated in separate chapters (Chapter 5.3 and 5.4). Finally, the surface properties of pulps and paper properties are combined in Chapter 5.5.

In Chapter 6, the results of the work are discussed. Also, further aspects related to this area are considered.

The objectives and results of each publication in the Appendices are summarised as follows:

- I “Surface characterisation of single mechanical fibres by contact angle measurement”
The effect of different treatments on the surface energy and acid/base properties of mechanical fibres is studied. The thesis includes an attempt to correlate these results and strength properties of paper.

- II “Surface characterisation of mechanical pulps by polyelectrolyte adsorption”
The charge properties of mechanical pulps are studied. A test method to characterise the charge of the pulp to indicate the titration end point by the Müték instrument is developed. The results are correlated to results obtained with an indicator dye. The

origin of the charge (xylan, pectin, lignin, extractives) is clarified. The relevance of this paper to the thesis is in finding out whether charge properties have an effect on the strength properties of mechanical pulps.

III “Precipitation of lignin and extractives on pulp fibres: Effect on surface chemistry, surface morphology and paper strength”

Lignin, extractives and metals on kraft pulp surfaces are examined by three surface sensitive techniques, ESCA, ToF-SIMS and AFM. The pH of the slurry is lowered to form precipitates (lignin, extractives and metals). The objective is to locate the adsorbed material on the surface and determine its chemical composition and morphology. The effect of precipitates on strength and bonding properties of the pulp sheets is examined.

IV “Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM”

The surface chemistry and topography of spruce mechanical pulps is investigated by ESCA and AFM. The surfaces are quite different from the bulk properties of the pulps. In most samples, the chemical composition of the pulps analysed by ESCA can be explained by morphology changes observed by AFM. These two sophisticated surface methods seem to describe different surface layers of pulps.

V “Lignin adsorption on cellulose fibre surfaces: effect on surface chemistry, surface morphology and paper strength”

The adsorption of kraft lignin on kraft pulp at neutral pH and the effects of calcium ions and cationic polyelectrolyte (PDADMAC) on the adsorption are studied by ESCA and AFM. Preadsorbed PDADMAC in the pulp does not enhance the adsorption of lignin, but without addition of polyelectrolyte the lignin is very weakly attached to the fibre surface. Addition of calcium ions results in higher coverage by lignin compared to sodium ions. The objective of this paper is to locate the adsorbed kraft lignin on the surface and determine its chemical composition and morphology. The effect of adsorbed kraft lignin on strength and bonding properties of the pulp sheets is also examined. Neither PDADMAC nor lignin alone increases the strength properties of pulp sheets significantly. However, together they clearly increase the bonding between fibres.

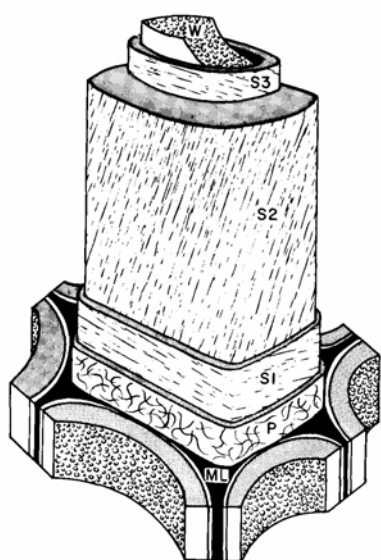
VI “Evaluation of surface lignin on cellulose fibres with XPS”

Throughout the thesis, the XPS/ESCA has been combined with solvent extraction in order to evaluate the surface lignin and extractives contents on the pulp surface. This article ascertains the usability of the ESCA spectrometer used for pulp samples, and describes two methods of analysis to monitor the pulp surfaces. The two methods are oxygen-to-carbon ratio (O/C) measured from the wide spectrum and aliphatic carbon (C1, C-C) measured from high resolution spectra. The reliability and reproducibility of the methods are studied. Both methods of analysis turned out to be consistent indicators of surface lignin content for a variety of extracted pulps.

3 BACKGROUND

3.1 Wood fibre structure

In the wood fibre, the microfibrils and matrix polymers are organised into laminae which are structured into cell-wall layers (Fig. 1) (Salmén 1985, Sjöström 1993). These layers differ from one another with respect to their structure as well as their chemical composition. The microfibrils wind around the cell axis in different directions either to the right (Z helix) or to the left (S helix) (Sjöström 1993).



Layer	Thickness	Angle
S3	~1 μm	50°-90°
S2	1-5 μm	0°-30°
S1	0.2-0.3 μm	50°-70°
P	0.1-0.2 μm	irregular
ML	0.2-1.0 μm	

Fig.1. Simplified structure of woody cell and the average layer thickness and microfibril angle, showing the middle lamella (ML), the primary wall (P), the outer (S1), middle (S2), and inner (S3) layers of the secondary wall, and the warty layer (W) (Sjöström 1993, original from Côté 1967).

The middle lamella (ML) is not an integral part of the cell wall but a lignin-rich bonding medium which interconnects the cells and also gives structural support to and imposes swelling restrictions on the fibre (Salmén 1985). The middle lamella, together with the primary walls on both sides, is often referred to as the compound middle lamella (ML+P) (Sjöström 1993). The lignin content is higher in the ML+P and in some cases in the S1 and S3 layers than in the other cell-wall layers. Lignin is more condensed or cross-linked in ML+P and probably has a higher molecular weight than the lignin in other fibre walls (Salmén and Ljunggren 1996). About 50% of the ML+P layer consist of pectic material (pectic acid,

galactan and arabinan), whereas the cellulose content is low, as shown for young tracheids from spruce wood (*Picea abies*) (Meier 1985). Recent studies with transmission electron microscopy have revealed that the middle lamella has a fine irregular network (Hafrén et al. 2000). After delignification, the structure of the middle lamella appeared to be compact and partly covered by a globular structure.

The primary wall (P) consists of an unoriented cellulose microfibril network (Salmén 1985). It has a high content (up to 15%) of protein and contains pectic substances (Salmén and Ljunggren 1996). The protein is indicated to be highly associated with the lignin in the primary wall, to such an extent that these polymers form a mechanically homogeneous mixture.

The much thicker secondary wall is nearly always made up of three distinct layers, such as S1, S2 and S3 (Fig. 1). The S2 is the thickest, being dependent on the location of the tracheid within the growth ring (Salmén 1985). The fibrils in each layer are built up of cellulose microfibrils in which the cellulose chain axis is arranged in parallel to the axis of the microfibril, thus giving a high reinforcing effect in its length direction (Salmén 1985). The outer S1 layer contains 3-4 lamellae where microfibrils form either a Z helix or S helix and the microfibril angle of the crossed fibrillar network varies between 50 and 70° (Sjöström 1993). In the middle S2 layer, the angle of fibrils is usually between 0 and 30° to the fibre axis. In the inner S3 layer, the fibrils are arranged at a larger angle to the fibre axis in both S helices and Z helices (50-90°) (Sjöström 1993).

Hemicelluloses act as a coupling agent between lignin and the microfibrils in the native fibre cell wall. Some of the hemicelluloses are located on the fibril surfaces in the interfibrillar spaces, and about one-third of hemicelluloses present in the secondary cell wall of black spruce is directly associated with the cellulose. No difference has been found between the cell-wall layers with regard to the hemicellulose-cellulose ratio (Salmén 1985). In softwoods, glucomannan is preferentially more associated with the cellulose and xylan is more associated with the lignin (Salmén 1985, Hardell and Westermarck 1981).

The warty layer (W) is a thin amorphous membrane located in the inner surface of the cell wall in all conifers and in some hardwoods, containing warty deposits of still unknown composition (Sjöström 1993).

3.2 Mechanical pulp surface and its characterisation

The main purpose of wood pulping is to liberate the fibres. This can be accomplished either mechanically, or combining chemical and mechanical treatments. In practice, mechanical pulp is produced by pressing wood logs against a revolving pulp stone (grinding), or by disintegrating wood chips in a disc refiner (refining) (Sundholm 1999). Chemimechanical pulping, in turn, involves a chemical treatment stage combined with mechanical fibrillation. Sulphite (Na_2SO_3) used in CTMP pulping introduces sulphonate groups into lignin, making lignin more hydrophilic and thus easier to soften (Lindhölm and Kurdin 1999). It has been proposed that the rupture of the fibre wall during CTMP refining takes place preferentially in the primary layer (P) and in the middle lamella (ML), whereas for TMP and PGW the separation occurs between primary and secondary walls, preferably between S1 and S2 layers (Fig. 2) (Franzén 1986, Cisneros et al. 1995, Salmén et al. 1999).

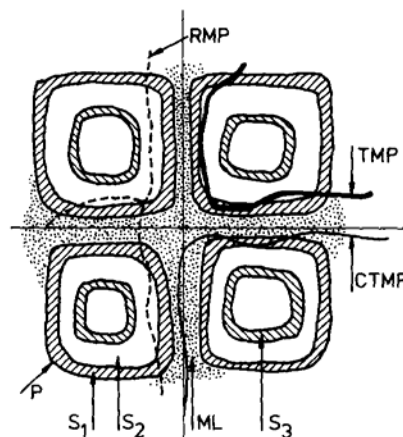


Fig.2. Typical kinds of fibre rupture in different high-yield pulping processes (Franzén 1986).

Mechanical pulping involves the conversion of raw wood into papermaking pulp by mechanical means which does not remove lignin from fibres (Roberts 1996). During PGW and TMP pulping, some hemicelluloses may dissolve (Sjöström et al. 1965). Due to presence of water, extractives are removed unless precipitated back to the surface.

In the development of theories and experiments aiming at understanding the papermaking properties of mechanical pulps, the fibre characteristics, such as fibre distribution and fibre

coarseness, are usually the main subject of interest (Karnis 1994, Mohlin 1997, Corson 2002). However, the chemical composition of the pulp surface can be very different from the bulk composition of the pulp.

Surface analysis methods

During recent years, ESCA or XPS (Electron Spectroscopy for Chemical Analysis/X-ray Photoelectron Spectroscopy) has been widely applied in analysing PGW and TMP pulp surfaces (Dorris and Gray 1978a-c, Barry et al. 1990, Hua et al. 1993, McDonald et al. 1999, Westermark 1999, Matuana et al. 2001). In particular, CTMP pulps have been investigated (Barry et al. 1990, Carlsson 1996, Koubaa et al. 1996, Börås and Gatenholm 1999a,b). Usually, the ESCA technique used involves extraction of the sample with a solvent, such as acetone or dichloromethane (DCM). The detection of oxygen and carbon before and after extraction enables the coverage of lignin and extractives on the sample surface to be determined. Lower lignin or higher carbohydrate surface coverage of CTMP pulps is favoured by a lower temperature in press-drying (170 to 140 °C) (Koubaa et al. 1996), a lower sodium sulphite charge during sulphonation (Börås and Gatenholm 1999b) and manufacture of steam explosion pulps instead of conventional ones (Hua et al. 1993). Xylan has also been found to be successfully adsorbed on the surface of CTMP pulp (Henriksson and Gatenholm 2002). A higher carbohydrate content in the pulps and the fines results in a paper with better physical strength properties (Hua et al. 1993, Luukko et al. 1999). According to Luukko et al. (1999), extractives are enriched on the surface of fines, and according to Mosbye et al. (2003) especially on the flake-like fines of TMP pulp.

Among the ESCA techniques, the Tougaard background analysis has also been applied to different pulps. This technique provides quantitative information on the depth distribution of surface lignin and extractives (Johansson 2002). For example, background analysis of oxygen has suggested that a thin film of extractives at least partially covers the TMP pulp surface. Another technique of ESCA involves selective labelling of lignin by mercurisation and determination of mercury by ESCA (Westermark 1999, Heijnesson Hultén and Paulsson 2003). According to these results, the lignin content of different pulps are slightly higher than that of the bulk lignin.

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) has recently been applied especially to analysing the surfaces of different fines, namely fibrillar and flake-like fines (Kleen et al. 2001, Kleen et al. 2002a, Kleen et al. 2003, Kangas et al. 2002). This technique provides information on the metal ions and on the chemical structure of lignin and extractives in the outermost surface layer of the pulp. Hence, ToF-SIMS has become an excellent complement to the ESCA technique. The results have shown that the fines fraction of TMP pulp contains more extractives, lignin and pectin than bulk fibres (Kleen et al. 2003). Also, the surface of fibrils and flakes of unbleached GW, PGW and TMP pulps are more covered by lignin and extractives than the surface of ray cells (Kleen et al. 2002a, Kangas et al. 2002). On the other hand, flake-like fines are more enriched with extractives in a CTMP pulp (Kangas et al. 2002). Peroxide bleaching has been found to decrease the surface coverage of extractives in different mechanical pulps, and the residual extractives seem to be adsorbed more on fibrillar fines than flake-like fines (Kangas and Kleen 2003).

Imaging techniques, such as AFM (Atomic Force Microscopy) have been used to study the surface morphology of mechanical pulps, revealing different fibre wall structures on the surface, namely fibrillar and globular parts (Hanley and Gray 1994, Niemi et al. 2002). The fibrillar and granular structures occurring on the fibre surface after one-stage TMP refining have been identified as P/S1 cell wall layers, whereas two-stage refining results in much more heterogeneous surfaces (Gustafsson et al. 2001). The origin of wood samples from which the pulp has been manufactured seems to have a greater effect on the revealed cell wall layer than the temperature or type of process used. In this paper, the TMP processed pulp was compared to RTS “low Retention, high Temperature, high Speed” processed pulp (Gustafsson et al. 2003). It has been reported that the surface roughness of pine chips increases with increasing refiner pressure (Snell et al. 2001). However, the interpretation of the globular structures detected on the mechanical pulp surfaces is somewhat unclear. These have been linked to e.g. extractives (unbleached CTMP (Börås and Gatenholm 1999a)), adsorbed xylan (xylan modified CTMP (Henriksson and Gatenholm 2002)) or lignin (original kraft pulps (Simola et al. 2000, Pereira et al. 2001, Simola-Gustafsson et al. 2001, Gustafsson et al. 2002)). Obviously, more work needs to be done with AFM to distinguish unambiguously between different wood components on wood pulp surfaces.

3.3 Kraft pulp surface and its characterisation

The chemical pulping process, aiming at effective removal of lignin while preserving the carbohydrates, takes place at high pressures and temperatures under aqueous alkaline, neutral or acidic conditions (Roberts 1996). Usually about 90% of the lignin is removed (Sjöström 1993). The surface lignin is reportedly difficult to remove from kraft pulp surfaces in successive bleaching stages (Laine 1996). The chemical composition of kraft fibres depends strongly on the wood material, pulping methods and bleaching chemicals used (Laine et al. 1994, Laine 1996, Laine et al. 1996, Halminen et al. 1998, Kleen et al. 2002b, Sjöberg 2002, Heijnesson Hultén and Paulsson 2003). The surface analysis methods used for kraft pulps have been well described by Laine (1996).

The secondary wall lignin is easier to degrade chemically and thus to dissolve than middle-lamella lignin. The structural differences of lignin, e.g. more reactive phenolic groups in the secondary wall and less cross-linking, have substantial effects upon the course of delignification. The secondary-wall lignin seems to contain much more cleavable bonds of the dominating β -O-4 linkages between lignin units, suggesting that the delignification preferentially occurs initially from the secondary wall lignin (Salmén and Ljunggren 1996).

3.4 Effect of wood components on strength properties of paper

Among the wood substances, xylan and glucomannan have been found to strengthen paper made from kraft pulp (Lindström et al. 1977). A high xylan content of the kraft pulp preferentially increases the *tensile strength* of the paper, whereas the *bonding strength* is not affected by the hemicellulose content of the pulps at the same density (Molin 2002). The quantity rather than chemical nature of hemicelluloses appears to determine the paper properties (Annergren et al. 1962). On the other hand, it has been reported that precipitated xylan on kraft pulp results in an increase in both tensile and bonding strength of paper (Sihtola and Blomberg 1975, Schönberg 2001, Sjöberg 2002). Xylan introduces new carboxylic groups into fibres. Fibres with a higher acid group content swell more, exposing larger surface areas with more potentially reactive sites available for interaction (Eriksson and Sjöström 1968). The increase in fibre flexibility and conformability increases the bonding of fibres (Laine 1996). The increase in strength properties after mannan sorption has been

explained by increased hydrophilicity of the fibres and thus improved bonding ability (Hannuksela et al. 2003). The effect of mannose and galactose containing guar gum and Locust bean gum on the dry strength is also well established (Leech 1954, Dugal and Swanson 1972).

A high lignin content in the pulp makes the fibre so stiff that bonding with another fibre is difficult. For example, Retulainen and Nurminen (1993) have shown that the chemical removal of lignin from CTMP by acid sodium chlorite treatment increases the flexibility, conformability and specific bond strength of long fibres. Precipitated kraft lignin on kraft pulp, in turn, has been reported to impair the strength and bonding properties of paper (Lindström et al. 1977, Springer et al. 1985, 1986). The precipitated kraft lignin seems to act as a filler or a non-bonding spacer in fibre crossings (Lindström et al. 1977).

A high content of extractives on pulp surfaces has been unambiguously connected to impaired strength properties of paper and fines (Brandal and Lindheim 1966, Luukko 1999, Sundberg et al. 2000, Rundlöf et al. 1995, 2000a,b). Although the amount of extractives is very low in the pulps (<1%), its deposition on the fibres can affect the quality of paper. Especially lipophilic extractives reportedly impair paper strength (Zhang et al. 1999, Sundberg et al. 2000), as well as dissolved (Zhang 2000) and colloidal substances (Rundlöf 2002). In particular, fatty acids (Brandal and Lindheim 1966, Kokkonen et al. 2002), fatty alcohols (Brandal and Lindheim 1966) and steryl esters (Kokkonen et al. 2002) seem to be the main components of extractives that have a harmful effect on paper strength. Both lignin and extractives are rather hydrophobic in nature. It has been suggested that adsorbed material prevents hydrogen bonding between fibres. Extractives also affect sheet formation (Kokkonen et al. 2002) and fibre-to-fibre friction (Garoff et al. 1999), which may also have an effect on the strength properties of paper.

Other components occurring in the papermaking process, such as neutral polysaccharides (Zhang 2000), lignans (Zhang 2000), alum, ferric chloride, defoamers (Springer et al. 1985, 1986) and increased salt concentration (Lindström et al. 1977) have also been reported to have harmful effects on paper strength.

It is evident that the surface chemical composition of fibres and fines affects the strength properties of paper. However, it must be kept in mind that the characteristics of paper are also

influenced by other factors, such as the distribution of fibre fractions in pulp (Lindholm 1980a, 1981a,b) and the type of fines (Lindholm 1980b, Westermark and Capretti 1988). Especially the proportion of fibrillar material is an important characteristic contributing to the tensile strength of a fines sheet (Luukko et al. 1999).

4 EXPERIMENTAL

4.1 Mechanical pulps

Unbleached PGW, TMP and CTMP spruce (*Picea abies*) pulps as well as peroxide bleached CTMP and TMP pulps were collected from pulp mills. Unbleached PGW and TMP pulps were peroxide-bleached in laboratory conditions and subjected to alkaline treatments without the addition of hydrogen peroxide (Fig. 3). The PGW pulp was also dithionite-bleached in laboratory conditions. After the laboratory treatments, pH was adjusted to 5.3 and the pulps were washed three times with water. As a reference, the unbleached PGW and TMP pulps were washed three times with deionised water. Notations and descriptions of the different pulps examined are given in Table 1 (Papers I, II, IV).

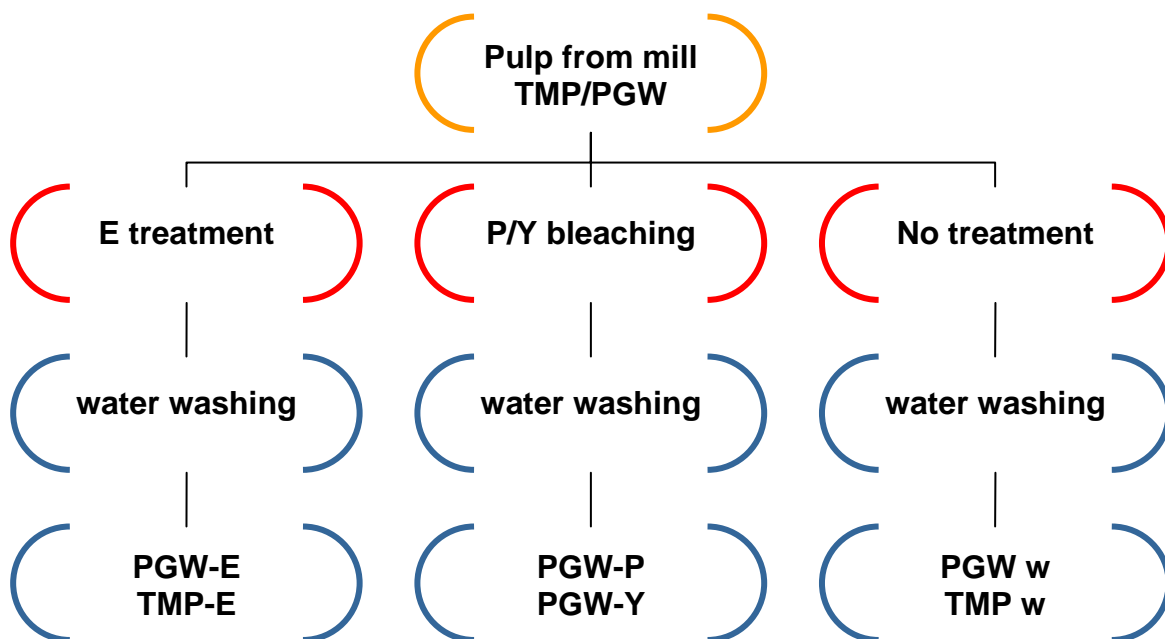


Fig.3. Alkaline treatment (E), peroxide (P) and dithionite (Y) bleaching of pulps in the laboratory. See Table 1.

Before the ozone treatment (PGW-Z), the PGW pulp was washed for 3 h with deionised water at 1% consistency and 60°C, followed by centrifugation (1500 rpm, 60 min). The pulp was ozone-treated for 55 min at 12% consistency, using an ozone dosage of 5.2%. The ozone consumption during the treatment was 3.6%. Initial and the final temperatures/pH were 23°C/pH 5.5 and 40°C/pH 2.7, respectively. Thereafter, the pH of the pulp was adjusted to 7

with 1 M NaOH, shives were removed by Somerville screening and the pulp was washed again for 2 h at 1% consistency and 60°C.

Table 1. Notations, properties and treatments of spruce mechanical pulps.

Notation	Description	Pulp properties and treatments
PGW uw	Unwashed pressure groundwood pulp from UPM-Kymmene, Kaukas Oy, Lappeenranta, Finland, (MEKKA pulp)	CSF 45 ml, d.w. 29 %, ISO-% 61
PGW w	Washed PGW	Pulp washed 3 times with deionised water
PGW-E	Alkaline-treated PGW	Treated in laboratory with NaOH at pH 11.2 for 1.5 h at 10 % consistency, 60°C*, ISO-% 59
PGW-P	Peroxide-bleached PGW	Bleached in laboratory, 3 % H ₂ O ₂ for 1.5 h at 10 % consistency, 60°C, pH 11.2*, ISO-% 70
PGW-Y	Dithionite-bleached PGW	Bleached in laboratory, 1.5% Na ₂ S ₂ O ₄ for 1h at 3% consistency, 60°C, pH 6*, ISO-% 65
PGW-Z	Ozone-treated PGW	See text, ISO-% 54
TMP uw	Unwashed thermomechanical pulp from UPM-Kymmene, Kaipola, Finland, (MEKKA pulp)	CSF 120 ml, d.w. 47 %, ISO-% 59
TMP w	Washed TMP	Pulp washed 3 times with deionised water
TMP-E	Alkaline-treated TMP	Treated in laboratory with NaOH at pH 11.2 for 1.5 h at 10 % consistency, 60°C*, ISO-% 57
TMP-P	Peroxide-bleached TMP	Bleached in laboratory, 3 % H ₂ O ₂ for 1.5 h at 10 % consistency, 60°C, pH 11.2*, ISO-% 65
TMP-P2	Peroxide-bleached TMP from UPM-Kymmene, Rauma, Finland, (FINE pulp)	CSF 35 ml, ISO-% 71
CTMP uw	Unwashed chemithermomechanical pulp from Metsä-Serla, Lielähti, Finland, (MEKKA pulp)	CSF 470 ml, d.w. 34 %, ISO-% 60
CTMP-P uw	Unwashed peroxide-bleached CTMP from Metsä-Serla, Lielähti**, Finland, (MEKKA pulp)	CSF 465 ml, d.w. 31 %, ISO-% 69

* After the treatments pH was adjusted to 5.3 and the pulps were washed three times with water

** M-real Lielähti at present

ISO-%: brightness of the pulp

In the experiments made with PGW (uw) pulp using different alkali treatment times, the pulp was first washed with deionised water at 1% consistency and 60°C at Åbo Akademi University (Pranovich et al. 2003). Thereafter, the pulp was alkaline-treated for 30/60/180/360 min at 1% consistency, using NaOH (pH 11.2 and 60°C).

Two laboratory pulps with freeness levels 24 and 129 CSF were made at Åbo Akademi University. The pulp with a higher freeness level was produced by using increased feeding pressure. PGW pulps were fractionated for the fractions +30, +50, +100, +200 and -200 mesh using the Bauer McNett apparatus (KCL 140:65).

4.2 Chemical pulps

ECF bleached kraft pulp made mainly from spruce was used in studying the adsorption of kraft lignin and model extractives. More detailed information on the pulp is shown in Table 2. The pulp was first refined for 50 min in a Valley beater (SCAN-C 25:76). The fines fraction (<200 mesh) was removed with a Bauer McNett apparatus (SCAN-M 6:69) and washed into sodium form according to the procedure described by Wågberg et al. (1989), Swerin et al. (1990) and Swerin and Wågberg (1994).

Table 2. Notations and treatments of kraft pulps.

Notation	Composition	Pulp properties and treatments
ECF (FINE softwood pulp)	83% spruce, 13 % pine, 4% hardwood, Metsä-Sellu*, Äänekoski, Finland	- Fully bleached pulp: Kappa 0.4 and ISO-% 86 after ECF bleaching sequence
TCF (NI softwood pulp)	70% spruce, 30 % pine, Metsä-Rauma*, Finland	- Unbleached pulp: Super Batch cooked (kappa 19, ISO-% 30, viscosity 930 mg/l) - Fully bleached pulp: Kappa 2.3, ISO-% 84 and viscosity 660 ml/g after O-O-Z-PO-Q-PO bleaching sequence
TCF (NI hardwood pulp)	94% birch, 3% aspen, 2% beech and 1% spruce, Mörrum, Sweden	- Unbleached pulp: RDH cooked (kappa 15.9, ISO- % 37, viscosity 1180 mg/l) - Fully bleached pulp: Kappa 4.7, ISO-% 89 and viscosity 760 ml/g after O-Q-P-Q-(PO)P bleaching sequence

* Oy Metsä-Botnia Ab at present
ISO-%: brightness of the pulp

Softwood pulps cooked with the Super Batch process and hardwood pulps cooked with rapid displacement heating (RDH), bleached in highly closed bleaching plants, were used in the recirculation experiments. More detailed information on the pulps and bleaching sequences is

contained in Table 2. Oxygen-delignified mill pulps were laboratory-bleached at conditions corresponding to those in the mills.

4.3 Adsorption experiments with chemical pulps

The kraft lignin used in the adsorption experiments was precipitated from black liquor, CURAN 100 (LignoTech AB, Sweden). Lignin was adsorbed into pulp at concentrations of 13, 330 and 1330 mg/g d.w. pulp. A more detailed description of how the lignin solutions were prepared and adsorbed into the pulp is found in Paper V. PES-Na was adsorbed into PDADMAC pre-treated pulp at concentrations of 10, 20, 40 and 80 mg/g d.w. pulp. The adsorption time both for PDADMAC and PES-Na was 1 h. The PDADMAC was adsorbed into pulp at 50 mg/g d.w. pulp. The polyelectrolytes used in the experiments were the same as those described in Paper II.

The sodium oleate (NaOl) used in the experiments was produced by Riedel-de Haën. Sodium abietate (NaAb) was manufactured from abietic acid (Sigma) according to the procedure described by Palonen et al. (1982). The concentrations of NaOl, NaAb and their 1:1 mixtures used during sorption were 1×10^{-6} , 1×10^{-5} , 1×10^{-4} , 1×10^{-3} , 1×10^{-2} and 0.5×10^{-1} M, which corresponded to 0.15, 1.5, 15, 150, 1500 and 7600 mg/g d.w. pulp for NaAb and 0.14, 1.4, 14, 140, 1420 and 7100 mg/g d.w. pulp for NaOl. The surface tension of liquids was measured with a Sigma 70 tensiometer from KSV Instruments Ltd (Helsinki).

Pitch adsorbed on the spruce kraft pulp was isolated with hexane from unbleached TMP pulp, as described by Sundberg (1995). In the experiments, PDADMAC was adsorbed at a concentration of 2 mg/g d.w. pulp at 1 mM NaCl. In the pitch adsorption, the pitch concentration was 5 mg/g d.w. pulp, NaCl or CaCl₂ concentrations of 1 mM and 100 mM were used and pH was adjusted to 6.5. After 2 hours, the pulp was filtered and washed again with a small amount of water.

When lower pH was exploited to produce precipitates, a softwood kraft pulp slurry from the second oxygen delignification stage and Z filtrate from the succeeding ozone stage were used (Paper III). In brief, the O₂ pulp slurry was diluted with water or acidic Z filtrate and heated to 70 °C. The pH was then adjusted to 5.0, 3.5 and 2.0 with H₂SO₄.

4.4 Methods to investigate surface properties

ESCA/XPS, AFM, a Wilhelmy balance, ToF-SIMS and FTIR-PAS were used to investigate the surface properties of pulps. Table 3 shows of the approximate analysis depths of the different methods.

Table 3. Methods used in the experiments and their analysis depths.

Method	1. Input radiation 2. Radiation detected	Application	Analysis depth
ESCA/XPS	1. X-ray 2. Photoelectrons from inner orbitals	Elemental composition and chemical states	Few atom layers, 4-10 nm
ToF-SIMS	1. Primary ions 2. Secondary ions, i.e. atoms, small and larger molecules	Elemental and molecular information	Sampling depth (~1 nm)
AFM/SPM	-	Topography	Outermost surface (~1 nm)
Wilhelmy balance	-	Contact angle between single fibre and liquid	Outermost surface
FTIR-PAS	1. Modulated light— 2. Acoustic signal	Molecular chemical information	3-8 μm (5 kHz), dependent on λ

4.4.1 ESCA/XPS

ESCA/XPS was first applied to pulp fibres by Dorris and Gray in 1978a-c and since then it has been used in numerous fibre studies. This technique yields information on the elemental and chemical composition of the surface. In this study, the most common approach was applied, i.e. ESCA was combined with solvent extraction to evaluate the surface lignin and extractives contents on the pulp surface (Papers I-VI). Both acetone (SCAN-CM 49:93) and dichloromethane (DCM) (SCAN-C 7:62) extractions were used as solvents. The measurements were performed with a Kratos Analytical AXIS 165 electron spectrometer (Manchester, England) using a monochromated Al K α X-ray source at the Center for Chemical Analysis, Espoo, Finland. The experimental procedure used for cellulose fibres is described in more detail in Paper VI. The principle of ESCA technique is described elsewhere (Briggs and Seah 1990, Turner 1997, Holmbom and Stenius 2000).

Different solvents are known to extract different components of extractives and even other wood components (Katz and Gray 1980, Ahmed et al. 1987, Laine 1996, Holmbom and Stenius 2000, Grüber et al. 2002). Usually, the choice of extraction solvent is critical (Holmbom and Stenius 2000). For gravimetric determination, the extraction solvent should be selective, that is, extract only the components of interest. It is known that acetone gives a complete extraction of wood resin components, but it also extracts other components: salts, sugars, and various phenolic compounds (including low-molar-mass lignin). Solvents with intermediate polarity, e.g. DCM, will extract some polar components in addition to true wood resin components. According to the results of the present study, extraction with acetone removes more material both from the bulk as well as from the surface than extraction with DCM (Paper IV, Fig. 4). The effect is more evident for extractives-rich mechanical pulps.

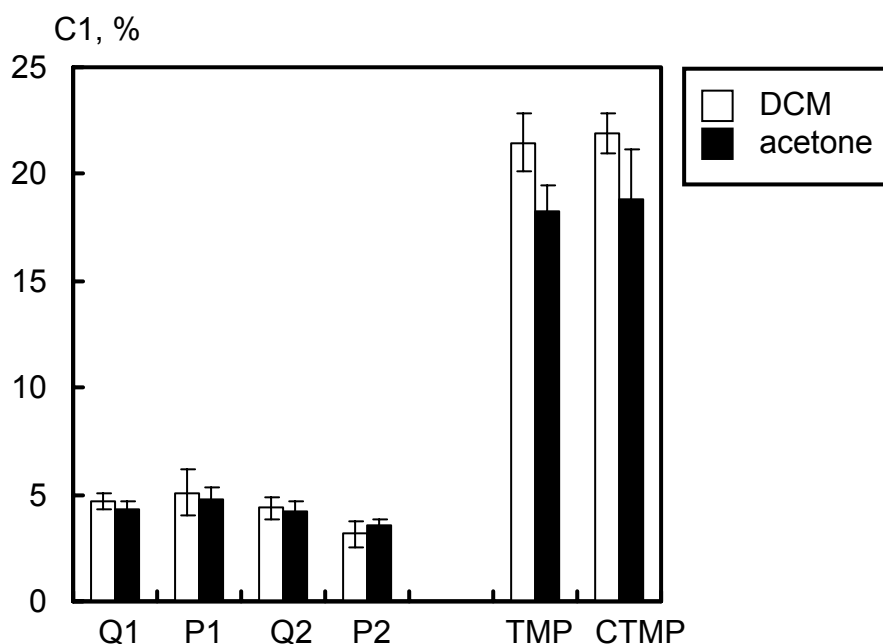


Fig.4. Comparison between DCM and acetone extraction for hardwood kraft (Koljonen et al. 2000) and mechanical pulp samples (Paper IV) by ESCA.

The quantification of surface lignin and extractives was based on C-C (C1 carbon) percentages instead of the more commonly used O/C ratios, since the former method was found to give more reproducible results under strictly controlled experimental conditions (Paper VI). The larger scatter, especially on extracted samples, in O/C ratios may be due to adsorbed water present on the hygroscopic fibre surface (Fig. 5B).

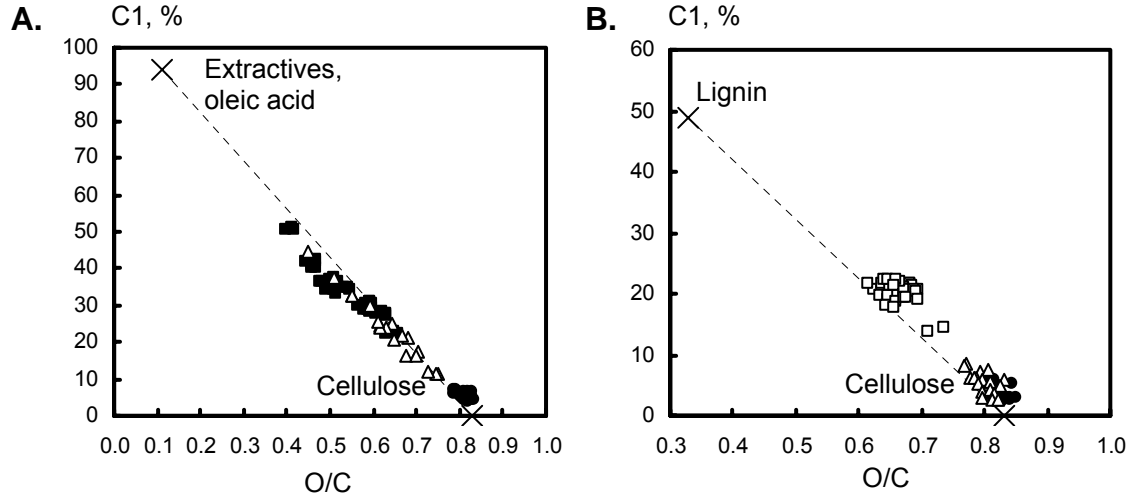


Fig.5. C1 as a function of O/C of the mechanical (■□), hardwood kraft (△) and softwood kraft (●) pulps A. before and B. after DCM extraction. Theoretical values for cellulose, lignin and extractives are from Laine (1996).

Knowing that pure cellulose contains no C1 carbon and pure mill wood lignin contains 49% C1 carbon (Laine 1996), the surface content of lignin can be estimated using the following equation:

$$\phi_{lignin} = \frac{(C1_{extracted\ pulp} - a) \times 100\%}{49\%} \quad (1)$$

Here, $C1_{extracted\ pulp}$ is the relative amount of the C-C component in the deconvoluted high-resolution C1s spectrum of the extracted pulp sample and a is the contribution to the C1 peak from surface contamination. The value used for a was 2%, which is the lowest relative amount of the C1 peak detected on the surface of the fully bleached pulp fibres with the ESCA instrument used. The surface content of extractives can be calculated from

$$\phi_{extractives} = (C1_{pulp} - C1_{extracted\ pulp}) \times 100\% \quad (2)$$

4.4.2 Wilhelmy balance

In Paper I, the dynamic wetting properties of single pulp fibres were measured using the Wilhelmy balance technique with a Sigma 70 tensiometer from KSV Instruments Ltd (Helsinki). Three solvent probes, water (ultra high quality water, UHQ), ethylene glycol (Riedel- de Haën, > 99.5%) and α - bromonaphthalene (Aldrich 98%), were used to calculate the dispersive-polar, Lifshitz van der Waals, and acid-base components of the surface tension. Measurements were made in an air-conditioned cabinet at room temperature.

Eq.3 was applied to calculate the contact angles from the recorded forces.

$$F = p\gamma\cos\theta + mg - (\rho_l - \rho_v)Vg \quad (3)$$

where F is the force acting on the fibre, p is the wetted perimeter, γ is the surface tension of the liquid, θ is the contact angle between fibre and wetting liquid, m is fibres mass, V is submerged volume and ρ_l, ρ_v are the liquid and vapour densities, respectively. The buoyancy force, $mg - (\rho_l - \rho_v)Vg$, was neglected (Hodgson and Berg 1988, Tiberg et al. 2001).

The receding contact angle was assumed to be zero, i.e. $\cos\theta_R=1$ (Klungness 1981, Krüger and Hodgson 1994, 1995, Hodgson and Berg 1988, Deng and Abazeri 1998). Therefore, the advancing contact angle, $\cos\theta_A$, was reduced to form:

$$\cos\theta_A = \frac{F_A}{F_R} \quad (4)$$

where F_A and F_R are the average advancing and receding forces, respectively. Three cycles were performed on each fibre. The results were calculated only from the first immersion. The other cycles were used to confirm that no marked changes in fibre properties occurred due to the repeated immersion and withdrawal of the fibres.

obtained when using the PCD than the dye indicator (Fig. 7). The reason for this systematic difference is probably that the end point of titrations with dye indicator was detected visually.

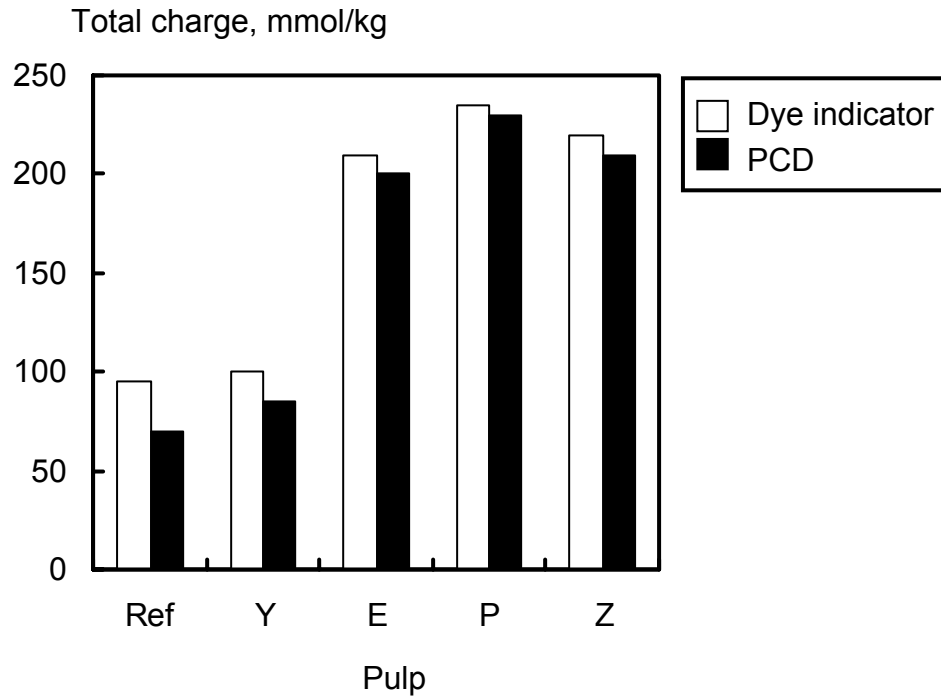


Fig.7. Total charge (polybrene adsorption) of different PGW pulps measured with dye indicator and PCD. The charge variation of the sample is approximately ± 5 mmol/kg.

The amount of elementary charge ($\mu\text{mol/g}$ or mmol/kg) in the pulp, σ , was calculated from:

$$\sigma = \frac{\left(\frac{V_{bt} - V_{tit}}{V_{bt}} \right) \times m_{poly} \times CD_{poly}}{m_{pulp}} \quad (5)$$

where V_{bt} and V_{tit} are the PES-Na consumption at the point of equivalence of the blank test and the pulp sample, CD_{poly} is the charge density of the polyelectrolyte and m_{poly} and m_{pulp} are the dry weights of the polyelectrolyte and the pulp sample. The amount of the non-adsorbed cationic polyelectrolyte, i.e. the equilibrium concentration of the cationic polyelectrolyte in the filtrate, c_{eq} is given by

$$c_{eq} = \frac{\left(\frac{V_{tit}}{V_{bt}}\right) \times m_{poly}}{V_{tot}} \quad (6)$$

where V_{tot} is the total volume of the filtrate.

Adsorption isotherms were determined at pH~7 with different excess dosage of cationic polyelectrolytes (Eqs. 5 and 6) (Wågberg et al. 1989). The amount of charge in the pulp was also determined as a function of pH (Eq.5 and pH 2-11).

4.4.4 ToF-SIMS

ToF-SIMS was used to study the chemistry of an adsorbed layer on kraft pulp after lowering the pH of the pulp slurry (Paper III). Both inorganic and organic compounds on the outermost surface of the pulp sheets were analysed. Special attention was paid to analysing the metal content and structure of lignin and extractives on the pulp surfaces.

Measurements were performed using the time-of-flight secondary ion mass spectrometer PHI TRIFT II (Physical Electronics Inc., Eden Prairie, USA) at Top Analytica Ltd., Turku, Finland. The instrument is described elsewhere (Schüler 1992). High-mass-resolution spectra in positive secondary ion mode over the mass range 10-2000 Da were acquired using a Ga liquid metal ion gun with 15 keV primary ions in a bunched mode. The primary ion current was 600 pA. Two areas of 200×200 mm² on each sample were analysed. The acquisition time was 5 min and time per channel 138 ps. The data were evaluated using the WinCadence Data Reduction software in off-line mode.

The metal content of the pulp sheet surface was determined using the main isotope, recalculated for the total isotope distribution, and using a separately determined response factor for each element (Kleen 2004). Identified structures of wood components are listed in Paper III in Table 4. The identification is based on studies made on model compounds of lignin (Kleen 2000a, b, Fukushima et al. 2001).

4.4.5 AFM/SPM

AFM has provided topographical information on surface structures with dimensions 10-100 nm that are present on the initially rough fibre surfaces. Throughout the work, AFM was extensively used to characterise the surface morphology of cellulose fibres and adsorbed materials (Papers III, IV, V, Koljonen et al. 2000). The principle of the AFM technique is described elsewhere (Colton et al. 1998).

Samples for AFM analysis were taken from the same sheets as for the ESCA measurements. AFM measurements were performed using a NanoScope IIIa Multimode scanning probe microscope (Digital Instruments, Inc. Santa Barbara, USA), at HUT, Espoo, Finland. The images were scanned in tapping mode in air using commercial Si cantilevers (Digital Instruments) with a resonance frequency of about 260-360 kHz. A free amplitude (A_o) of about 20 nm and a set-point ratio (r_{sp}) between 0.4-0.6 was used. r_{sp} is the ratio between the set-point amplitude (A_{sp}) and A_o . No image processing except flattening was made. Images of at least ten different fibres were scanned for each sample. Areas of $1.5 \times 1.5 \mu\text{m}$ and $3.0 \times 3.0 \mu\text{m}$ of each fibre were investigated. The phase image technique was chosen since it reveals more details of the fibre structure than the topography image (Fig. 8).

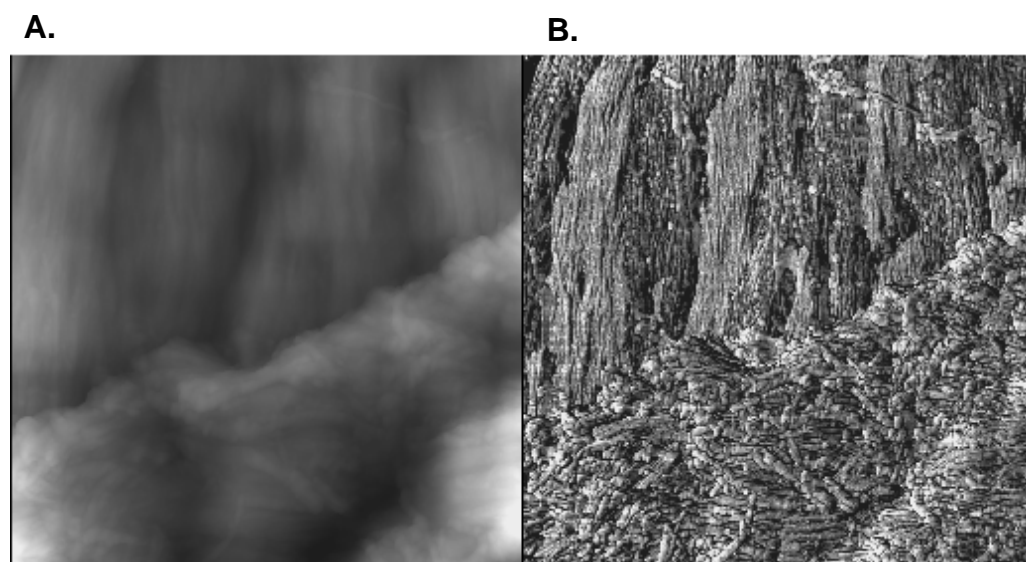


Fig.8. A. Topography and B. phase image on PGW fibre surface. The image size is $3\mu\text{m} \times 3\mu\text{m}$.

In most of the images no clear phase contrast between different components was found and hence they were distinguished mostly on the basis of structural differences. In Fig. 8B a clear

phase contrast is, however, also observed. Since rather light tapping was used, this contrast is most probably due to differences in hydrophobicity between the areas. The tip adheres more strongly to the hydrophilic areas which will thus appear darker in the image.

4.5 Other analyses and accuracy of measurements

4.5.1 Paper properties

Mechanical pulp sheets were prepared according to SCAN-M 5:76 and tested for density (SCAN-P 7:75), ISO brightness (SCAN-P 3:39), light scattering and adsorption coefficients (SCAN-C 27:76), tensile strength (SCAN-P 38:80) and tear strength (SCAN-P 11:73). Hot disintegration was performed according to SCAN-M 10:77 and the Canadian standard freeness (CSF) of the pulps was measured according to SCAN-M 10:77.

After adsorption of kraft lignin (Paper V) and model compounds of extractives, handsheets were prepared on a semiautomatic sheet former equipped with a circulation water system. The sheets were tested for density (SCAN-C 28:76), ISO brightness (SCAN-P 3:39), light scattering and adsorption coefficients (SCAN-P 8:93), tensile strength (SCAN-P 38:80) and Scott Bond value (Tappi 833 om-94). An in-plane tear-test to measure fracture energy was carried out as described by Kettunen (2000).

Standard handsheets in Paper III were tested for tensile index, tear index, wet zero span, Scott Bond, light scattering, absorption coefficient, opacity and Gurley air flow resistance according to EN ISO-5270.

4.5.2 Other analyses

The WRV of the pulps was analysed according to standard SCAN-C 62:00 in water. For some samples also 0.5 M NaCl solution was used.

Klason lignin was analysed by the sulphuric acid method (KCL 115b:82, Browning 1967). Acetone (SCAN-CM 49:93) or dichloromethane (SCAN-C 7:62) was used to remove

extractives from pulps. Extracts of unbleached PGW pulp were analysed by gas chromatography (Örså and Holmbom 1994).

The carbohydrate composition of mechanical pulps was determined after acidic hydrolysis by high-performance liquid chromatography (Puls et al. 1985, Hausalo 1995). The content of xylan was calculated from the amounts of analysed monosaccharides assuming that xylan: methylglucuronic acids : arabinose = 8 : 1.6 : 1 (Fengel and Wegener 1983). The pectin content was calculated from the galactouronic acid (GalA) content. The detection limit for glucuronic acids (GlcA) was rather high (~1 mg/g). Usually, only traces of GlcA were observed. When estimating the charge densities of the carbohydrates, the monomeric molecular masses of 208, 194 and 194 g/mol were used for methylglucuronic acids (MeGluA), GalA and GlcA, respectively. The degree of esterification for GalA in fibres was assumed to be 80% (Holmbom et al. 2000). On the other hand, it was assumed that 20% of the total content of GalA carries free carboxyl groups in unbleached TMP and PGW pulps. For unbleached CTMP pulps, it was assumed that 50% of the total GalA carry free carboxyl groups. This assumption was made based on the FTIR results, according to which ~20% of galactoglucomannan was deacetylated during CTMP pulping. Alkaline treatment and peroxide bleaching were assumed to demethylate all the methyl ester groups (Paper II).

Hexenuronic acids were determined using the HUT method as described by Tenkanen et al. (1999). In this acid hydrolysis method, the hexenuronic acid groups are selectively converted to formic acid and furan derivatives (2-furoic acid and 5-carboxy-2-furaldehyde), and UV spectroscopy is used for quantification of formed derivatives.

FTIR was used to study the chemical changes of the mechanical pulps (Paper II). The measurements were performed using a Bio-Rad FTS 6000 spectrometer (Massachusetts, USA) equipped with a photoacoustic (PA) detector (MTEC, USA). Samples were purged for 5 minutes with helium between the measurements. The spectra were collected in the rapid scan mode using a 5 kHz mirror velocity and a spectral resolution of 8 cm⁻¹. The analysis area was ~ 1 mm² and sample depth for 5 kHz mirror velocity 3-8 µm depending on the wavelength. 400 scans were accumulated prior to Fourier transformation. All spectra were baseline corrected at 3750, 1850 and 830 cm⁻¹.

4.5.3 Accuracy of measurements

95 % confidence level was used for paper properties. If only two parallel measurements were performed, the average difference was calculated.

Only three to nine parallel points per sample were usually investigated since the surface measurements are rather expensive and time- consuming. Therefore, the inaccuracy of the measurements was estimated with the confidence level of 95%, assuming that measurements are normally distributed. Eq. 7 was applied in the measurements:

$$\bar{x} \pm (x_{max} - x_{min}) \times F \quad (7)$$

where

\bar{x} is average of the measurements,
 x_{max} is a maximum and
 x_{min} is a minimum value of the measurements.

Table 4 shows the correction factors, F, used as a function of the number of measurements, n. If \bar{x} is the expected average value and x_v the average of n measurements, the correction value F is a quantile of 0.975 for distribution $(x_v - \bar{x}) / (x_{max} - x_{min})$.

Table 4. F values.

n	2	3	4	5	6	7	8	9	10
F	6.4	1.3	0.72	0.51	0.40	0.33	0.29	0.26	0.23

Wider deviations were usually obtained for the extractives coverages than for lignin coverages of the pulps because the calculation procedure used sums both the variations of unextracted and extracted samples.

5 RESULTS

In the following, the results obtained with mechanical pulps and chemical pulps are dealt with separately. First, the surface of lignin (Chapter 5.1) and the extractives of the pulps (Chapter 5.2) are reviewed, and then the pulp charge (Chapter 5.3) and the surface energy of single fibres (Chapter 5.4) are discussed. Furthermore, an attempt is made to explain the strength properties of paper with the surface properties of fibres (Chapter 5.5). The experiments made with model compounds were expected to give information on the behaviour of lignin and extractives on both mechanical and chemical fibre surfaces, and also on the effect of individual wood components on paper properties.

5.1 Surface lignin

5.1.1 Mechanical pulps

Fig. 9 shows the surface coverage of lignin on an industrial (CSF 45) and two laboratory-made PGW pulp sheets (24 and 129 CSF), and their fibre fraction sheets analysed by ESCA. Fractions +30-+200 seem to have almost the same surface coverage of lignin, whereas the fines fraction is more covered by lignin (Koljonen et al. 1997). The surface coverage of lignin is slightly lower for pulp produced by grinding with low feeding pressure. However, no clear difference is observed between pulps with different freeness levels.

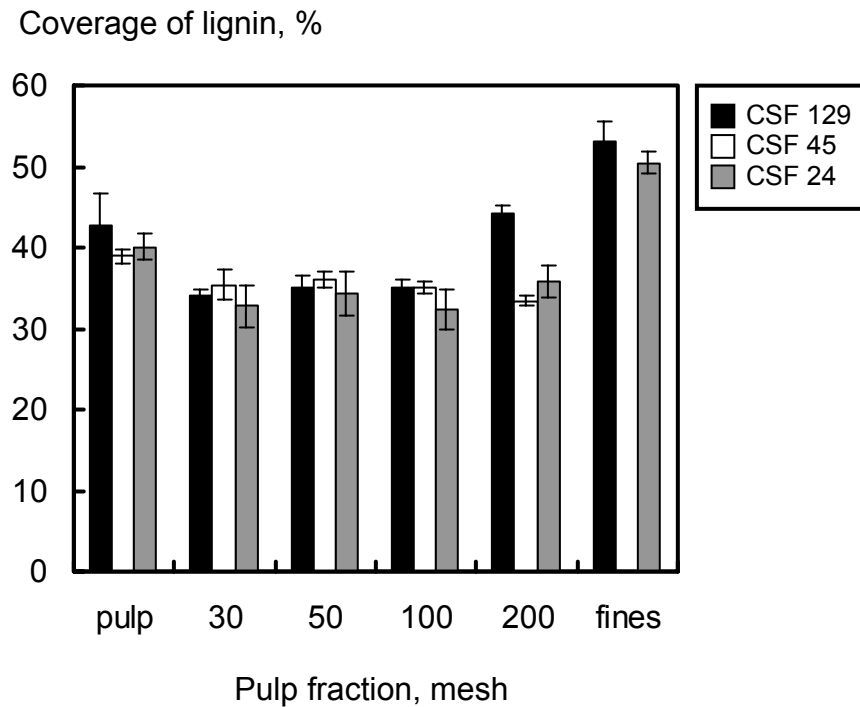


Fig.9. Coverage of lignin on PGW pulps by ESCA with different freeness levels (Koljonen et al. 1997). The fines fraction includes all particles that passed through a 200 mesh screen.

A comparison between these results and Klason lignin values indicated that lignin is slightly enriched on the surface of the mechanical pulps (Paper IV, Koljonen et al. 1997). The fines fraction seemed to be slightly more enriched with lignin than other fractions. The fines fraction includes all the pulp particles that passed through a 200 mesh screen. In this work, different fractions of fines were not investigated separately.

The AFM results illustrated that both pressure grinding (PGW) and chip refining (TMP) exposed different cell wall layers (Paper IV). The surfaces of unbleached PGW and TMP pulp fibres consisted of both granular and fibrillar structures. Although the freeness levels of unbleached PGW and TMP pulps were quite different, distinct differences between these pulps could not be observed with AFM or ESCA. Unlike the PGW and TMP pulps, the surfaces of unbleached CTMP pulp fibres were almost fully covered by irregular granular material (Fig. 10a). This granular layer was interpreted to originate from the middle lamella and the primary wall (Paper IV). Only in a few images part of the S2 layer was detected.

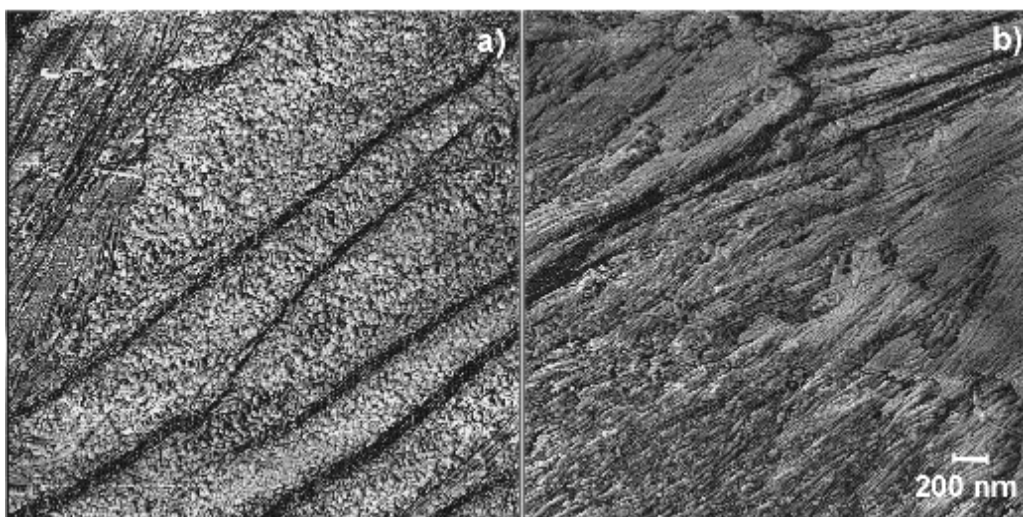


Fig.10. AFM phase images of a) unbleached CTMP pulp and b) peroxide-bleached CTMP pulp. The image size is $3\mu\text{m} \times 3\mu\text{m}$. Peroxide bleaching clearly modifies the fibre surface.

The effect of different treatments on the surface coverage on lignin in various pulps was thoroughly investigated (Paper IV, Koljonen et al. 1997). The pulps were also studied by FTIR before and after DCM extraction (Fig. 11B). The following summary of results is based on the ESCA, AFM, FTIR and bulk composition results (Paper IV, Fig. 11):

Alkaline treatment (E) and dithionite bleaching (Y). The surface content of lignin as well as the total content of lignin remained approximately the same (Fig. 11A). No effect on the topography of PGW and TMP fibres was observed.

Peroxide bleaching (P). The surface content of lignin remained approximately the same on PGW and TMP pulps (Fig. 11A). No clear effect on the topography of the fibres was observed. On the other hand, the granular layer was removed from the CTMP fibre surface after peroxide bleaching, exposing the underlying structure (Fig. 10b). However, the surface content of lignin determined by ESCA was not reduced. This suggests that peroxide bleaching of sulphonated CTMP pulp in some way modifies the lignin- and pectin-rich surface, and that lignin occurs also in a non-granular form on the surface of mechanical pulps.

Ozone treatment (Z). In contrast to the other treatments, the lignin coverage was strongly reduced after ozone treatment, while the total content of lignin was not reduced (Fig. 11A). The lignin/cellulose ratio was also reduced after treatment as determined by FTIR-PAS (Fig.

11B). This suggests that the ozone treatment used in this study primarily oxidises and/or reduces the lignin on the fibre surface. The AFM results show that before ozone treatment the pulp surface was covered with a granular phase. After the treatment, patches of fibrous material were observed (Paper IV).

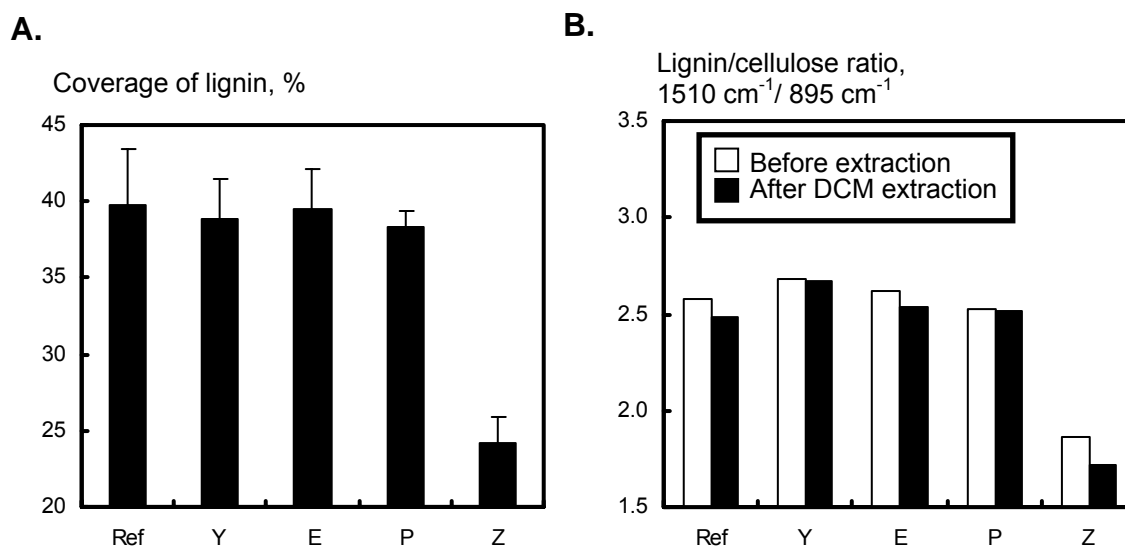


Fig.11. A) Coverage of lignin by ESCA and B) intensity ratio of 1510 cm⁻¹ and 895 cm⁻¹ by FTIR-PAS in PGW pulps. The average difference between two measurements in FTIR-PAS measurements is ~20 %.

5.1.2 Adsorbed kraft lignin on chemical pulps

Kraft lignin was adsorbed into fully bleached kraft pulp (Paper V). Addition of calcium was found to result in a very high surface coverage by lignin. Because kraft lignin was easily washed away with water, PDADMAC was used to increase the retention of kraft lignin. The adsorbed kraft lignin on the PDADMAC adsorbed pulp was detected as granules on the fibre surface. Granules were also detected when the pH of the slurry, containing fibres and liquor, taken after oxygen bleaching was reduced using either sulphuric acid or sulphuric acid and Z filtrate (Fig. 12, Paper III). Most of the precipitated lignin was found on the pulp surface after sheet forming. The adsorbed material was mainly kraft lignin.

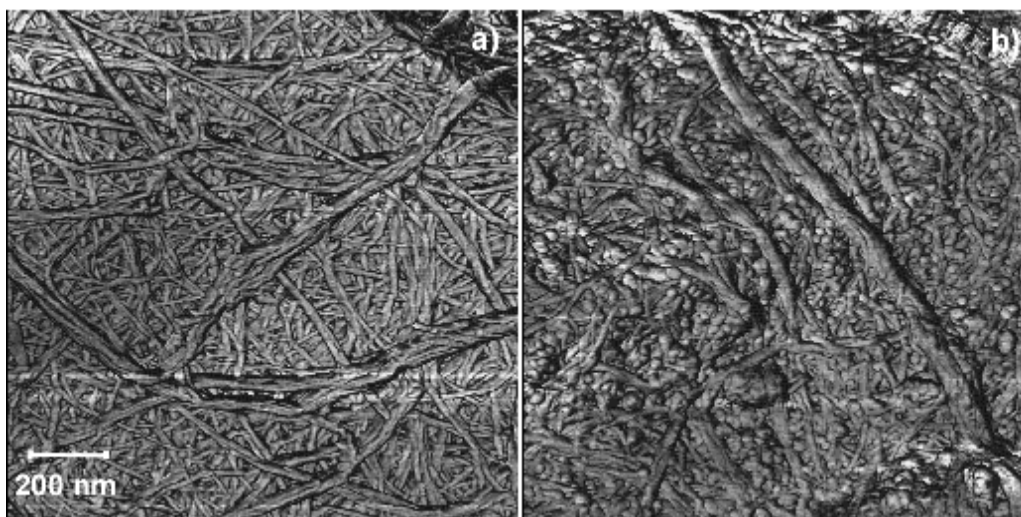


Fig.12. AFM phase images ($1.5 \times 1.5 \mu\text{m}^2$) of a) reference pulp sheets and b) after pH adjustment to 2.0 using H_2SO_4 .

Under acidic conditions ($\text{pH} < 6$), large amounts of lignin precipitated onto the pulp surface (Fig. 13A, Paper III). Surprisingly, neither the relative content of lignin nor its chemical structure seems to depend on the dilution filtrate used (Fig. 13A) although the Z-filtrate contained a high amount of Ca ions. Based on earlier findings, a high calcium ion content should increase the amount of lignin found on the surface. The precipitated lignin mainly originated from the oxygen filtrate (Fig. 13B).

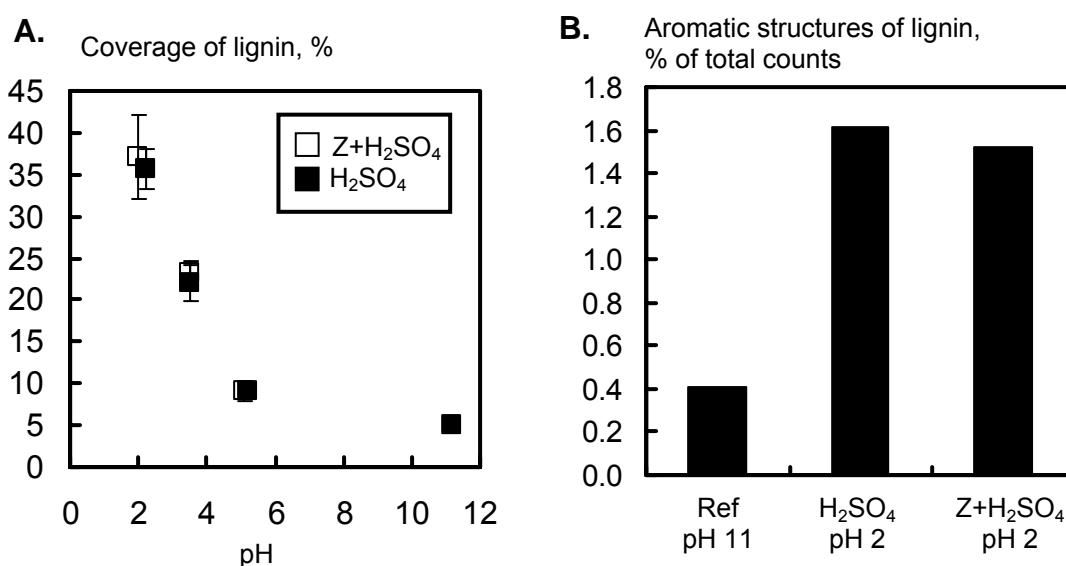


Fig.13. A. Surface coverage by lignin on pulp sheets as a function of precipitation pH determined by ESCA and B. percentage of aromatic structures of lignin (77 Da + 137 Da + 151 Da) from total counts determined by ToF-SIMS (Paper III).

5.2 Surface extractives

5.2.1 Mechanical pulps

Fig. 14 shows the surface coverage of extractives of the different PGW fibre fractions. The surface coverage of extractives increases towards smaller fraction size. The surface coverage of extractives seems more evenly distributed compared to the PGW pulp with a freeness level of 129 CSF.

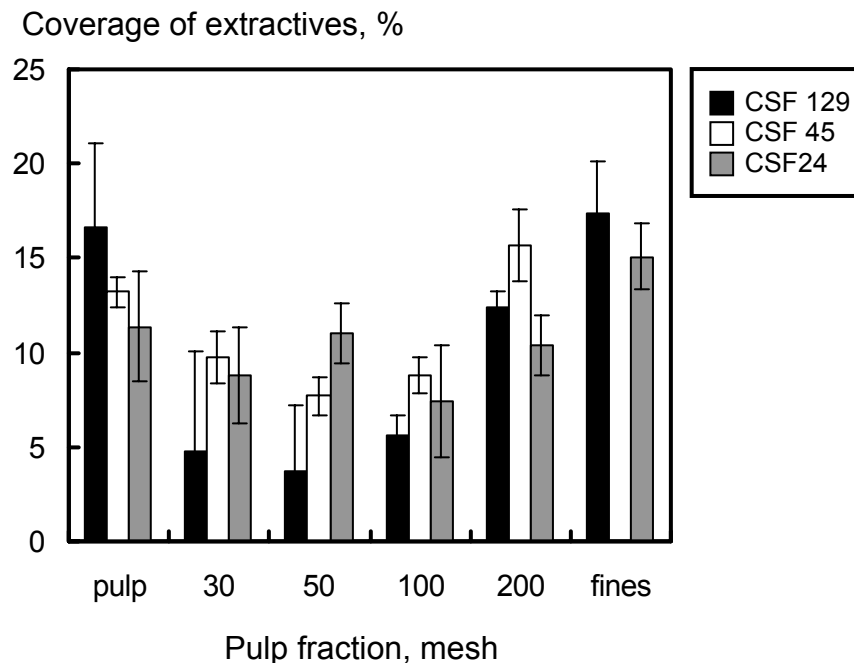


Fig.14. Surface coverage by extractives for PGW pulps of different freeness levels (Koljonen et al. 1997). The fines fraction includes all particles that passed through a 200 mesh screen.

The results indicated that the extractives content is significantly higher in the surface region than in the bulk (Paper IV, Koljonen et al. 1997). While the total extractives content in the pulp is 1-2%, the coverage by extractives on the surface varied between 15% and 30%. Especially the fines fraction is enriched with extractives. The fines fraction includes all the pulp fractions that passed through the 200 mesh wire (e.g. ray cells, fibrils etc.).

Because extractives on the pulp surface cannot be effectively detected with the FTIR-PAS method without isolating extractives from the pulp (Fig. 11B), and since it is not yet possible to distinguish the extractives component in the AFM images, ESCA and ToF-SIMS are the

only techniques to reveal changes on the fibre surface. The following observations are a summary derived from the ESCA and bulk results (Paper IV) for differently treated mechanical pulps (Fig. 15, Paper IV).

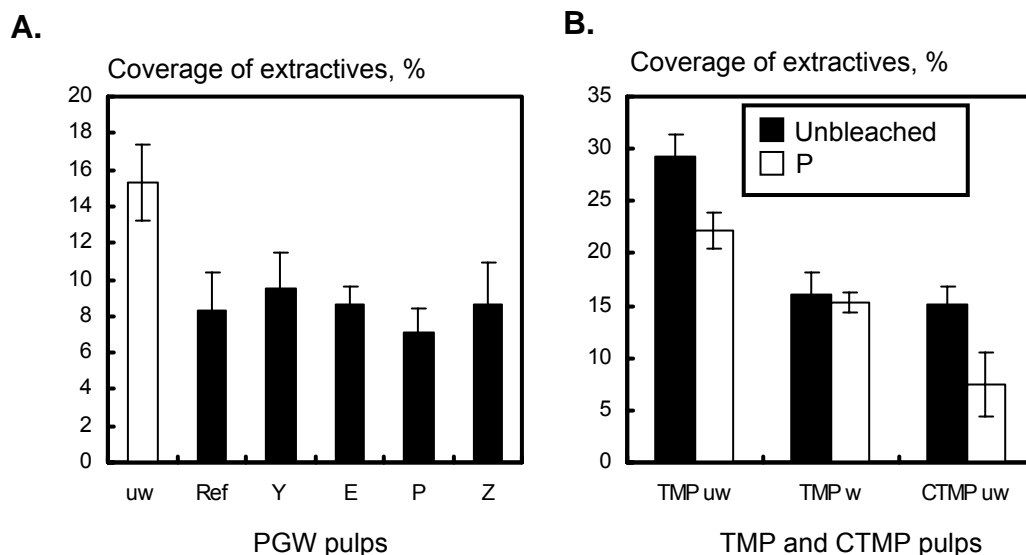


Fig.15. Effect of different treatments on surface coverage of extractives of mechanical pulps determined by ESCA.

The extractives contents on the unwashed and unbleached PGW and CTMP pulps ranged between 13-17%, whereas for the corresponding TMP pulps the content was even higher (27-32%) (Fig. 15). Washing of the pulps with water decreased the surface extractives content by 10-15%. The results indicate that the higher the content of extractives in the pulp, the greater the amount of surface extractives found on the surface. The reason why the extractives of TMP pulp are not washed out effectively to the level of PGW pulp is not known. Because washing is not effective, there are more extractives in the TMP fibres before and after different treatments than in other pulp surfaces. Because the fines structures of TMP and PGW pulps are different, the washing efficiency of the fines with water may be different.

As shown in Fig. 15A, alkaline treatment (E), peroxide bleaching (P), dithionite bleaching (Y) or ozone treatment (Z) do not decrease the extractives content on the PGW pulp surface. Only a small amount of extractives was removed from the surfaces of the TMP pulps that were peroxide-bleached and thereafter washed with water (Fig. 15B). However, peroxide bleaching was found to reduce the content of surface extractives by about 50% on the unwashed TMP and CTMP pulps (Fig. 15B).

5.2.2 Adsorbed components on chemical pulps

The adsorbed extractives after lowering the pH either with sulphuric acid or sulphuric acid and Z filtrate could be detected with ESCA and chemically characterised with ToF-SIMS. More extractives were found on the outermost pulp surfaces prepared at pH 2 than on those prepared at pH 11 (Fig. 16).

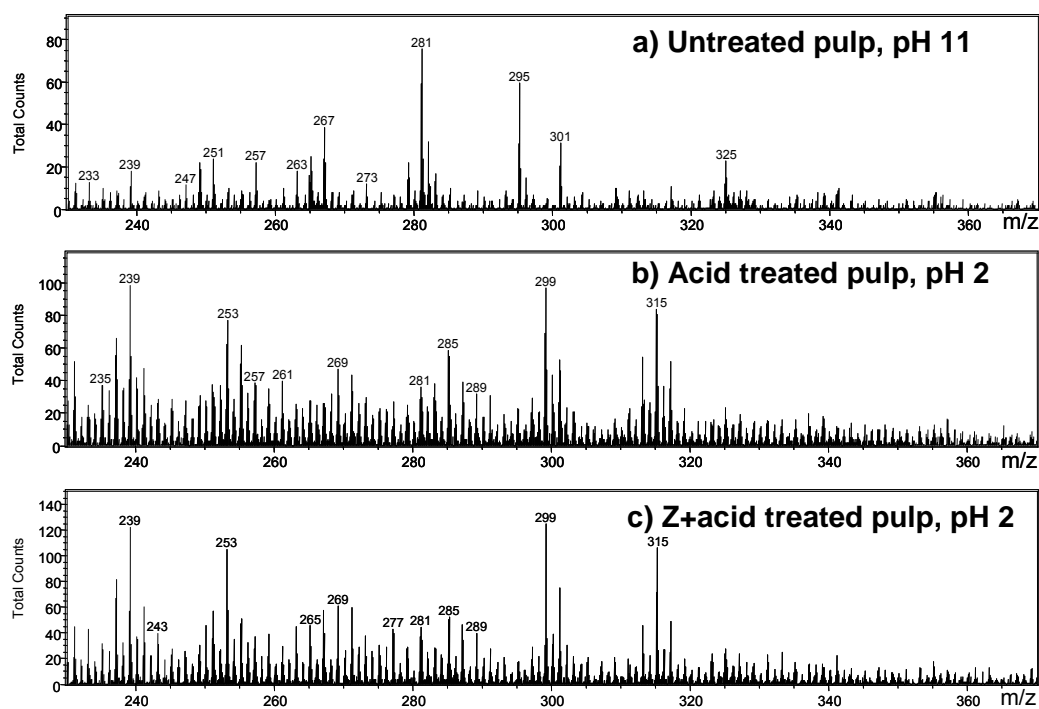


Fig.16. Part of positive ToF-SIMS spectra of a) reference, after precipitation with b) H_2SO_4 and c) H_2SO_4 and Z effluent, showing the extractives on the outermost surface. More saturated fatty acids from C16:0 to C19:0 precipitate in both treatments, i.e. palmitic acid (239 Da, 257 Da), *anteisoheptadecanoic* acid (253 Da, 271 Da), stearic acid (267, 285) and a C19:0 fatty acid (281 Da, 299 Da).

The main part of the precipitated extractives could, however, be easily washed away with water during sheet forming (Paper III), showing that the way the pulp is treated/washed before analysis is of great importance for the surface coverage on the pulps.

The model compounds sodium oleate (NaOl), sodium abietate (NaAb) and a mixture of these (1:1) were adsorbed on the ECF bleached kraft pulp (Fig. 17). These compounds are typical of the soaps formed in alkaline pulping when fatty and rosin acids are hydrolysed (Ström et al. 1990). In mechanical pulping, on the other hand, the content of free soaps is low, but neutral

compounds, including unhydrolysed fats and free acids (“pitch”), are dispersed in the process liquid. The adsorbed amount of extractives on the fibre surface was determined by ESCA, and the surface tension of the fibre suspension was measured to obtain the critical micel concentration (cmc). The adsorption took place at pH~7-8. Fig. 17 shows that in the presence of small amounts of these surfactants, i.e. approximately below the cmc, no appreciable sorption into the fibres is observed. As the concentration exceeded the cmc (>0.001 M), the coverage increased.

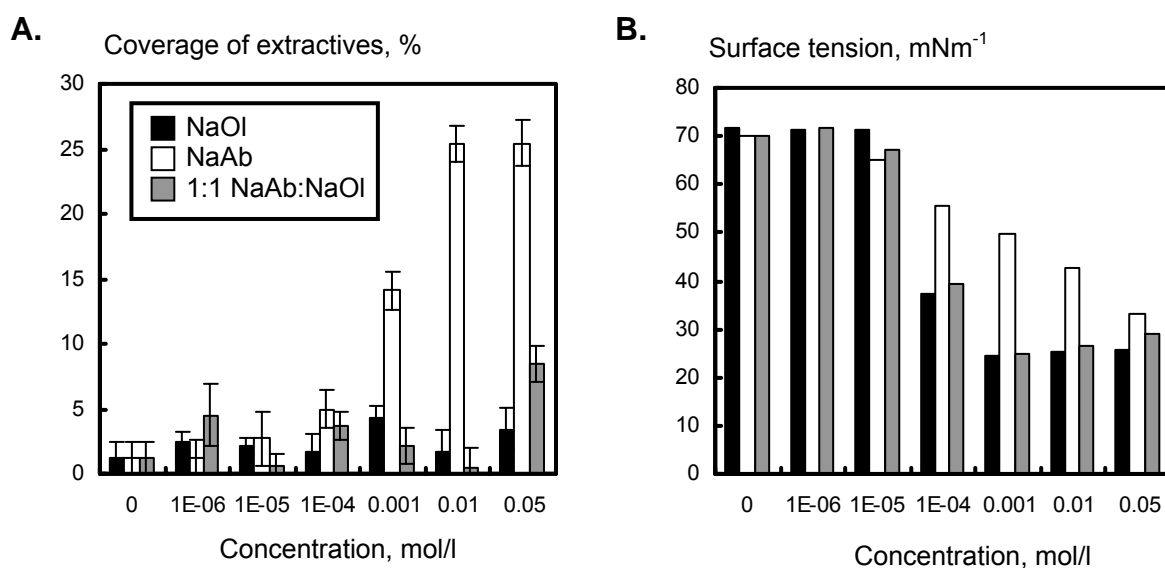


Fig.17 a) Surface coverage of extractives on the kraft pulp surface by ESCA and b) surface tension of pulp suspension. Cmc values in water for NaOI 0.00048 mol/l, NaAb 0.010 mol/l and 1:1 NaAb:NaOI 0.001 mol/l (Palonen et al. 1982).

The surface chemical composition of the samples after the adsorption of pitch extracted from unbleached TMP was also determined (Fig. 18). Different electrolytes (Na and Ca) and electrolyte concentrations were used. The adsorption measurements were performed approximately at pH 7. A cationic polymer, PDADMAC, was pre-adsorbed on the surface to enhance the adsorption. PDADMAC is commonly used as a fixing agent in order to promote aggregation of colloidal material with the fibres. As expected, the coverage of pitch increased when PDADMAC was pre-adsorbed or Ca ions were present in the solution. Surprisingly, a higher concentration of NaCl had no clear effect on the surface coverage of pitch.

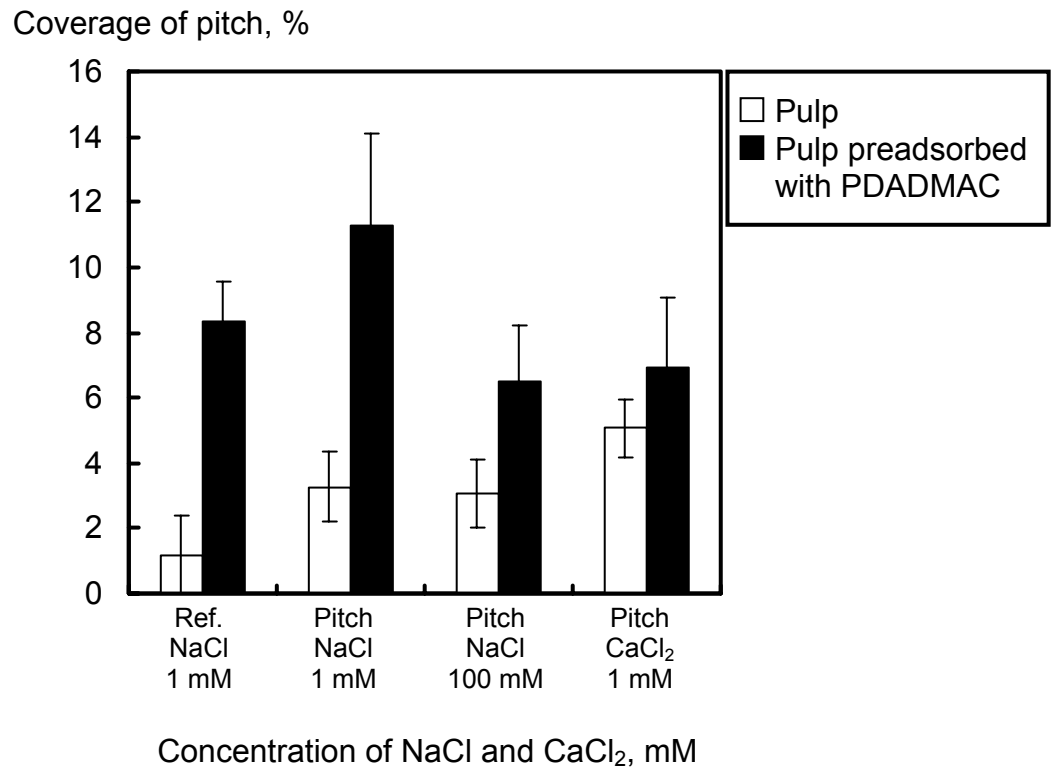


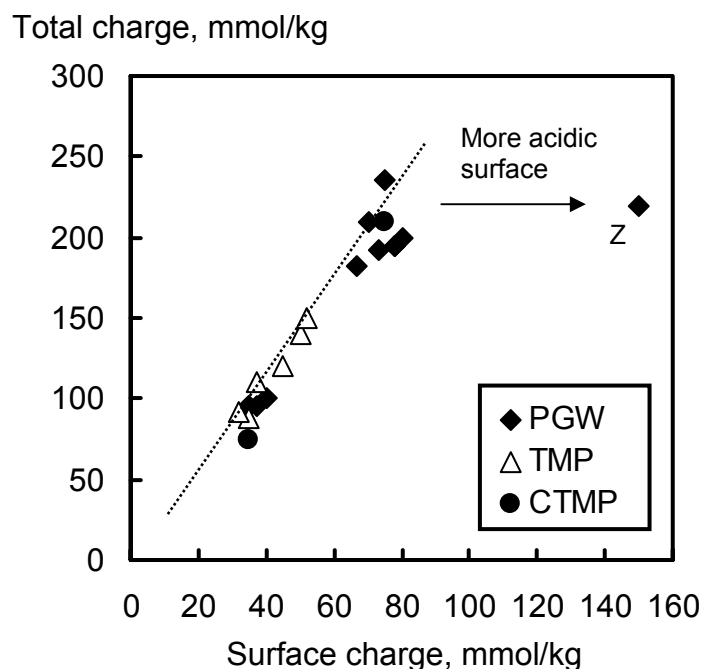
Fig.18 Effect of electrolyte, electrolyte concentration and PDADMAC on the coverage of pitch (P) on kraft pulp surface by ESCA. Pitch concentration is ~5 mg/g dry weight pulp.

5.3 Pulp charge

Mechanical pulps

The results of pulp charge determinations for mechanical pulps are presented in Paper II. Methylglucuronic acid (MeGluA) in xylan and galactouronic acid (GalA) in pectin, together with sulphonic acids in CTMP, were found to account for 30-90% of the charge for mechanical pulps. Charge distributions in unbleached PGW and TMP were quite similar. Unbleached CTMP, which contained sulphonate groups, had the highest charge of all. It is well known that the pulp charge has an effect on the swelling of the pulp as well as the adsorbed amount of cationic additives, and thereby on the bonding properties of the pulp.

The total charge determined by polybrene adsorption (M_w 8000) is plotted against the surface charge determined by PDADMAC (M_w 100 000-300000) in Fig. 19.



In most of the pulps, about 35% of the charged groups are accessible to a high M_w polyelectrolyte, whereas about 70% of the groups are accessible to PDADMAC after ozone treatment. An increase in polymer adsorption, i.e. pulp charge, may also partly be explained by changes in topography caused by the ozone treatment.

The treatments caused the following changes in charge profiles:

Dithionite bleaching (Y). Both the surface and total charge were only moderately increased.

Alkaline treatment (E) and peroxide bleaching (P). Both the amount of the surface and total charge increased two to threefold over that of the untreated pulp sample. The main reason for this is the demethylation of methyl ester groups in pectins, which results in the formation of carboxyl groups bound to the pectins and release of methanol into the surrounding solution (Fig. 20). The alkaline treatment appears to be mainly responsible for the major part of the charge increase, while peroxide bleaching introduces some more carboxyl groups into the pulp.

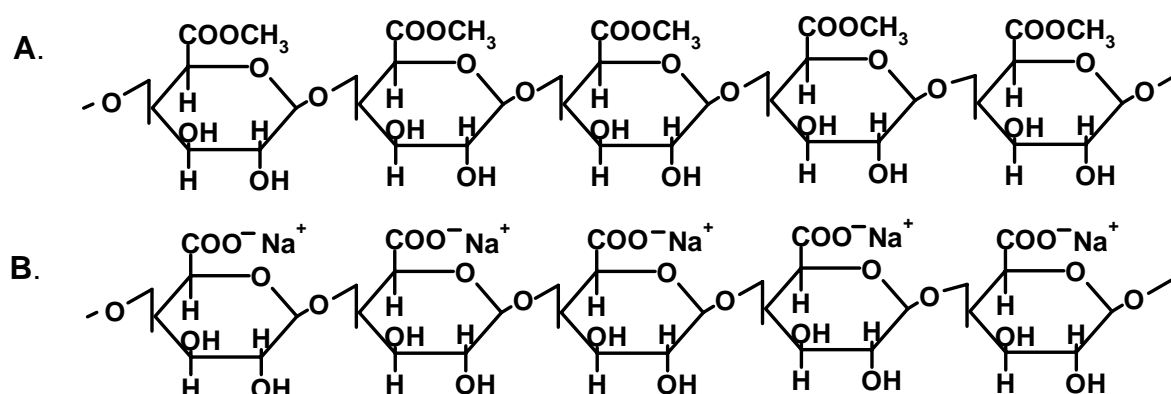


Fig.20. Methyl esterified galactouronic acid groups in pectin (A) are demethylated in an alkaline environment. Pectate (B) and methanol are formed.

Ozone treatment (Z). Not only the total charge but especially the surface charge of the PGW pulp was markedly increased. The outermost surface of the ozone-treated pulp is more acidic than that of the unbleached PGW pulp. The increase in the charge is most probably due to formation of carboxylic groups in lignin (Fig. 21).

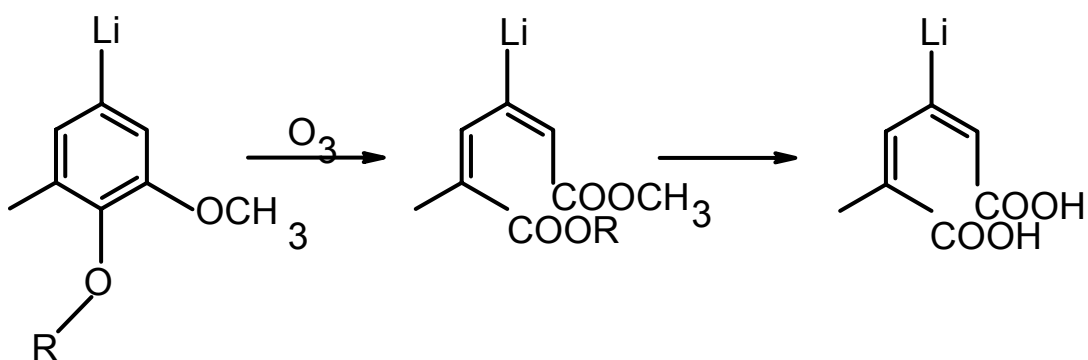


Fig.21 Formation of muconic acid structures in lignin (Li) after ozone treatment.

Although most of the carboxyl groups originate from xylan and pectin, some of the acidic groups originate from carboxyl groups attached to lignin and maybe also extractives. Some acidic groups bound to another wood component may be covered by a high amount of extractives, and/or may also hinder the hydrolysis of methyl ester groups in pectin in alkaline conditions. This phenomenon was observed with TMP-P pulps (Fig. 22).

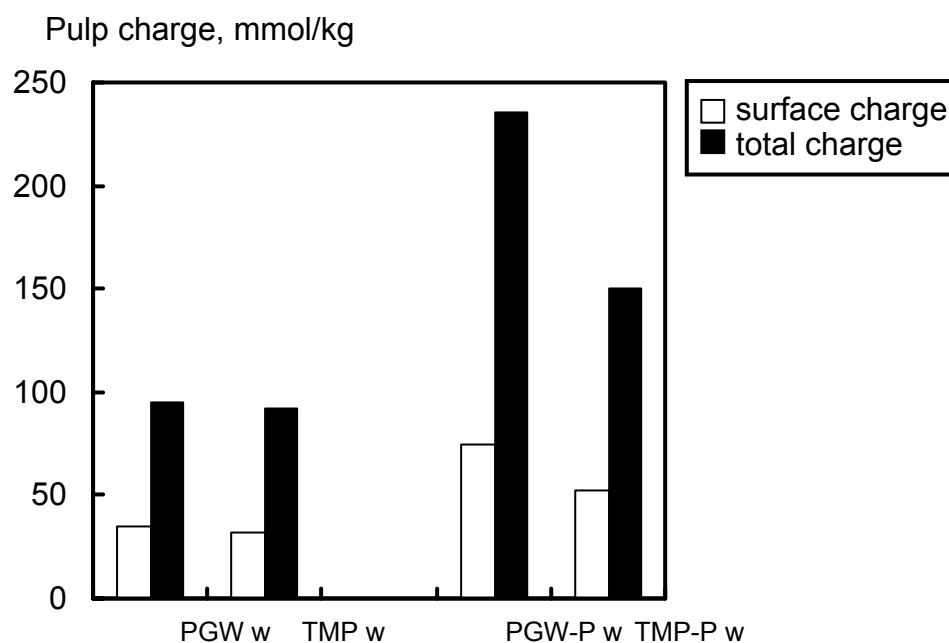


Fig.22. Effect of peroxide bleaching on charge of mechanical pulps (Paper II).

Chemical pulps from closed mills

No clear differences were observed between the charges of pulps from a highly closed mill and open-system laboratory softwood and hardwood pulps (Fig. 23). Most of the carboxylic groups in kraft fibres originate from hexenuronic acids (HexA) in xylan (Buchert et al. 1993), whereas a minor part consists of the MeGluA that has not been converted to HexA. Approximately 80% of the charges have been reported to originate from uronic acids (MeGluA and HexA), while ~20% appears to be lignin-bound weaker acid groups (Laine 1996). Fig. 23 shows that about 50 mmol/kg originates from other structures than HexA.

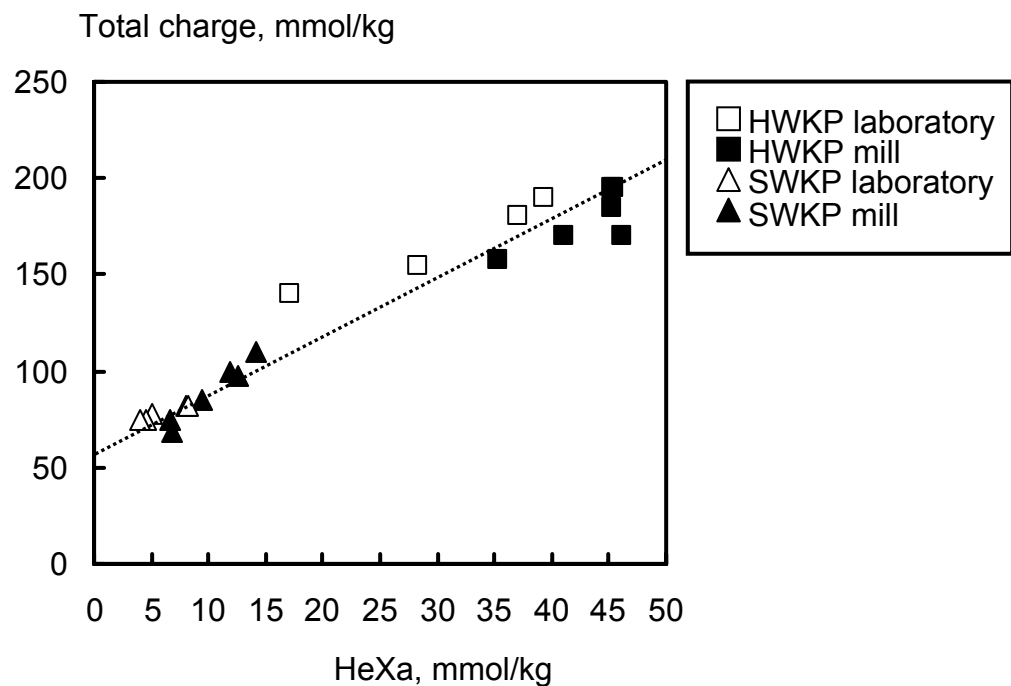


Fig.23 Correlation between total charge and hexenuronic acids (HexA) for hardwood (HWKP: O-Q-P-Q-(PO)P) and softwood (SWKP: O-O-Z-PO-Q-PO) kraft pulps. Total charge was determined by polybrene adsorption.

5.4 Surface energy of single fibres

The surface energy properties of the mechanical pulps were evaluated by contact angle analysis made on single fibres applying the Wilhelmy technique (Paper I). Water, ethylene glycol and α -bromonaphthalene were used as wetting liquids. The Good-van Oss approach was used to obtain the dispersive, acid and base components of surface energy. Values for solvent probes proposed by Della Volpe and Siboni (2000, 2001) were applied. According to these researchers, water is predominantly acidic in character (γ_L^+/γ_L^- 4.3:1). This differs from the conventional assumption by van Oss (1994) that the base and acid parameters of water are equal (γ_L^+/γ_L^- 1:1). Furthermore, the van Oss-Chaudry-Good approach (Lee 1996) was used to obtain the Lewis acid-base (AB) and Lifshitz- van der Waals (LW) contribution to the work of adhesion (W_a).

The results revealed that the Lewis base parameters of the fibres examined are substantially greater than the Lewis acid parameters (Paper I). If water is predominantly acid, the basic groups on the fibres will interact more strongly with water than with the acid groups. Therefore, the water/fibre interaction is predominantly due to the basic groups in the fibres. However, this does not exclude the possibility that the fibres may contain even a lot of acid groups that do not interact with water, as shown in Chapter 5.3.

The increased hydrophilicity was due to an increase in the Lewis base parameter of the fibres, i.e. the exposure of more basic groups in the fibres resulted in increased adhesion of the acid water (Fig. 24). Additionally, the removal of extractives from the fibre surface increased the basicity/ hydrophilicity. The differences seen in adhesion values were due to the changes caused mainly in acid-base (W_a^{AB}) interactions, whereas the Lifshitz-van der Waals (W_a^{LW}) interactions did not change to any greater extent. Among the unbleached fibres, CTMP fibres were found to be the most hydrophilic ones, resulting in the lowest contact angle between water and fibres. The lignin-modifying treatments, such as ozonation, sulphonation and sulphonation followed by peroxide bleaching, also increased the hydrophilicity of the fibres.

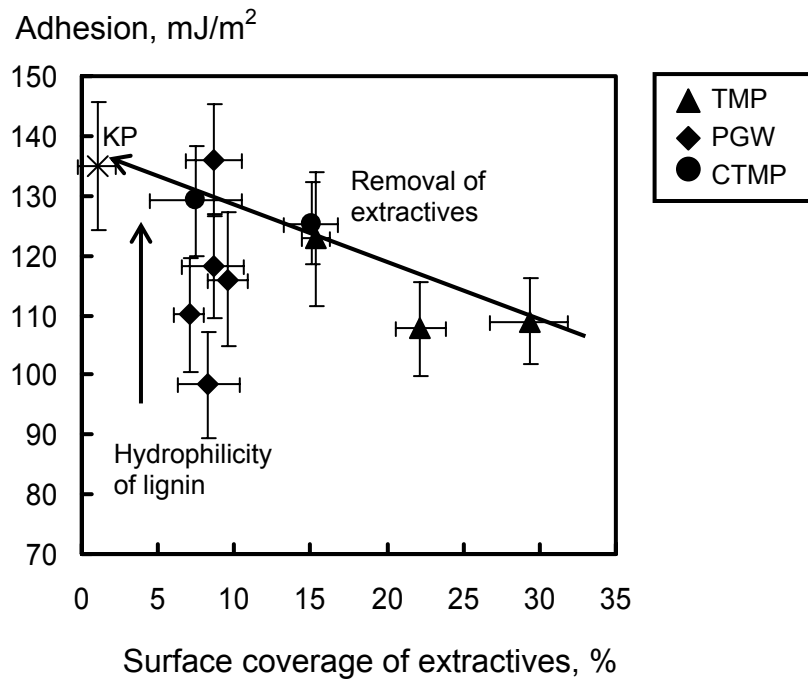


Fig.24. Work of adhesion between fibres and water as a function of the surface coverage of extractives. KP is fully bleached softwood kraft pulp (FINE pulp). Arrows indicate trends.

5.5 Effect of surface properties of fibres on strength properties of paper

5.5.1. Mechanical pulps

Mechanical pulp strength is strongly affected by the fines content, i.e. the freeness of the pulp, which makes comparison of the different mechanical pulps difficult. However, some attempts were made to find correlations between the surface properties of pulps and paper properties.

To examine the effect of the charge properties of pulp on the strength properties of paper, a test series with PGW pulp was made in which the time of alkali treatment was changed (Fig. 25). The demethylation of methyl ester groups in pectins results in the formation of carboxyl groups bound to the pectins, which is a time-dependent phenomenon (Pranovich et al. 2003). As Fig. 25 shows, both tensile strength and total charge of the pulps were increased. The acidic group content seems to become constant at high values of paper strength. The constancy of the acidic group content may be due to the dissolution of material containing acid groups from the cell wall as fast as or faster than new acidic groups are being generated (Katz and Scallan 1983). The prolonged alkaline treatment may also delaminate the fibre wall.

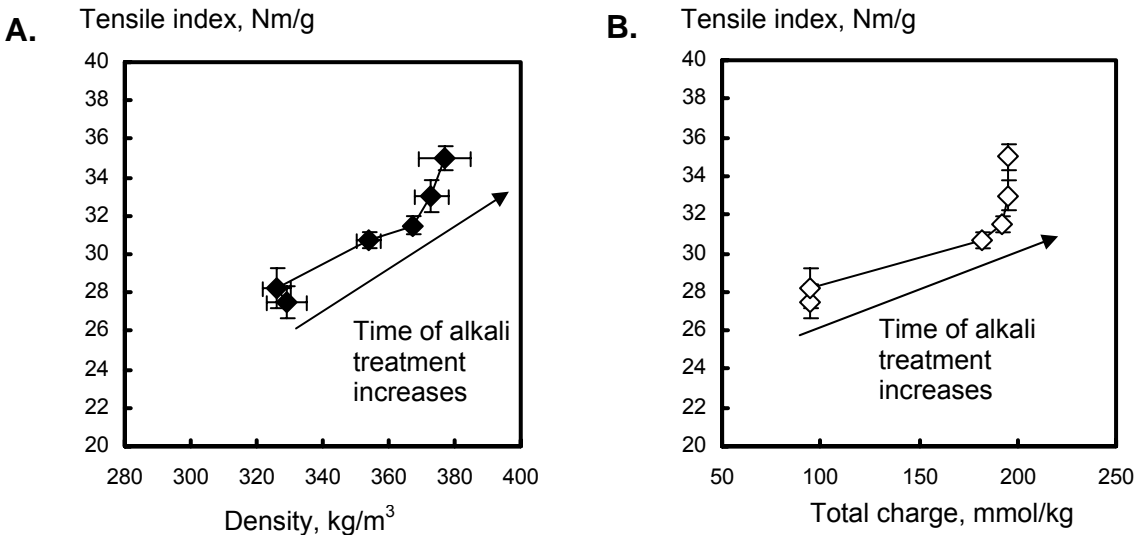


Fig.25. Tensile index A. as a function of density and B. as a function of charged groups for PGW samples where time of alkali treatment was 0, 0.5, 1, 3 and 6 hours.

Fig. 26 shows that there is a clear correlation between the tensile strength and density of the paper sheet for all pulps. A linear correlation between tensile index and density *within the*

same pulp grade shows that fibre dimensions have not changed. The effect of treatments on tear strength was found to be related to density in a similar way, but the increase was not so evident. The high-freeness CTMP pulps, because of their low fines content, have low density and tensile index (Fig. 26B), but high tear strength. The tensile strength indexes are affected by fibre length, fibre strength, the number and strength of fibre-to-fibre bonds (RBA and SBS), while the tear index is also affected by the total number of fibres involved in the tear itself (Rothenberg et al. 1981).

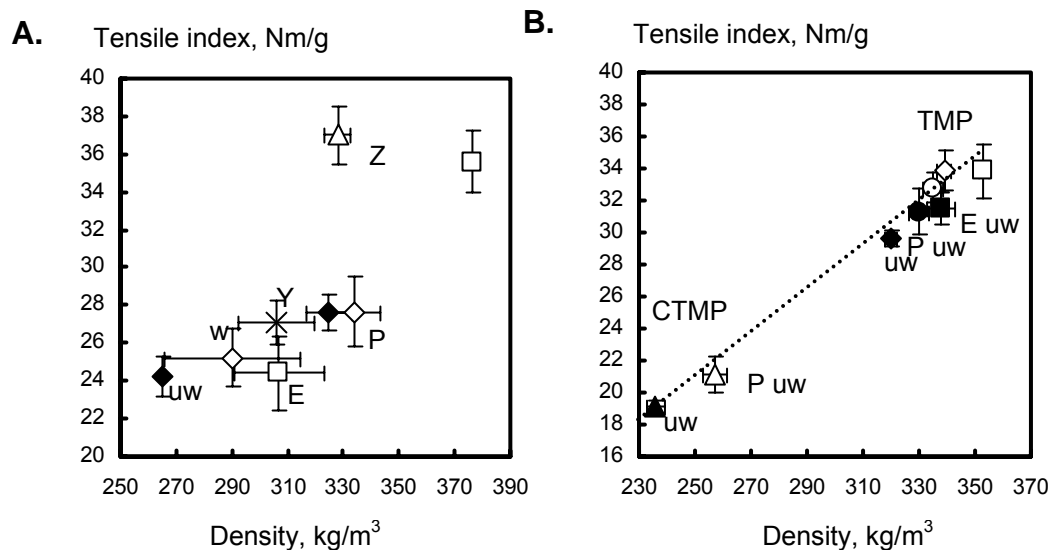


Fig.26. Tensile index as a function of density for A) PGW pulps and B) TMP and CTMP pulps. Open symbols represent water-washed (w), alkali-treated (E), peroxide-bleached (P) or ozone-treated (Z) pulps, whereas filled symbols represent the unwashed (uw) pulps. The effect of washing of TMP pulp on strength properties is seen in Fig. B. The line indicates the trend.

Water washing of the TMP pulps was found to increase both tensile strength and density. Among the PGW pulps, ozone-treated pulps differed clearly from the others (Fig. 26A). The effects of treatment can be caused mainly by (Retulainen and Nurminen 1993):

- a. an increase in RBA due to enhanced fibre conformability,
- b. an increase in SBS due to a change in chemical conditions on the fibre surface and/or
- c. an increase in the number of fibres.

Oxidative treatment with ozone resulted in a significant increase in the tensile index of PGW pulp, but not in the tear index (Fig. 26A). The main reason for the improvement is the

increase in density of the handsheet. This increase is related to both fibre flexibility and, possibly, interfibre bonding (SBS). It has been suggested that the increase in the chemical bonding ability is the main mechanism after ozone treatment of mechanical pulp rather than fibre flexibility (Lindholm 1977). The introduction of carboxyl groups (E, P) improved strength values, but not to the same degree as ozone treatment (Fig. 26A). The development of density suggests that the relative bonded area (RBA) increases progressively with increasing carboxyl content. With decreasing yield the number of fibres per gram and the total surface area also increase. The increase in the RBA of fibres is due to the increased conformability.

Mechanical fines can affect both light scattering and bonding. Therefore, the relative bonded area cannot be determined from light scattering properties as for kraft pulps (Stratton 1991). The difference in the amount of fines *between various pulps* is clearly seen in Fig. 27.

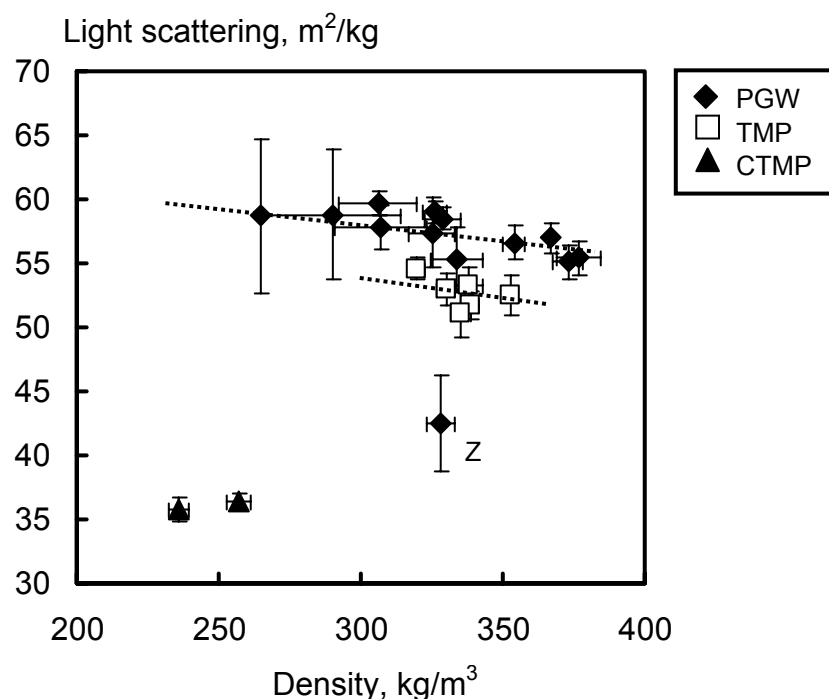


Fig.27. Light scattering as a function of density for mechanical pulps. The lines indicate trends.

However, the change in light scattering was fairly stable during the development of sheet density for PGW and TMP pulps (Fig. 27). On the other hand, changes in light scattering may be caused by modification of the fibre surface structure at the wavelength scale of light. This is the case especially in ozone-treated PGW pulp which scatters less than other PGW pulps.

Furthermore, during alkaline and ozone treatment there was a noticeable yellowing of the pulps, with a resultant brightness decrease, which can affect the light scattering value. It is known that the Kubelka-Munk theory cannot be applied to distinguish changes in light scattering coefficient from changes in light absorption (Retulainen and Nieminen 1996).

It has been shown that a decreased degree of bonding in sheets made solely from fines results in an increase in the optically active surface area and thus in the light scattering coefficient (Luukko et al.1999). This, in turn, suggests that the decrease in light scattering seen in Fig.27 could be also due to a decrease in the extractives content.

WRV values were measured in water and in 0.5 M NaCl solution and plotted as a function of total charge (Fig. 28). The difference between the WRV values of water and NaCl solution gives a measure of how much the water retention is based on osmotic pressure as a consequence of counter ions dissociating from the fibre. Fig. 28 shows that only a very small portion of the water retention can be explained by the fibre charge. The results confirm that fibres swell more after introduction of carboxylic groups.

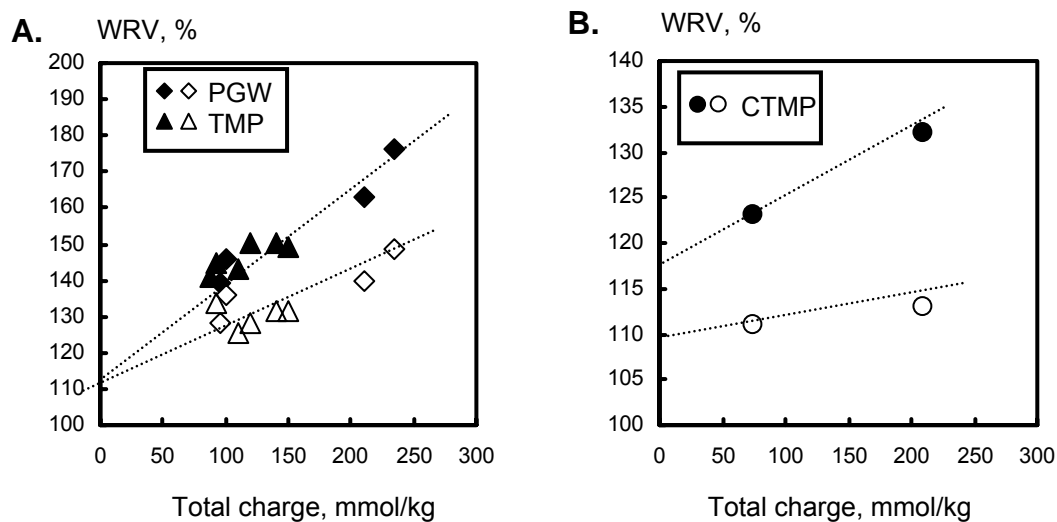


Fig.28. Water retention value (WRV) as a function of total charge for A. PGW and TMP pulps and B. CTMP pulps. Filled symbols represent WRV values measured in distilled water and open symbols represents WRV values measured in 0.5 mM NaCl. Total charge was measured by polybrene adsorption. The lines indicate trends.

A quite good correlation between tensile index and coverage of extractives is obtained within the same pulp groups (Fig. 29).

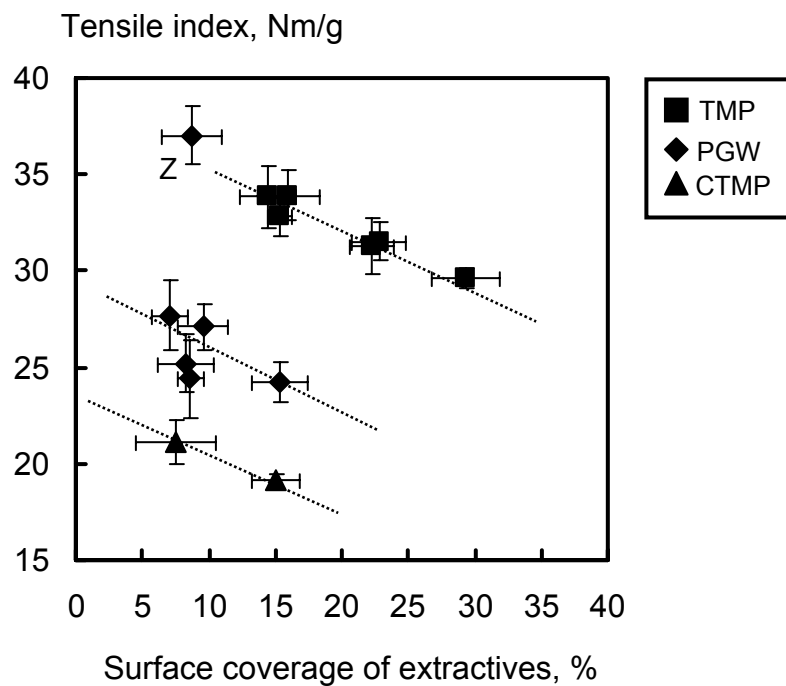


Fig.29. Tensile index as a function of coverage of extractives by ESCA. The lines indicate trends.

5.5.2 Adsorbed material on chemical pulps

Kraft lignin or PES-Na on PDADMAC covered surface

The effect of adsorbed kraft lignin on the Scott Bond value of paper sheets is illustrated in Fig. 30A. PDADMAC impairs the bonding between fibres. Its high molecular weight and charge density probably cause flocculation of fibres, which results in weak zones in the sheets and thereby lower tensile index, as demonstrated with TMP pulp fines (Rundlöf 2002). On the other hand, when PDADMAC was pre-adsorbed onto the fibres before addition of lignin, the Scott Bond increased, showing that the otherwise anionic and hydrophobic component may form a complex with cationic polyelectrolyte, producing an effect opposite to that of pure adsorbed kraft lignin. The same effect was verified with anionic polyethylene sulphonate (PES-Na), though the effect was weaker. This suggests that it is the complex of anionic and cationic polyelectrolytes formed between fibres that increases the bonding between fibres.

At a small coverage of NaOI, the bonding of the fibres was increased until a certain concentration ($c > 0.01$ M) was reached (Fig. 30B, no PDADMAC added). Thereafter, the bonding decreased noticeably. The same effect was seen also with NaAb and the 1:1 NaOI:NaAb mixture. The increase at low levels of surfactant or surfactant mixture addition may be caused by the lubrication effect between fibres.

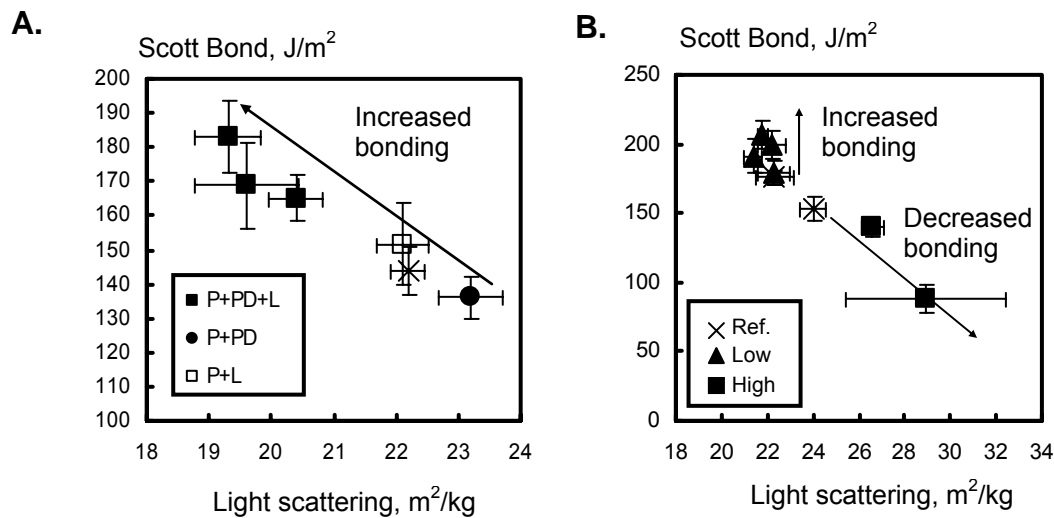


Fig.30 Scott Bond as a function of light scattering coefficient for A) kraft lignin series and B) NaOI series. At high levels of addition, NaOI (B) and PDADMAC (A) impair bonding, while at low levels of addition, NaOI (B) and PDADMAC-kraft lignin complexes (A) strengthens the paper. Arrows indicate trends.

The in-plain tear (IPT) test was also used to determine the bonding ability of kraft fibres. Kettunen (2000) found a common trend for reasonably well-bonded papers where IPT work was found to be almost directly related to damage width. Measured variations arose from variations in fibre length and fibre strength. The translation of reference pulps (open symbols) to the right from the trend line results from the removal of fines from the pulps before treatment (Fig. 31).

The results were in good agreement with the Scott bond results, showing that combinations of kraft lignin-PDADMAC and PES-Na-PDADMAC increase the bonding between fibres, whereas model compounds of fatty acid (NaOI) and resin acid (NaOIAb) and a mixture of these (1:1) decrease bonding at high levels of addition.

6 DISCUSSION

Untreated mechanical pulps

The contact angle results in Paper I showed that the mechanical fibres from the same sample were extremely heterogeneous, indicating that there are small-scale variations in the outermost surface of fibres. This is because fibres rupture at different points of the fibre wall, and the treatments directed at them are not always evenly distributed. Since the tensiograms give information on the chemical distribution, the roughness of the fibre surface and alteration in perimeter, it is difficult to specify the exact cause of the changes.

The different parts of the fibre wall were clearly revealed by AFM (Paper IV). The S2 layer was observed in both PGW and TMP pulps. The more irregular phase was interpreted to consist of the primary wall or middle lamella. It is difficult to give any exact proportions of cell wall layers on the surface since only ten images were measured. The results are in good agreement with earlier results, according to which the rupture of the TMP and PGW fibre wall occurs between primary and secondary walls, preferentially between the S1 and S2 layers (Fig. 2).

The surface of unbleached CTMP differed from those of unbleached PGW and TMP pulps. The surface of CTMP pulp was more hydrophilic and basic (Lewis base parameter) (Paper I), contained more acidic groups (Paper II) and was more covered by lignin and a granular structure (Paper IV). The charge is partly due to sulphonic groups introduced into the pulp (Beatson et al. 1984, Peng et al. 1992), but also partly due to demethylation of methyl ester groups in pectin. During manufacture of CTMP pulp, the pH is apparently so high (pH>9) that demethylation could also take place. The granular layer was interpreted to originate from the middle lamella and the primary wall. It is also possible that the sulphonated lignin may exhibit granular structures. However, the content of sulphur detected in the surfaces was rather low for CTMP pulps (S_{2p}=0.20-0.30 %, sulphonic acid ~50 mmol/kg). This supports the hypothesis that fracture occurs in non-sulphonated regions, as suggested earlier (Börås and Gatenholm 1999b). On the other hand, the sulphonated lignin layer, because of its high hydrophilicity, may be removed from the surface region during pulping. Nevertheless, the results revealed by different techniques are supported by recent studies according to which the

middle lamella has a fine irregular network (Hafrén et al. 2000), and the rupture of the fibre wall during CTMP refining takes place preferentially in the primary layer (P) and in the middle lamella (ML) (Fig. 2).

The unbleached fibres were predominantly basic (high Lewis base parameter values), whereas the Lewis acid parameter seemed to be clearly lower (Paper I). If water is assumed to be predominantly acid, the basic groups on the fibres will interact more strongly with water than with the acid groups. Therefore, the water/fibre interaction is predominantly due to the basic groups in the fibres. Consequently, the fibres may contain a lot of acid groups that do not interact with the water. Indeed, the polyelectrolyte titration results showed that acidic groups were introduced in the fibres during the treatments (Paper II). Supporting the surface energy results presented in this thesis work, numerous wood fibres and wood surfaces have also been found to be more basic than acidic using the Wilhelmy technique/ wetting approach (Wågberg and Annergren 1997, Shen et al. 2000, Wålinder 2002).

Chemically treated mechanical pulps

When mechanical pulp is bleached with lignin-preserving chemicals, such as peroxide or dithionite, a certain amount of easily reducible chromophores is removed, while practically no lignin is released from the pulps (Holmbom et al. 1991, Gellerstedt 2001). In this study, the surface lignin content of mechanical pulps indicated the same trend. However, the outermost surface of CTMP was an exception. The granular layer disappeared from the CTMP fibre surface after peroxide bleaching, exposing the underlying structure. However, the surface content of lignin determined by ESCA was not reduced. This would, indeed, support the notion that sulphonated lignin dissolves during bleaching, but some lignin in non-granular form is retained on the surface of CTMP pulps.

Hemicelluloses and pectins are modified during peroxide bleaching. According to the polyelectrolyte titration results (Paper II), the amount of carboxylic groups in unbleached PGW pulp was doubled by the alkaline treatment, while the peroxide bleaching introduced a somewhat larger amount of these groups. The results are in agreement with earlier results, according to which methyl ester groups in pectin are demethylated (Fig. 20) (Holmbom 1997, Pranovich et al. 2003), and carboxyl groups are introduced into lignin (Engstrand et al. 1991,

Holmbom 1991, Kuys 1992, Sundberg 2000, Pranovich et al. 2003). On the other hand, the introduction of acidic groups after alkaline treatments made in the laboratory was not so clear for TMP pulp. The alkaline treatment of TMP pulp probably does not demethylate all the methyl ester groups in pectin, or the high content of extractives of the TMP pulp may prevent polyelectrolyte from penetrating into the fibres. ESCA measurements of these pulps support the latter suggestion, since more extractives were found on the surface of the TMP pulps than on the PGW pulps (Paper IV). It has been noted earlier that the extractives are not always removed from the pulp in alkaline conditions and during peroxide bleaching (Muustranta et al. 1998).

In contrast to peroxide bleaching, dithionite bleaching did not change the charge density of the PGW pulp. The mild acid conditions during dithionite bleaching have no effect on the methyl ester groups in pectin. Dithionite is known to simply reduce the easily reduced chromophores, such as quinones in lignin (Gellerstedt 2001).

The ozone treatment clearly modified the surface of PGW pulp, introducing new carboxylic groups (Paper II), notably increasing the hydrophilicity and Lewis base parameter of fibres (Paper I) and decreasing the amount of granules on the fibre surface (Paper IV). The formation of carboxylic structures was indicated by an increase in the C4 and C3 bands in the high-resolution C1s spectrum after DCM extraction. It is known that ozone reacts mainly with lignin, breaking unsaturated bonds to produce carbonyl and carboxyl end structures, thereby increasing the hydrophilicity of fibres (Rothenberg et al. 1981, Katz and Scallan 1983). The formation of new carboxylic groups and muconic acid structures in lignin fractionated from TMP pulp after ozonation has been identified by the NMR technique (Robert et al. 2000). Thus, the increase in acidic groups after ozone treatment of the PGW pulp most probably is due to carboxylic acids bound to lignin, although this could not be directly verified from the polyelectrolyte titration results. It must be kept in mind that an increase in polymer adsorption, i.e. pulp charge, may be partly explained by changes in morphology on the fibre surface after ozone treatment (Paper IV). Modification of the surface after ozone treatment of high-temperature TMP pulp has also been observed with transmission electron microscopy (Kibblewhite et al. 1980).

Extractives on mechanical and chemical pulp surfaces

The large amount of extractives on the fibre surface is very likely due to reprecipitation of dissolved extractives occurring during mechanical pulping (latency removal, screening) and during fractionation with the Bauer McNett apparatus. In particular, the fines fraction was enriched with extractives. A high content of extractives (concentration above cmc), low pH (Paper III), presence of cationic polyelectrolyte and a high content of calcium were found to increase the adsorption of extractives on the pulp (Chapter 5.2). Extractives contain free fatty and resin acids and, hence, affect the amount of carboxylic groups. However, their contribution to the charge in mechanical pulp fibres or fines has been found to be quite low, about 0-1.5 mmol/kg (Sundberg et al. 2000, Mosbye et al. 2002).

For both mechanical (Paper IV) and chemical pulps (Paper III), water washing effectively reduced the content of extractives. This is in accordance with earlier results (Allen and Maine 1978, Lloyd et al. 1990, Suckling et al. 1990). Water washing removes a large portion of colloiddally dispersed resin as well as some of the resin on the mechanical pulp fibres. Since extractives were not removed as efficiently from the TMP pulp as from PGW pulp, it is possible that extractives are washed differently from various fines (flake-like, ray cells, fibrillar) (Luukko 1999, Mosbye 2003, Kangas et al. 2002, Kangas and Kleen 2003). However, the composition of fines fractions were not characterised in detail in this work.

It has been shown earlier that the adsorption of colloidal extractives increases at low pH (Back 2000, Mosbye et al. 2003). pH also has an influence on the washing efficiency (Ekman et al. 1990). It is known that neither fatty and resin acids nor neutral lipophilics, such as triglycerides and steryl esters, are efficiently washed away from the pulp at pH 5.5, whereas at pH 8 fatty and resin acids are more effectively removed than neutral lipophilics.

The precipitation of dissolved extractives in the filtrate onto the pulp (Paper III) is readily explained by their colloidal behaviour (Allen 1975, Palonen et al. 1982, Suckling et al. 1990). While the corresponding acids are very insoluble, fatty and rosin acid soaps are surfactants, i.e. they are very soluble and form micelles above a critical micelle concentration (cmc) (Ekwall and Lindström 1941, Harva 1951, Palonen et al. 1982). Above the cmc, the solubility of neutral extractives is enhanced by solubilisation in the micelles. Micelle formation depends on the pH, temperature and electrolyte concentration of the surrounding solution. At pH above

6, the acids are almost fully dissociated and the total solubility of extractives increases, at high pH perhaps even to the extent that the cmc is exceeded and neutral extractives are solubilised. When pH is lowered below pH 8 (pH 8-6), dissolved soaps precipitate as resin and fatty acids, or are not dissolved out of the fibre surface, because they are mainly present in undissociated form in the fibres (Suckling et al. 1990).

The precipitation of electrostatically stabilised particles of extractives by calcium ions is well known (Sundberg 1995, Back 2000). The negatively charged particles are stabilised by repulsion between the diffuse ion double layers around them. They aggregate if these repulsive forces are screened by adding a sufficient amount of electrolyte. The amount of electrolyte needed for destabilisation depends on the counter-ion valence. Cationic polyelectrolytes are also used as “fixing agents” in the industry. A commonly accepted view of the mechanism of action of these cationic polymers is that they fix anionic wood polymers or anionically stabilised colloidal particles to cellulose fibres or cellulosic fines in the papermaking pulp by activating or neutralising the particle charge (Wågberg and Ödberg 1991).

In this study, attempts were also made to detect extractives with AFM by examining both unextracted and extracted mechanical pulp samples, but structures that could be associated with extractives on the fibre surface could not be clearly identified. Since extractives were detected by ESCA, it is possible that some of the non-fibrous material observed in the AFM images consists of extractives, but this cannot be verified by AFM. Darker areas were also seen on the surface of kraft fibres after lowering the pH (Paper III). These darker areas detected in the AFM phase images may also be extractives, although it could not yet be definitely ascertained how extractives can be identified in AFM phase images.

The equations for calculating the surface coverage by extractives and lignin are valid, provided that extractives and lignin are distributed on the fibre surface in patches thicker than the ESCA analysis depth (Paper IV). Recent studies of mechanical pulp fibres using Tougaard analysis have shown that extractives may in some cases form monomolecular films, which may at least partially cover the fibre surface, whereas lignin on the cellulose surface most probably occurs in the form of patches, which are thicker than 10 nm (Johansson 2002). These results indicate that the calculation of the surface coverage of lignin is correct, while it may be

somewhat uncertain in the case of extractives. The ToF-SIMS observations also suggested that the extractives cover the pulp as a thin layer (Paper III). Typically, the escape depth of electrons from organic material detected by ESCA is such that 95 % of the information comes from a 5-7 nm thick surface layer. The depth of analysis of static SIMS is typically ~ 1 nm. Hence, the information provided by these surface techniques comes from different depths in the pulp surface. Obviously, ESCA will be sensitive both to pure lignin and lignin below a very thin layer of extractives, which may nevertheless be so thick that ToF-SIMS will not detect lignin below it.

Lignin on mechanical and chemical pulp surfaces

The surface content of lignin was equal to the average content of lignin in the mechanical pulp fibres. However, the lignin-rich middle lamella may cover the outermost surface of the fibres, as was shown for the unbleached CTMP pulp. Although the amount of lignin is not significantly changed, the lignin is modified. Especially sulphonation, ozone treatment and peroxide bleaching made the lignin more hydrophilic (Paper I). Low pH (Paper III) and a high content of calcium were found to increase the adsorption of kraft lignin on the kraft pulp (Paper V, Maximova and Stenius 2001, 2004a, Li 2003). However, circulation of effluents in highly closed bleaching plants did not cause any precipitation of lignin on the surface (Koljonen et al. 2000).

The granular and fibrillar structures on the surface of unbleached PGW and TMP pulps are mainly interpreted as lignin and cellulose/hemicellulose, respectively. This assumption is logical, since residual lignin on kraft pulp fibres (Simola et al. 2000, Simola-Gustafsson et al. 2001, Pereira et al. 2001, Gustafsson et al. 2002) as well as adsorbed lignin (Chapter 5.1.2) have been detected in granular form by AFM. However, mechanical pulps consist of several wood constituents, such as pectin, xylan and extractives, which have not been identified by AFM. It has also been proposed that adsorbed xylan on CTMP pulp fibres has a granular structure (Henriksson and Gatenholm 2002). In the present study, the granular structure was found to occur mainly on unbleached CTMP, for which there is no reason to assume that large amounts of xylan would be initially present on the surface, or that xylan would have precipitated on the surface. Since no clear differences between unextracted and extracted

samples were detected by AFM, we may assume that in this case the observed changes are not related to extractives to any significant extent.

The precipitation of lignin on kraft pulp fibres can at least partly be explained by its colloidal behaviour (Lindström 1980, Rowan and Scott 1992). In particular, the part of the lignin with high molecular mass has been reported to form particles of colloidal dimensions (Sundin and Hartler 2000). A low NaCl concentration further promotes the formation of large lignin fragments (Norgren et al. 2001). Because the carboxylic groups in the lignin (and, at very high pH, also phenolic hydroxyls) are ionised, kraft lignin dispersion will be stable at high pH. When pH is lowered, the charge decreases and the dispersed lignin becomes unstable and coagulates, which may result in precipitation onto the pulp.

Effect of chemical structure of pulp surface components on properties of paper made from mechanical pulps

The charge of fibres was found to be one of the main contributors to the strength of mechanical pulps. Ozone and alkaline treatment and peroxide bleaching were found to increase the tensile index. A major reason for the improvement was the increase in density of the handsheet. This increase was related both to fibre flexibility and, possibly, interfibre bonding (SBS) in ozone treated PGW pulp, whereas the relative bonded area (RBA) and conformability increased for alkaline and peroxide-bleached pulps. These results are in agreement with earlier results, according to which modification of lignin by breaking of cross-linked bonds with acid chloride, peracetic acid or ozone treatment leads to increased formation of hydrophilic groups. Thus, the pulp fibres become more swelling, flexible and conformable (Rothenberg et al. 1981, Carlsson et al. 1983). The mechanism of aromatic ring cleavage in the lignin matrix is believed to be the main factor increasing the flexibility of the fibre. Alkali strengthening of mechanical pulps by introducing new carboxylic groups which result in increased swelling is also a well-known phenomenon (Katz et al. 1981, Katz and Scallan 1983, Korpela 2002).

If the charge increases in a pulp, the osmotic pressure inside the pulp increases and more water is transported into it, i.e. it swells more. This most probably leads to stiffening of the free fibre in solution. It seems reasonable to assume that such a swollen fibre, when dried, will

not go back to its original shape but will remain more flexible and/or expose more contact area with other fibres than before acquiring a high charge.

The strength of paper made from mechanical pulps was also affected by the extractives. A critical value of 45% for surface coverage by extractives on thermomechanical fines (TMP), above which the tensile strength index begins to decrease, has been reported by Rundlöf et al. (2000b, 2002). Luukko (1999) has also shown that the tensile strength of the TMP fines sheet decreases with an increase in the surface content of extractives, a critical value being ~25 %. The results obtained in the present study suggested, however, that there is no such critical value for surface coverage of extractives on the pulp, i.e. the higher amount of extractives on the surface results in lower tensile strength.

Effect of adsorbed components on properties of paper made from chemical pulps

No clear traces of any precipitates in kraft pulps (Fuhrmann et al. 2000) or on the surfaces of these pulps (Koljonen et al. 2000) were observed. These pulps were collected from highly closed kraft mills and compared with laboratory-washed (“open-system”) samples.

Nevertheless, dissolved components may precipitate from bleaching filtrates, for example, if a poorly washed pulp from an alkaline stage is fed into an acidic stage, or if an acidic filtrate is recirculated to an alkaline stage. Therefore, material was precipitated on the pulp surfaces by lowering the pH of a pulp slurry taken after the oxygen delignification stage (Paper III). A distinct precipitation of kraft lignin was observed. The precipitated material impaired the strength and bonding properties of the kraft pulp. Especially the SBS was decreased by the precipitated material.

On the other hand, the results of another study suggest that precipitated kraft lignin alone does not significantly change the strength properties of pulp sheets (Paper V). A possible reason for this is that the lignin is easily washed with water after adsorption, as suggested earlier by Maximova and Stenius (2001). The results are in agreement with earlier results, according to which kraft lignin has no or mainly a negative effect on bonding (Lindstöm et al. 1977, Springer et al. 1985, 1986).

By adsorbing first the cationic polymer before the anionic polyelectrolyte, such as kraft lignin and polyethen sulphonate, PES-Na, the strength properties increase markedly. The cationic polyelectrolyte and the negatively charged kraft lignin form a complex akin to a water-rich gel on the fibre surface and thus increase the bond area after drying.

This effect has been thoroughly studied with kraft lignin and cationic starch by Maximova et al. (2002, 2004b), suggesting that the adsorption of complexes is highly dependent on the sequence in which lignin is added. Formation of complexes by polycations and polyanions has reported been to improve the strength of the paper in the following combinations: cationic starch and anionic carboxymethylcellulose (CMC) (Retulainen and Nieminen 1996), cationic PDADMAC and anionic CMC (Zhang et al. 2001), cationic polyamideamine epichlorohydrin (PAE) and anionic CMC (Gärdlund et al. 2003a,b), cationic polyallylamine hydrochloride (PAH) and anionic polyacrylic acid (PAA) (Gärdlund et al. 2003a,b) as well as cationic C-PAM and CMC/A-PAM (Koljonen et al. 2003). The net charge of the complex seems to be the one factor that alters the adsorbed amount (Gärdlund et al. 2003a, Maximova et al. 2004b).

No clear correlation was found between the strength properties and the amount of model compounds of extractives on the kraft fibre surface. At a small coverage of extractives, the bonding between fibres was increased until a certain concentration (about 0.01 mol/l of the model extractive) was reached, after which the bonding decreased noticeably.

One possibility is that at very low concentrations the adsorption of surface-active extractives leads to increased surface charge and stronger fibre-to-fibre bonding. Above a certain critical concentration the surface-active extractives “condense” due to hydrophobic interactions on the surface to form more coherent domains, resulting in weaker bonding between the fibres when dried. These domains reduce polar interactions or hydrogen bonding between the fibres. Indeed, it has often been suggested that the lipophilic compounds are adsorbed onto the fibre surface, preventing hydrogen bonding between fibres (Brandahl and Lindheim 1966, Sundberg et al. 2000, Rundlöf 2002). Although this type of adsorption behaviour has not been directly verified for this particular system, it is a general characteristic of surfactant adsorption on solid surfaces. The formation of aggregates at a certain critical concentration at the surface is analogous to the formation of micellar aggregates by surfactants in solution at

the critical micelle concentration, which is usually much higher than the concentrations that lead to aggregation on the surface.

It has also been shown earlier that anionic surfactants may increase the strength properties of paper made from sulphite pulp (Touchette and Jenness 1960) and unbleached sulphate pulp (Christensen 1969). On the other hand, negative effects of surfactants (resin acids, fatty acid) on the strength properties of paper made from mechanical pulps have been demonstrated (Brandahl and Lindheim 1966, Sundberg et al. 2000, Kokkonen et al. 2002). Depending on the type of pulp (kraft/mechanical or unbleached/bleached), these anionic compounds seem to behave/adsorb differently (Touchette and Jenness 1960, Christensen 1969, Friberg et al. 1975).

7 CONCLUSIONS

Generally, the results of the thesis show that a combination of ESCA, ToF-SIMS and AFM techniques yields a comprehensive picture of the chemistry and morphology of pulp fibre surfaces. Hence, these surface techniques are eminently suitable for studying pulp surfaces and precipitates on them.

Mechanical pulps

The coverage of extractives on mechanical pulps was clearly higher than the extractives content in the bulk. The large amount of extractives in the fibre surface very likely is due to re-precipitation of dissolved extractives during mechanical pulping (latency removal, screening) and during fractionation with the Bauer McNett apparatus. A large amount of extractives is found particularly in the fines fraction. Water washing removed extractives efficiently from both mechanical and chemical pulps. The removal of extractives from the fibre surface increased the basicity/ hydrophilicity of fibres.

The lignin coverage of mechanical pulps was equal to the average content of lignin in the mechanical pulp fibres. However, the lignin-rich middle lamella may cover the outermost surface of the fibres, as was shown with the unbleached CTMP pulp. Although the amount of lignin is not changed, the lignin appears to be modified. Especially sulphonation, ozone treatment and peroxide bleaching were found to introduce acidic groups into the lignin, making it more hydrophilic. The lignin-modified treatments, such as ozonation, sulphonation and sulphonation followed by peroxide bleaching, also increased the hydrophilicity of the fibres. The increased hydrophilicity was also due to an increase in the Lewis base parameter of the fibres, i.e. the exposure of more basic groups in the fibres resulted in increased adhesion of the acid water.

The way mechanical pulps are produced significantly influences their charge. Alkaline treatment mainly hydrolysed the methyl ester groups in pectin, while peroxide bleaching also increased the lignin-bound carboxyl groups. Ozone treatment produced new carboxyl groups, especially on the surface of the pulp. Introduction of sulphonate groups during CTMP pulping clearly increased the content of acidic groups in CTMP over that in PGW and TMP.

Approximately 35 % of the charged groups were found to be accessible to PDADMAC, whereas in the ozone-treated pulp up to 70 % of the charges were located on the surface.

Methylglucuronic acid (MeGluA) and galactouronic acid (GalA), together with sulphonic acids in CTMP, accounted for 30-90% of the charge for mechanical pulps. Some of the acidic groups originate from carboxyl groups attached to lignin and possibly also extractives. A high amount of extractives seems to cover some acidic groups bound to another wood component, and may also hinder the hydrolysis of methyl ester groups in pectin in alkaline conditions.

The charge of the fibres was found to be one of the factors contributing to the strength of mechanical pulps. The amount of acidic groups affects the water adsorption and the adsorbed amount of cationic additives, and in this way has an influence on the bonding properties of the pulp. Ozone and alkaline treatment and peroxide bleaching were found to increase the tensile index.

The main reason for the improvement was the increase in density of the handsheet. This increase was related to both fibre flexibility and, possibly, interfibre bonding (SBS) in ozone treated PGW pulp, whereas the relative bonded area (RBA) and conformability increased for alkaline and peroxide-bleached pulps. In addition to the charge properties, removal of extractives on the surface and the hydrophilicity of lignin also made the fibres more hydrophilic, increasing the adhesion between fibres and water.

Adsorbed components on kraft pulps

The combined ESCA, ToF-SIMS and AFM results suggest that the precipitated lignin formed a thick granular phase on the pulp surface, while the precipitated extractives formed a very thin film that may cover a large part of the pulp surface, including the lignin. The film is probably considerably thinner than the thickness of surface layers probed by ESCA.

A high content of extractives (concentration above cmc), low pH, presence of cationic polyelectrolyte and a high content of calcium were found to increase the adsorption of extractives on the pulp.

Low pH and a high content of calcium were found to increase the adsorption of kraft lignin on the kraft pulp. Acidification seems to be more important than the actual metal composition of the solutions used in acidification of the pulp, i.e. acidification is detrimental to the effectiveness of washing. This needs to be taken into account when filtrates are recycled in the bleaching or washing of pulps.

Precipitated kraft lignin alone did not significantly affect the strength properties of the pulp sheets. A possible reason for this is that the lignin was easily washed with water after adsorption. However, lowering the pH of a pulp slurry taken after the oxygen delignification stage resulted in a clear precipitation of kraft lignin. As a result of the precipitation, the strength and bonding properties of the kraft pulp were impaired. Especially the specific bond strength (SBS) was decreased by the precipitated material.

Adsorbing first the cationic polymer (PDADMAC) before the anionic polyelectrolyte, such as kraft lignin and polyethene sulphonate, PES-Na, the strength properties increased markedly. The cationic polyelectrolyte and the negatively charged kraft lignin form a complex akin to a water-rich gel on the fibre surface and thus increase the bond area after drying. In conclusion, the effect of adsorbed material on paper properties is complex and so far by no means fully understood.

No clear correlation was found between the strength properties and the amount of extractives on the kraft fibre surface. At a small coverage of extractives, the bonding between fibres was increased until a certain concentration was reached, after which the bonding decreased noticeably.

No clear traces of any precipitates on the surfaces of these pulps were found when comparing samples collected from highly closed kraft mills with laboratory-washed samples. Any precipitates formed by extractives on the pulp surface are probably washed out by the modern and efficient washing equipment that many bleaching plants are equipped with today.

RECOMMENDATIONS FOR FUTURE WORK

The following recommendations for future work are suggested:

- In this work, the introduction of carboxylic groups was found to increase the swelling of the otherwise stiff mechanical pulp. More flexible and conformable fibres are needed to increase bonding between fibres. The adsorption of carboxylic-rich polyelectrolyte may, however, mainly modify the surface and not change the flexibility of fibres.
- Another way to enhance the bonding clearly is to modify the lignin structure by breaking the cross-linked bonds. For this purpose, acid chloride, peracetic acid and ozone are commonly used.
- The use of polyelectrolyte complexes made of polycation and polyanion polyelectrolytes may increase the bonding between mechanical pulp fibres, as was shown here with the kraft fibres. The gel-like structure formed by these complexes probably acts as a glue between fibres. The polyelectrolyte complexes have already shown promising results for pulp mixtures made of 50:50 kraft and mechanical pulps (Koljonen et al. 2003).
- More AFM work is needed to understand properly the role of extractives on the surface of mechanical pulp fibres and how they are distributed on the surface.
- Among the ESCA techniques, the Tougaard background analysis technique should be applied to different pulps to give quantitative information on the depth distribution of surface lignin and extractives.
- ToF-SIMS is a powerful tool giving valuable information on the chemistry of the surface, while ESCA gives an indication of the proportions of lignin and extractives on the surface. ToF-SIMS is an excellent complement to the ESCA technique.

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