Preferred citation: J. Laine, R. Hynynen and P. Stenius. The effect of surface chemical composition and charge on the fibre and paper properties of unbleached and bleached kraft pulps. In **The Fundametals of Papermaking Materials**, *Trans. of the XIth Fund. Res. Symp. Cambridge, 1997*, (C.F. Baker, ed.), pp 859–892, FRC, Manchester, 2018. DOI: 10.15376/frc.1997.2.859.

The effect of surface chemical composition and charge on the fibre and paper properties of unbleached and bleached kraft pulps

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ABSTRACT

The objectives of this research were (i) to obtain a comprehensive description of the surface chemistry of cellulosic fibres by thermodynamic and spectroscopic methods, (ii) to use this description to clarify the effect of kraft cooking as well as ECF and TCF bleaching on the surface chemical and adhesive properties of cellulosic fibres, (iii) to clarify and understand the connection between the fibre surface properties and some key sheet properties (e.g. tensile strength).

The charge, surface energy and hydrophobic material in the surface of cellulosic fibres (mainly pine, *Pinus sylvestris* and birch, *Betula verrucosa)* were studied by potentiometric titration, determination of polyelectrolyte adsorption isotherms, determination of contact angles of single fibers and ESCA.

Lignin (remnants of middle lamellae or reprecipitated during cooking) is enriched in the surface of unbleached kraft pulp fibres. The fraction of surface lignin removed by oxygen or hydrogen peroxide is much smaller than the total decrease in lignin content. Ozone removes both bulk and surface lignin, while the effect of chlorine dioxide depends on the number of treatments. The low reactivity of surface lignin is due to condensed lignin structures and/or to lignin-carbohydrate complexes.

Unbleached fibres contain uronic acids (4-O-methylglucuronic acid and hexenuronic acid, both with p$K \approx 3.4$) and a weaker acid (p$K \approx 5.5$). The amount of the weak acid correlates with the amount of lignin in the fibre. Oxygen delignification increases the accessibility of acid groups in pine, but does not change the relative amounts weak and strong acid. Hexenuronic acid is removed by ozone and chlorine.

Extractives are reprecipitated during cooking and washing. Hence, their surface concentration is always much higher than their total concentrations in the fibres.

Adhesion of water to unbleached fibres increases slightly with increasing degree of delignification during the cook, and increases strongly after oxygen delignification. The correlation of adhesion to the amount of hydrophobic material in the fibre surfaces and to sheet properties needs to be further clarified.

Sheet tensile strength correlates strongly to the total charge of the fibres. This can be explained as follows: (i) The swelling, and hence the flexibility of rewetted fibres increase with increasing charge. (ii) Increasing flexibility promotes the conformability of the fibres. (iii) This results in the formation of denser paper sheets with higher relative bonded area and higher tensile strength.

For the fibres used in this study, the intrinsic fibre-fibre bond strength did not vary much between fully bleached fibres. In order to get an independent evaluation of intrinsic bond strength, some studies of adhesion between model cellulose surfaces were made using a surface force apparatus (SFA). It was found that both swelling and adhesion depend on relative humidity.

Swelling of rewetted fibres is governed by (i) the hydration and entropic swelling of fibre polysaccharides, (ii) the Donnan equilibrium created by dissociating groups in the fibres, (iii) the irreversible interfibrillar bonding when the fibres are dried ("hornification"), (iv) the resistance of the fibre cell walls to the swelling pressure. Swelling increases with charge even at ionic strengths that are so large that effects of the Donnan equilibrium are suppressed. Thus, the charge affects not only the Donnan equilibrium but also hornification, which decreases when the content of ionizable groups in the fibres increases. Hardwood fibres swell more than softwood fibres because their charge content is higher, and because their cell walls are thinner and contain more hemicellulose, i.e. their elastic response to swelling is weaker. For softwood, the effect of coarseness on fibre flexibility and bonding properties is stronger than for hardwood.

INTRODUCTION

There is an urgent need for a better insight into how changes in fibre structure and chemistry affect the papermaking process and the properties of paper and board. The reason for this need are the efforts to develop economically viable minimum impact pulping and papermaking processes. In addition to systematic improvement of the primary raw materials (wood and pigments), these efforts include the use of modified or new pulping and bleaching processes and chemicals, reduction of water consumption, use of paper with lower grammage, and recycling of fibres. It is obvious that these developments will both depend on and have a strong impact on the properties of the fibres delivered to the paper machine.

Extensive data on the strength and ligth scattering properties of different papers as well as on the morphological properties of different types of fibres are available. However, many other properties have been much less comprehensively studied, although they can be expected to yield a deeper understanding of the connection between fibre characteristics and the nature of the fibre network in paper and board. Such properties are, for example, the charge, energy and chemical composition of fibre surfaces, the porosity, flexibility and swelling of fibres, and the heterogeneity of fibres in typical pulps. In particular, systematic studies of the same pulp by several different methods of characterisation are virtually non-existent.

With this background in mind, the objectives of the research presented in this paper were: (i) comprehensive description of the surface chemistry of cellulosic fibres based on thermodynamic and spectroscopic investigations, (ii) clarification of the effect of cooking and bleaching on the surface chemistry and adhesion of cellulosic fibres, and (iii) understanding of the connection between the fibre surface properties and some of the key features of the final product (e.g. sheet strength). The paper summarises results from several earlier papers [1-8] and presents some new data and conclusions.

Strength and morphological properties (fibre length, fibre width, cell wall thickness) of fibres have many times been found to strongly influence the physical properties of paper [9-11]. For example, all these factors are included in Page's tensile strength equation [10]. On the other hand, it has been shown that fibre chemistry has a great influence e.g. on the bonding properties of paper [12, 13]. Therefore, it is quite evident that both physical and chemical properties of fibres affect bonding ability of fibre network, i.e. the extent of bonded area and the strength of fibre-fibre bonds.

Molin and Alfredsson [14] showed that the tensile index of industrially bleached kraft fibres correlates with the rewetted zero-span tensile index. They also found that the rewetted zero-span index is a measure of both the strength of single fibres and the extent of deformation in the fibres (amount of kinks and curls). Fibre strength is an important factor also for the tear strength of paper [11]. When the bonding level is low, fibres pull out from the sheet and fibre length plays a significant role with regard to tear strength, whereas at higher bonding levels the importance of intrinsic fibre strength may increase considerably. Several properties, both chemical and physical, influence the fibre strength. Thus, it has been hypothesised that e.g. degree of crystallinity, degree of polymerisation of cellulose and the number of weak points affect the intrinsic fiber strength [15, 16].

By definition, coarseness is affected by cell wall thickness, cell wall density and fibre width. Paavilainen [9] found for European softwood fibres that differences in coarseness are mainly explained by variations in the cell wall thickness. She also showed that cell wall thickness of softwood fibres is the dominant morphological factor with regard to flexibility of wet fibres as well as bonding properties of the fibre network [9]. As shown by Emerton [17] and Scallan [13], cell wall plasticization also increases with increasing degree of swelling. It has often been assumed that variations in the swelling and flexibility of cellulosic fibres are due to variations in the hemicellulose content [16, 18]. Indeed, the presence of strongly hydrated nonionic polymers in the cell wall will certainly be one factor that governs the amount of water that penetrates into the fibres when dry pulp is immersed into water. Swelling is also controlled by the amount of anionic groups that are bound to the fibre wall [13, 19, 20].

It has been recognised for a long time that the extent of swelling, generated either through mechanical stress or by dissociation of ions, is related to the bonding properties of paper [17, 21]. The penetration of water affects the flexibility of wet fibres by loosening the cell wall structure through debonding and separation of solid elements (microfibrils, lamellae). Fibre flexibility controls their conformability. The increase in conformability facilitates bonding due to the fact that a higher fraction of fibre surfaces can get close enough to form fibre-fibre bonds [17, 22]. The improved bonding leads to a higher paper density, and is also reflected in the light scattering properties and tensile strength of paper.

During the beating process, fibres are subjected to mechanical stress that causes several effects, such as delamination of the cell wall, formation of fines, fibrillation and straightening of fibres. These all are key factors that improve bonding properties during beating. It has been suggested that one of the important effects of refining is "molecular fibrillation", i.e. that part of the polymer chain remains attached to the fibre surface so that wood polymers are not completely dissolved during beating [17, 23, 24]. This kind of swelling of the surface regions of fibres improves fibre-fibre bonding as well. However, although the presence of a swollen carbohydrate layer seems to be clearly established (e.g. detected by surface force apparatus [25]), the contribution of the physical state of surface hemicelluloses to the strength of paper is still incompletely understood.

MATERIALS

Pulps

Unbleached softwood pulps (pine, Pinus sylvestris) were prepared in a laboratory digester at the Laboratory of Pulping Technology, Helsinki University of Technology. The cook was carried to different degrees of delignification, producing pulps with kappa numbers in the range 18 to 57 [1, 3, 8]. The initial charge of effective alkali was 20, 22 or 26%, the sulfidity was 30% and the liquid/wood ratio was 5.0. The temperature was raised from 20 °C to the cooking temperature of 173 °C in 80 minutes. The duration of the cook varied according to the effective alkali used and the target kappa number.

Unbleached softwood (pine, Pinus sylvestris) and hardwood (birch, Betula verrucosa) pulps analysed in [5] were cooked in a laboratory digester to kappa numbers 25.9 and 18.2, respectively. The conditions used were (pine, birch): effective alkali 18, 18%; sulfidity 35, 30%; maximum temperature 170 °C, 165 °C.

Laboratory bleached pulps. Unbleached softwood kraft pulp (Pinus sylvestris) with kappa number 25.9 was bleached in the laboratory using sequences OZEP, OPZEP, ODEDED and DEDED (O = oxygen, P = peroxide, Z = ozone, D = chlorine dioxide, E = extraction in alkali). The kappa numbers, viscosities (dm^3kg^{-1}) and brightnesses (% ISO) of the pulps were: OZEP: 2.9; 700; 74.1, OPZEP: 0.8; 650; 85.1, ODEDED: 0.4; 805; 86.8, DEDED: 0.8; 1005; 81.9. Full details of the pulp properties and bleaching procedures are given in [4, 8].

Industrial bleached softwood and hardwood kraft pulp fibres. These pulps were obtained in the dried state from Finnish pulp mills. Both ECF (oxygen and chlorine dioxide based bleaching) and TCF (oxygen and hydrogen peroxide based bleaching with and without ozone) bleaching sequences had been used in the manufacture of these pulps. Details on the pulp properties are given in [7].

Cationic Polyelectrolytes

The cationic polymers used in the polyelectrolyte titrations were poly(1,5-dimethyl-1,5-diazaundecamethylene)bromide ("Polybrene") with $M_w \approx 8 \cdot 10^3$ from Sigma, and poly(dimethyldiallylammonium)chloride (poly-DMDAAC) from Allied Colloids. The charge densities of the polymers were 5.35 meq/g and 6.19 meq/g, respectively. Polybrene was used without further purification. The poly-DMDAAC was purified by ultrafiltration. Two purified samples with M_w $(4 \pm 1) \cdot 10^4$ and $(2 \pm 1) \cdot 10^5$ were used.

Other Chemicals

All chemicals were analytical grade and used without further purification. The water was ion exchanged, distilled and de-gassed.

EXPERIMENTAL METHODS

Potentiometric Titration

Potentiometric titrations were performed using a computer-controlled automatic system for collection of high-precision emf data. The system is a modernised version of the set-up described in [26]. The cell arrangement essentially follows the description given in [27]. The titration vessel was kept in a thermostated bath at 25.00 ± 0.05 °C. pH was measured with a glass electrode and a Ag/AgCl reference electrode prepared by the method described by Brown [28]. The accuracy of the potentiometer was ± 0.05 mV. The maximum accepted drift in the measured emf was 0.6 mV/h.

The titrations started from a neutral pulp suspension (≈ 8% w/w) to which a known amount of HCl was added from a precision burette. The ionic strength was kept constant (0.1 M NaCl). The resulting suspension was titrated by generating hydroxyl ions coulometrically. A full titration (≈ 50 coulometric additions of OH^-) usually took about 3 days.

Following the method pioneered by Sillén [29] the results were analysed in the following way. The initial excess of protons was determined using Gran plots [30].

Then the total concentration of acid groups, C_B, the concentration of free hydrogen ions, $[H^+]$, the total amount of dissociated acid groups in the suspension, C_H, and the quantity

$$Z_{exp} = \frac{C_H - [H^+] + K_w / [H^+]}{C_B} \tag{1}$$

were calculated for each titration point (K_w = ionic product of water). Z_{exp} is the total fraction of protons released by the fibres. The results were analysed by fitting $Z_{exp}(-\log[H^+])$ to theoretical values for Z, calculated from

$$Z_{theor} = \frac{\sum_{p,i} p[B]_i}{C_B} = \frac{\sum_{p,i} p[H]^{-p}[H_pB]_i K'_{pi}}{C_B} \tag{2}$$

where p is the number of protons assumed to be bound to the acid $(H_pB)_i$, $[B]_i$ is the concentration of dissociated acid and K'_{pi} is the apparent dissociation constant of the acid. The intrinsic dissociation constants K_{pi} were calculated from

$$K_{pi} = K'_{pi} e^{\psi F / RT} \tag{3}$$

where the surface potential ψ was calculated from the total charge and capacitance of the cellulose, using the constant capacitance model of the electrical double layer at the fibre surface. The experimental data were fitted to model assumptions regarding the number of different acidic groups in the fibres by adjusting the K_{pi} values and the total capacitance of the double layer. The fitting was done using the program FITEQL, version 2.0 [31], which minimises the overall variance of the difference $C_B(Z_{exp} - Z_{theor})$. Full details of the potentiometric procedure and data analysis are given in [3].

Polyelectrolyte Adsorption

Polyelectrolyte adsorption was measured by titration using the method described by Wågberg et al. [32, 33]. This involves the following steps: (i) Pulps in their Na^+ form are immersed in dilute NaCl at the desired pH. (ii) Polycation solution is added and the suspension is stirred for 30 min (which is sufficient to reach acceptable adsorption equilibrium). (iii) The remaining amount of polycation in solution is determined by titration with a solution of an anionic polymer, using a dye indicator to detect the end point of the titration. (iv) For each pH value, a full adsorption isotherm is determined.

After a sharp initial rise, the isotherms level off to a slowly and linearly rising saturation level. The slow rise is attributed to conformational changes, once a stoichiometric adsorption reaction has taken place. The amount of polymer corresponding to neutralisation of the accessible charge on the fibres is determined by extrapolation of the linear part of the isotherm to zero polymer concentration [33]. Details of the experimental procedure are given in [5].

ESCA Analysis

ESCA spectra were recorded using spectrometers from Kratos Analytical at the Institute for Surface Chemistry, Stockholm and the Centre for Chemical Analysis, Helsinki University of Technology. Monochromatised Al K_α radiation was used to excite the electrons. The effect of the sampling depth was analysed by changing the angle of analysis, α, *i.e.* the angle between the plane of the paper sheet and the analyser. For the ESCA analysis, laboratory sheets were made directly from the pulps according to the standard method SCAN-C 26:76. The sheets were drum dried at 70 °C for 2h.

An area of 0.8x0.5 mm was analysed, usually at three different locations in the sheet for each sample. The carbon C1s peak was deconvoluted by fitting Gaussian curves using the software supplied with the spectrometers. The following chemical shifts relative to C-C (C1) were used: 1.7 ± 0.2 eV for C-O (C2), 3.1 ± 0.3 eV for O-C-O or C=O (C3), 4.4 ± 0.3 eV for O=C-O (C4) and 6.5 ± 0.3 eV for the shake-up band of aromatic carbon (detected only for lignin samples). The surface chemical composition was evaluated by calculating the total O/C atomic ratio from the C1s and the O1s peaks or the relative amount of different carbons (C1-C4) in the C1s peak.

The surface coverage of extractives, ϕ_{extr}, and lignin, ϕ_{lignin}, were calculated from the O/C atomic ratios using the method described in [34]. If the thickness of the patches of the extractives is greater than the deepest sampling depth ($\geq$ 10 nm when $\alpha = 90^\circ$), ϕ_{extr} can be estimated from the O/C atomic ratios using the equation

$$\phi_{extr} = \frac{\text{O/C(before extraction) - O/C(after extraction)}}{\text{O/C(extractives) - O/C(after extraction)}} \tag{4}$$

where O/C(extractives) is estimated from the spectrum of a model extractive compound. Similarly, if the thickness of the regions where lignin is located is greater than the ESCA analysing depth, the lignin surface coverage can be calculated from

$$\phi_{lignin} = \frac{\mathrm{O/C\,(pulp\ sample) - O/C\,(carbohydrates)}}{\mathrm{O/C\ (lignin) - O/C\,(carbohydrates)}} \tag{5}$$

where O/C(pulp sample) is the O/C atomic ratio of a pulp sample analysed after extraction with solvent and O/C(lignin) is the O/C value of a lignin model compound. Lignin and extractive mixtures isolated from the pulps were used as model compounds. Extracted bleached kraft pulp, which contains practically no lignin and extractives, was analysed to get a value for O/C(carbohydrates). Further details on ESCA analysis can be found in [1, 4].

Contact Angles

The dynamic contact angles of single fibres was measured using a modification of the method described in [35]. The fibres were suspended vertically in the liquid/air interface from a KSV Instruments Sigma 70 electrobalance. The balance, which is connected to a microcomputer, measures the force acting on the fibre with a sensitivity of ± 1 μN.

The wetting liquid is contained in a glass cup on a movable stage so that the liquid can be moved up and down the fibre. The stage moves at a constant velocity (0.7 -0.9 mm/min) over a 0.5 - 1.0 mm section of the fibre. For water, 40-50 fibres were measured for each pulp; for other liquids 15 fibre/pulp were found sufficient. The instrument was set in a hood at constant humidity and temperature.

The liquid meniscus can be observed during the measurement through a video camera equipped with a microscope lens. This made it possible to measure the diameter, and hence the average perimeter P of the fibres. Neglecting buoyancy effects, the contact angle θ then can be calculated from

$$F = \gamma P \cos\theta + mg - (\rho_l - \rho_v)Vg \tag{6}$$

where F is the force acting on the fibre, γ is the surface tension of the liquid, m is the mass of the fibre, g is the gravitational acceleration, ρ_l and ρ_v are the liquid and vapor densities, and V is the volume of submerged fibre.

In some cases it was difficult to obtain an accurate value of the fibre diameter. Then the following procedure was used [35]. For water and many other liquids of interest the receding contact angle on cellulosic fibres is close to zero. Assuming that $\theta_{receding} = 0$, the advancing contact angle can be calculated from

$$\cos \theta_{advancing} = \frac{F_A}{F_R} \tag{7}$$

where F_A and F_R are the forces measured when the liquid advances or recedes over the surface.

The thermodynamic work of adhesion of the liquid (l) to the fibre (s) was calculated from the Young-Dupré equation

$$W_{sl} = \gamma_l(1+\cos\theta) \tag{8}$$

Measurements were made for three liquids: distilled water, ethylene glycol and 1-bromonaphthalene. This made it possible to divide the adhesion into Lifschitz - van der Waals (LW) and Lewis' acid-base (AB) components by the method described e.g. by van Oss [36]. Thus, it is assumed that the adhesion can be calculated from:

$$W_{sl} = \gamma_{sl}(1+\cos\theta) = 2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_l^{+}\gamma_s^{-}} + \sqrt{\gamma_l^{-}\gamma_s^{+}}) \tag{9}$$

where γ^+ and γ^- are the acid and base parameters and γ^{LW} the Lifschitz-van der Waals component of the surface tension. If these quantities are known for three liquids, the corresponding quantities for the solid can be calculated from the three equations obtained by substitution of the contact angles of the liquids into eq. (9). The LW and AB parts of the adhesion to each liquid is given by

$$W_{sl}^{LW} = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} \tag{10}$$

$$W_{sl}^{AB} = 2(\sqrt{\gamma_l^{+}\gamma_s^{-}} + \sqrt{\gamma_l^{-}\gamma_s^{+}}) \tag{11}$$

Surface Force Measurements

A Mark II surface force apparatus [37] was used to measure the forces between cellulose surfaces. The surfaces were prepared by deposition of trimethylsilyl cellulose (TMSC) on hydrophobized mica using the Langmuir-Blodgett (LB) technique. The TMSC-film was desilylated in the atmosphere above a 10% aqueous HCl solution before the measurements. This resulted in pure cellulose films. The relative humidity (rh) in the chamber surrounding the cellulose surfaces was changed by placing a beaker with different saturated salt solutions on the bottom of the chamber. The salt solutions used were: $MgCl_2$ (rh 33%), $Ca(NO_3)_2$ (rh 54%) and KCl (rh 86%). P_2O_5 was used to achieve 0% rh. The measuring procedure, data treatment and surface preparation are described in detail in [38].

Other Analyses

The following standard methods were used to characterise and modify the bulk properties of the fibres. Kappa number: SCAN-C 1:77, brightness: SCAN-C 11:75, viscosity: SCAN-CM 15:88, PFI-mill beating: SCAN-C 24:67, separation of fines: Bauer-McNett, SCAN-M 6:69. Coarseness and fibre length were measured using a Kajaani FS-100 fibre analyser. The fibre width was determined manually with a projection microscope (100 fibres/sample) [9]. Wet fibre flexibility was measured by the Steadman method [39]. Fibre elastic bulk modulus was evaluated by the method described in [20]. The kappa numbers were converted to lignin content (L, %) according to L = (kappa number)/6.546 [40].

Residual rosin and fatty acids were removed by extraction with dichloromethane (DCM). The content of extractives in the pulps was analysed according to the standard method SCAN-C 7:62.

Handsheets were prepared and tested against SCAN standards, except that Scott bond was measured by the TAPPI UM 403 method. The zero-span tensile index was determined on both dry and rewetted paper strips using the Pulmac apparatus [41].

RESULTS

ESCA Analysis

Figure 1 shows the fraction of the surface of softwood kraft fibres that is covered by lignin after various steps in the cooking and bleaching process [1, 4]. The surface concentration of lignin is generally several times higher than the amount of lignin in bulk. However, the surface content decreases as cooking is carried out to lower total lignin contents and, of course, also in the bleaching sequences. PFI-mill beating reduces the surface lignin content to a larger extent for the fibres with higher kappa number, but considerable amounts of lignin remain in the surface even after beating [2]. These results agree well with surface studies by mechanical peeling which show that the surfaces of unbleached kraft pulp fibre surfaces contain lignin-rich particles [42-44]. Surprisingly, the enrichment of lignin was not markedly affected by the alkalinity in the cook [1]. On the other hand, the final pH values of the black liquors varied only slightly at a given degree of delignification.

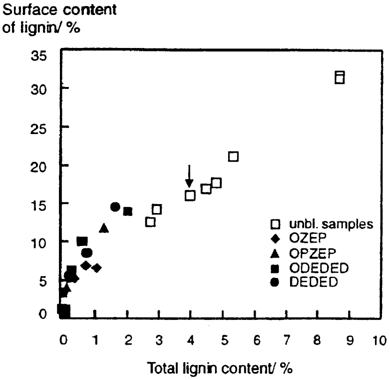

Figure 1: Degree of coverage of the surface by lignin as a function of the total lignin content in softwood kraft pulps [1, 4].

Analysis of the dependence of the lignin content on the depth of the ESCA analysis (angular dependence of electron intensity) shows that the relative amount of electrons emitted from carbon atoms in the lignin increases when the analysis depth decreases from about 10 to about 3 nm (Fig. 2) [1]. Thus, the surface layer of lignin appears to be very thin. The source of this layer of lignin may be strongly adhering residues of the middle lamella or reprecipitation in late stages of the cook [43, 45].

The development of the surface concentration of lignin in TCF and ECF bleaching processes is summarized in Figure 3 [4]. While *oxygen delignification* reduces the total lignin content by about 50%, the surface lignin concentration decreases by only about 15%. *Ozone* removes surface lignin at least as effectively as it removes bulk lignin. *Peroxide* hardly affects the surface lignin. For example, while in the sequence OPZEP the total removal of lignin in the peroxide steps is about 35%, the surface concentration of lignin is reduced by only about 10%. Chlorine dioxide treatment reduces the surface lignin concentration efficiently and results in lowest final lignin concentrations.

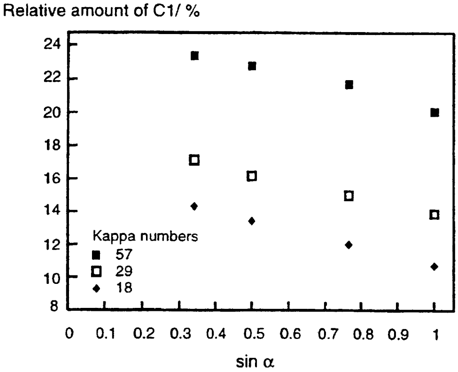

Figure 2: The relative amount of alkyl carbon as a function of sin α (analysing depth) for extracted softwood kraft pulp samples with different lignin contents [1].

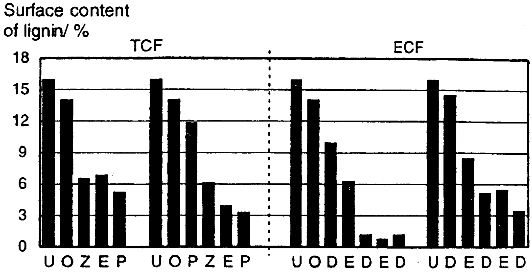

Figure 3: The lignin content of the surface of softwood kraft pulp fibres in TCF and ECF bleaching sequences [4].

Figures 1 and 3 show that only small amounts of lignin are removed from the surface in the first stages of bleaching (total lignin content 4 → 1%). As bleaching proceeds, a significant drop in the surface lignin content occurs when the total lignin content is about 1% [4]. At the end of the sequences, the total lignin concentration is always low, but viscosities of the pulps (see the materials section) differ considerably. After the conventional kraft cook the surfaces contains lignin structures that are difficult to remove by the chemicals normally used early in the ECF and TCF bleaching sequences (oxygen, peroxide, chlorine dioxide). The differences between the effects of different chemicals on surface lignin indicate that this lignin is condensed or that it contains low amounts of free phenolic hydroxyl groups [46, 47]. The source of this lignin may be reprecipitation and/or middle lamella remnants.

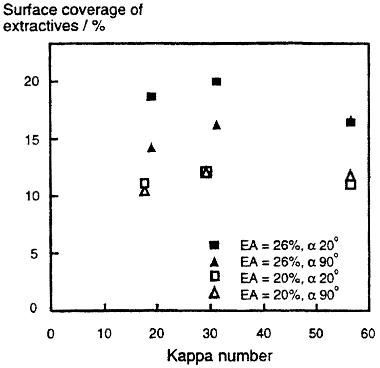

Figure 4: Degree of coverage of the surface by extractives as a function of the total lignin content in softwood kraft pulps [1].

The total amount of DCM-extractable material in the unbleached fibres varies between 0.09 and 0.17 w-%, while the surface content of extractives ranges between 11 and 17% [1]. Thus, the content of extractives in the surfaces is very high, in some cases up to 100 times higher than in the bulk of fibres. The amount of surface extractives increases with increasing excess alkali, but it does not depend on the degree of delignification (Fig. 4) [1]. It was shown by Ström et al. [48] that solubilized wood extractives reprecipitate on the surfaces of fibres when the concentration of micelles formed by surface active components in the extractives decreases during washing. The solubility of mixed fatty acid/rosin acid soaps and their solubilization capacity for neutral extractive compounds depends on the ionic strength and pH [48, 49]. Therefore, the effect of alkali dosage on the surface content of extractives is not unexpected.

Figure 5 shows that *oxygen delignification* strongly reduces the amount of extractives in the fibre surface [4]. After the oxygen stage, the amount of extractives in the ODEDED sequence is about half of that in the DEDED sequence. *Ozone* and *chlorine dioxide* do not reduce the content of surface extractives, while it always decreases when the fibres are treated with *hydrogen peroxide*. Note that the content of extractives in the surface even in fully bleached pulps may be quite high. This may be of importance for the binding properties of fibres.

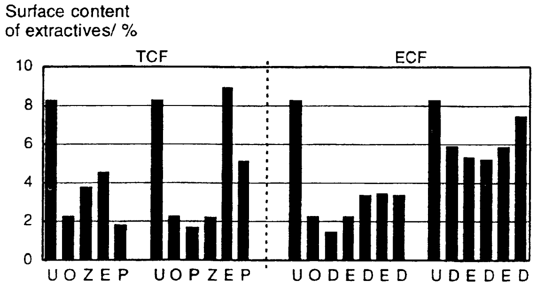

Figure 5: The development of the amount of extractives in the surface of softwood kraft pulp fibres in TCF and ECF bleaching sequences [4].

There are some indications that the solubility and solubilization of neutral substance may explain some of the trends observed in Figure 5. However, definite conclusions about the physico-chemical background of the effects require more detailed analysis of the extractives in the fibres, in solution and in the washing water.

Adhesive Properties

Figure 6 shows how the work of adhesion between water and softwood fibres depends on the total degree of coverage of the surface by extractives and lignin. It can be concluded that the adhesion of water to unbleached fibres decreases somewhat when the amount of non-polar material in the surface increases. Oxygen delignification strongly increases adhesion, but subsequent treatments do not significantly affect the surface energies.

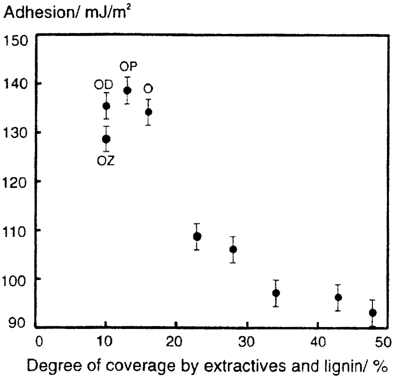

Figure 6: The adhesion between water and softwood fibres as a function of the total degree of coverage of the surface by extractives and lignin. The bars indicate the variability of fibres within the same sample.

Figure 7 shows the LW and AB components of the water/fibre interactions. The trends are quite clear. Decreasing the amount of non-polar material in the surface does not significantly affect the LW interactions but the AB interactions increase strongly, in particular after oxygen delignification. On the other hand, differences between different bleaching stages after oxygen delignification are not significant.

As shown by the error bars, the heterogeneity of the fibre material in pulps imply that contact angle measurements are inherently uncertain. Hence, adhesion measurements of this type should be supplemented by direct measurements on model surfaces. Figure 8 shows the adhesion between model cellulose surfaces in air, as measured by the surface forces apparatus. Adhesion increases with increasing humidity, but at the same time also the thickness of the cellulose layer increases, indicating that swelling also plays an important role in governing the total interaction between the surfaces.

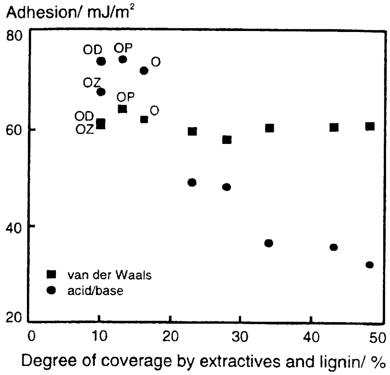

Figure 7: The LW and AB components of the adhesion between water and softwood fibres. The bars indicate the variability of fibres within the same sample.

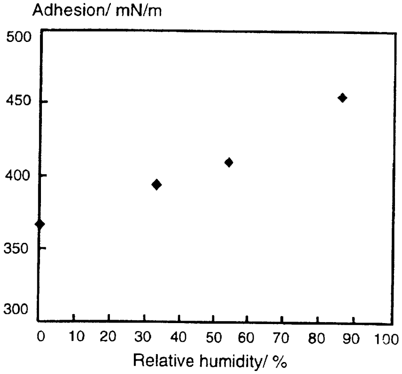

Figure 8: The adhesion between model cellulose surfaces in air as a function of relative humidity.

Total and Surface Charge of Fibres

Pulp	Effective alkali %	Kappa number	Lignin %	pK_1	pK_2	Total charge µeq/g	Acids µmol/g
Unbleached	20	17.7	2.70	3.37	5.71	70	65
Unbleached	26	19.0	2.90	3.41	5.43	65	55
Unbleached	22	34.7	5.30	3.40	5.50	90	75
Unbleached	20	56.6	8.65	3.37	5.68	130	115
Unbleached	26	56.7	8.66	3.39	5.48	110	100
U		25.9	3.96	3.32	5.59	100	85
O		13.2	2.01	3.30	5.51	110	90
OZ		7.0	1.07	3.35	5.49	60	55
OP		8.6	1.31	3.31	5.48	105	85
OD		4.2	0.64	3.35	5.44	60	55
OPZEP		0.8	0.12	3.32	5.55	55	40
DEDED		0.8	0.12	3.28	5.57	55	40

Table 1: The dissociation constants and amount of acidic groups in softwood kraft pulps, determined by polyelectrolyte adsorption ("total charge") and by potentiometric titration ("acids") [3, 6]. U = initial unbleached pulp used in bleaching experiments, P = peroxide, Z = ozone, O = oxygen, D = chlorine dioxide, E = extraction by alkali.

Table 1 summarizes the results from titrations of different softwood kraft pulps. The fibre charge in the pH interval 2-8 is due to the dissociation of two types of acidic groups, one with p$K \approx 3.3$, the other with p$K \approx 5.5$ [3, 6]. Taking into account that the ionic strength is 0.1 mol dm^{-3}, the lower pK value is typical for uronic acids. The content of the weaker acid correlates with the amount of residual lignin in the unbleached pulps. ECF and TCF bleaching do not change the chemistry of the fibres in the sense that the same acids are also found after oxygen, peroxide, ozone or chlorine dioxide treatments (Table 1). However, the relative amount of weaker and stronger acid somewhat depends on the bleaching procedure [6]. It was recently shown that during kraft pulping a significant proportion of the initial 4-O-methylglucuronic acid side groups in xylan is converted to hexenuronic acid [50]. However, the p*K* values of these two acids differ so slightly that separate p*K* values and concentrations of these acids in mixtures cannot be determined potentiometrically.

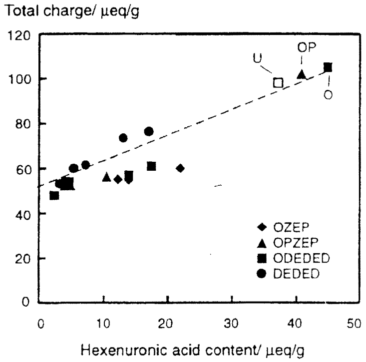

Figure 9: Relationship between the total amount of charge (determined by adsorption of cationic polyelectrolyte) and the amount of hexenuronic acid groups in softwood kraft pulps [6].

A higher alkalinity in the cook slightly reduces the total charge on the fibres at a given degree of delignification. The charge decreases considerably as cooking is prolonged to lower kappa numbers (Table 1) [3]. These changes largely are explained by the extent of dissolution of xylan and lignin. The situation is different in the ECF and TCF bleaching [6]. While carbohydrate losses and concomitant dissolution of lignin somewhat reduces the amount of charge, the decrease is primarily due to the selective reaction of hexenuronic acid side groups of xylan with the electrophilic bleaching chemicals ozone and chlorine dioxide (Figs. 9 and 10). Indeed, according to Buchert et al. [51], hexenuronic and 4-O-methylglucuronic acids are unreactive in peroxide and oxygen treatments, while hexenuronic acid side groups are decomposed by chlorine, chlorine dioxide and ozone.

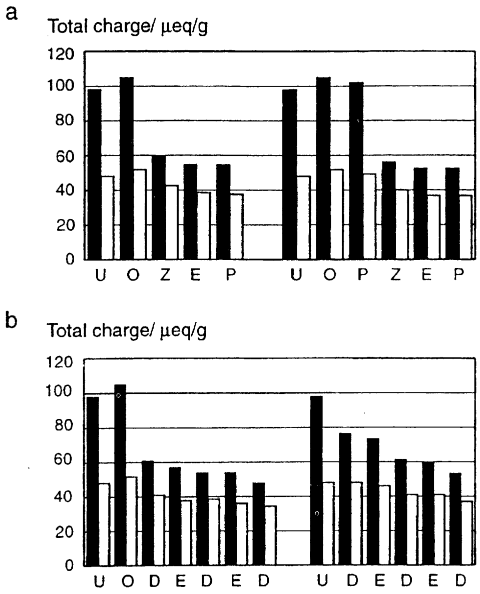

Figure 10: Change in the total charge of fibres at pH 7.5 after different bleaching stages in (a) TCF and (b) ECF bleaching of softwood kraft pulp. The total charge was determined by adsorption of polyelectrolyte ($M_W \approx 8\cdot10^3$) before (■) and after (□) selective hydrolysis of hexeneuronic acid groups [6].

Unbleached birch pulp contains the same acids as pine but the total content of acidic groups is higher due to higher content of uronic acids in birch. The relative amount of the stronger acid is also higher in birch than in pine [5]. The accessibility and location of the charges are different for birch and pine (Fig. 11), which may imply different binding properties of these pulps. A smaller fraction of the charge in softwood fibres than in hardwood fibres is accessible to polyelectrolytes with high molecular weight (Fig. 11). This may be due to differences in pore size distribution but also to the fact that the external surface of birch kraft pulp is more acidic than that of pine kraft pulp.

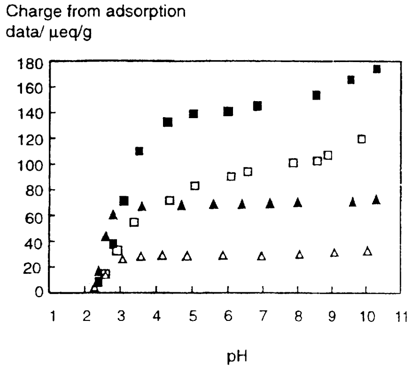

Figure 11: Accessibility of acidic groups in unbleached birch (■, ▲) and pine (□, △) kraft pulps as determined by adsorption of cationic polyelectrolytes. ■, □: $M_W \approx 8 \cdot 10^3$, △, ▲: $M_W \approx 2 \cdot 10^5$ [5].

Fibre and Paper Properties of Bleached Pulps

Figure 12 shows the effect of charge on the water retention value (WRV) of industrially produced ECF and TCF bleached hardwood kraft pulps [7]. The level of swelling increases with the amount of charge in the pulps. The result agrees with previous reports that swelling is partly controlled by the number of anionic groups bound to the fibre wall [13, 19, 20, 52]. However, the WRV increases with the content of ionizable groups, even in 0.5 M NaCl, i.e. when the osmotic pressure effects of the small counter-ions (Donnan equilibrium) are effectively suppressed. As shown in [7], irrespective of the hemicellulose content, the total charge and the water retention value correlate for both hardwood and softwood pulps. This indicates directly that neither the swelling of hemicelluloses nor the Donnan equilibrium can completely explain why the WRV of rewetted fibres increases strongly with total charge. One explanation is the degree of hornification, the extent of which has been found to be depend on the amount of ionized carboxyl groups in the pulps [53].

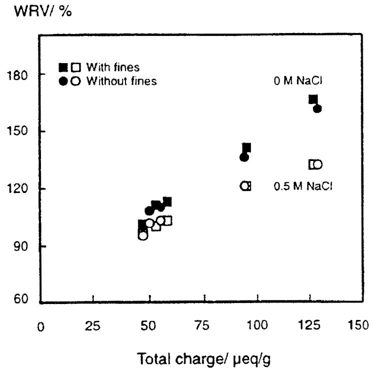

Figure 12: Effect of charge on the water retention value (WRV) of ECF and TCF bleached industrial hardwood pulps in their Na+ form, pH ≈ 7.5 [7].

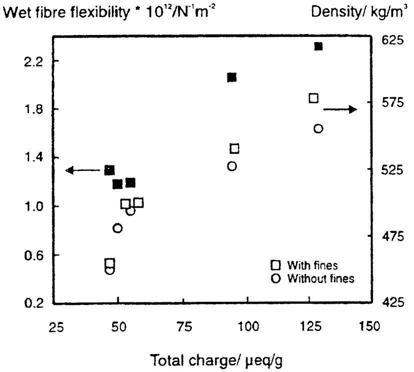

Figure 13: Wet fibre flexibility and density of paper as a function of total charge of industrially produced ECF and TCF bleached hardwood kraft pulps. All pulps were in their Na+ form [7].

As expected from Figure 12, there is also a linear correlation of wet fibre flexibility with the total charge (Fig. 13). This shows that penetration of water causes debonding and separation of solid elements (microfibrils, lamellae), thereby loosening the cell wall structure.

Figure 14 together with 12 and 13 shows that swelling, flexibility, RBA and tensile strength all correlate linearly with total fibre charge. It can be concluded that the observed relationship between paper properties and the amount of charge is due to the effect of charge on the swelling and flexibility of fibres. When their conformability increases the fibres can get closer to each other and more fibre-fibre contacts are formed [17, 22]. Fibres remain in contact with one another at their places of crossing during drying of paper [54]. Thus, when fibres are flexible and fines swell, the degree of compaction (Fig. 13), and the area of fibre-fibre bonding in dry paper sheet increases (Fig. 14). The increase in bonding is reflected in the tensile strength of paper (Fig. 14).

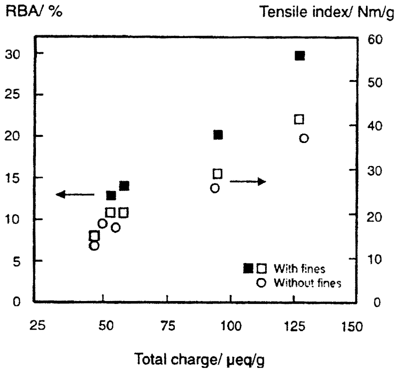

Figure 14: Relative bonded area (RBA) and tensile strength of paper as functions of the total charge of industrially produced ECF and TCF bleached hardwood kraft pulps. All pulps were in their Na^+ form [7].

Beating increases the swelling of pulp (Fig. 15). Mechanical treatment results also in the formation of fines which are expected to affect swelling. However, although the fines fraction plays an important role with regard to the WRV and °SR, the variations seen in Figure 15 cannot be explained by variations in the fines content only. They are also related to the electrochemical properties of fines and fibres, which affect both the state of swelling of pulps and the coagulation of fines [55, 56].

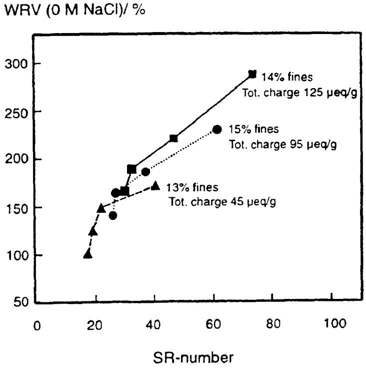

Figure 15: Changes in SR-number and water retention value (WRV) during PFI-mill beating of industrially produced bleached hardwood kraft pulps with different total charge. All pulps were in their Na+ form [7].

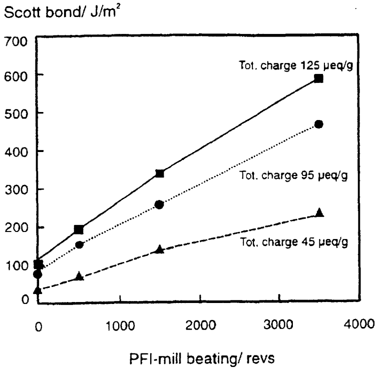

Figure 16: Changes in bonding ability during PFI-mill beating of bleached industrial hardwood kraft pulps with different total charge. Pulps were in their Na+ form [7].

If long-range electrostatic effects are screened by salt addition (0.5 M NaCl), the differences in the WRV's between different samples do not change during the PFI-mill beating. Thus, charge as such does not influence the creation of new surfaces and particles during mechanical treatment of fibres [7]. As expected, bonding can be affected by beating (Fig. 16). However, bonding develops faster the more ionizable groups the pulp contains.

DISCUSSION

We have shown that it is possible to follow in detail both the development and accessibility of charge as well as the amount of hydrophobic material in fibre surfaces during cooking and bleaching. This makes it expedient to discuss the relationship between these properties and paper properties on a more reliable footing than has perhaps been hitherto possible. The discussion will focus on the importance of intrinsic bond strength relative to the total bonded area. The situation is complex, since factors that affect the intrinsic bond strength (amount of hydrophobic material, polar and dissociating groups in the fibres) at the same time also affect the swelling properties and flexibility of the fibre. Thus, it is difficult to separate effects of bonded area and intrinsic bond strength from each other.

The studies of contact angles indicate that the extent of cooking and different bleaching sequences do not very strongly affect the adhesive properties of laboratory prepared fibres. However, variations in pulp and paper properties of fibres prepared at the laboratory are much smaller than the variability found between industrially produced pulps from the same wood but of different origin. Furthermore, the material studied is still rather limited, i.e. a comparison of a broad range of different types of fibres with totally different surface chemical compositions could result in a higher variation in the surface energies of fibres.

In bleached pulps the hemicelluloses located on the outer surface layers of fibres are expected to be of greater importance than lignin to fiber-fiber bonding. Extractives may also affect the bonding strength, even in the case of fully bleached pulps, because they are strongly enriched in the surface regions of the fibres [4, 7]. Indeed, it has been shown that changing the amount of extractives in the pulps significantly affects the tensile strength of paper [12].

It has been suggested that in addition to submicroscopic surface physical properties (smoothness, flexibility), the carbohydrate composition, the degree of polymerisation and the physical state of hemicelluloses on the surfaces of fibres are of great importance for bonding strength [57]. The intrinsic bond strengths, as evaluated using Page's tensile strength equation [10], are higher for bleached hardwood (≈ 3.7 N/mm^2) than for softwood samples (≈ 2.2 N/mm^2) [7]. The concentration of ionizable groups in the outermost surface of the fibres is higher in hardwood than in softwood. Thus, the difference in intrinsic bond strength may be a reflection of a higher hemicellulose content or a higher charge density of the outermost surface layers of hardwood fibres.

For the same type of fibre (hardwood or softwood) the calculated intrinsic bond strength is almost independent of the surface charge [7]. However, the swelling of the surface regions of fibres should affect the fibre/fibre bonding. For example, surface force measurements indicate that even for pure cellulose, the swelling properties may be of considerable importance (Fig. 8). It has been suggested that wood polymers may be strongly solvated but remains partially attached to the fibre surface ("molecular fibrillation") [23]. Measurements of the forces between surfaces covered by high or low charge density xylan indicate that when xylan is adsorbed from an aqueous solution with low salt concentration (10^{-3} M KBr), the swelling of the polymer layers is significantly affected by the charge density of the polymer. i.e. the higher the charge density the greater the swelling [58]. However, the addition of salt considerably decreases the expansion of the polymer, especially in the case of highly charged xylan.

Not only Page's tensile strength equation but also some other methods have been used to evaluate the specific bond strength [59]. For example, the Scott bond/ RBA ratio should give some indication of the specific bond strength. Furthermore, the elastic breaking strain (tensile strength/ elastic modulus of paper) should be proportional to the breaking strain value of the inter-fiber bonds. Re-evaluation of the data shown in [7] indicates that the amount of charge does not affect the bonding strength if the specific bonding strength is expressed as the ratio Scott bond/ RBA, i.e. independent of the sample, the ratio Scott bond/ RBA is about 370 and about 460 J/m^2 for unbeaten hardwood and softwood pulps, respectively. On the other hand, it is evident that the elastic breaking strain increases as a function of charge, implying that opening of inter-fiber bonds is somehow connected to the electrochemical properties of pulps. Nevertheless, one arrives at the conclusion that factors affecting swelling and fibre conformability (electrochemical properties, cell wall thickness) seem to be more important. Thus, for example the correlation between RBA and tensile strength supports the conclusion that bonded area rather than intrinsic bonding strength is responsible for the differences in bonding ability of the bleached kraft pulp fibres described here and in paper [7].

The relationship between the total charge and the tensile strength of paper can be explained as follows: (i) The swelling of rewetted fibres (and fines) increases with increasing charge. (ii) Fibre flexibility increases with increasing swelling. (iii) Increasing flexibility promotes the conformability of the fibres. (iv) The increased conformability results in the formation of denser paper sheets with higher relative bonded area and higher tensile strength.

The swelling and wet fibre flexibility increases more rapidly with charge for hardwood than for softwood. In both cases, swelling increases with the amount of ionizable groups (carboxyls) even at ionic strengths that are so large that effects of the Donnan equilibrium are suppressed. Extrapolation of the swelling data to zero charge on the fibres shows that fibres that contain no ionizable groups still swell strongly. Indeed, 40-60 % of the swelling seems to be due to other factors, such as the ability of nonionic hydrophilic polymers to swell with water.

Swelling is limited by the elastic properties of the cell walls [7, 20]. Thus, our results show that swelling is larger for hardwood than for softwood fibres not only because their charge is higher, but also because the cell walls are thinner and contain more hemicellulose, i.e. their elastic response to swelling is weaker.

For softwood, not only the amount of charge but also fibre coarseness influence fibre flexibility and bonding properties more strongly than for hardwood. For the hardwood samples investigated, the morphological properties of the fibres did not vary very much. It seems that with regard to the pulp and paper properties the charge on the fibre is of greater importance for bleached hardwood than for bleached softwood kraft pulps.

The amount of energy required to reach a certain bonding level by beating decreases considerably when the mechanical action is combined with a high concentration of ionizable groups. This may be due to both the swelling pressure created by ionization and to decreasing hornification. It is evident that the properties of the fibre network in the paper formed by bleached kraft pulp can be managed mechanically, by controlling the amount of charge (ionizable groups) or by a combination of these factors.

It seems that the swelling of rewetted fibres is governed by the following: (i) the water uptake (hydration and osmotic swelling) of fibre polysaccharides (ii) the

Donnan equilibrium created by dissociating groups in the fibres, (iii) the extent to which interfibrillar bonding increases when the fibres are dried ("hornification"), (iv) the ability of the fibre walls to resist the swelling pressure. The charge not only affects the Donnan equilibrium, but also hornification which decreases when the amount of ionizable groups in the fibres increases.

CONCLUSIONS

The amount of charge (i.e., the amount of ionizable groups bound to the cell walls) in bleached kraft pulps correlates with the WRV, the wet fibre flexibility and the bonding properties of paper. In fully bleached fibres of the same type, the differences in the intrinsic bond strength are small. From these correlations, it can be concluded that the relationship between the total charge of fibres and tensile strength of paper can be explained as follows:

(i) Swelling of the rewetted fibres (and fines) increases with increasing charge.

(ii) Fibre flexibility increases with increasing swelling.

(iii) Increasing flexibility promotes the conformability of the fibres. This results in the formation of denser sheets with higher relative bonded area (RBA) and higher tensile strength.

Swelling and wet fibre flexibility increase faster with charge for hardwood than for softwood. In both cases, swelling increases with charge even when long-range electrostatic interactions (Donnan effects) are suppressed. The swelling of hardwood fibres, with their thinner cell walls and higher hemicellulose content is more extensive than the swelling of softwood fibres. Thus, the swelling of rewetted fibres is governed by the following factors:

(i) the swelling of fibre polysaccharides,

(ii) the osmotic pressure created within the fibres when small ions dissociate from the fibre surfaces,

(iii) the extent to which interfibrillar bonding increases when the fibres are dried ("hornification"),

(iv) the ability of the fibre cell walls to resist the swelling pressure.

The amount of ionizable groups in the fibres not only affects the Donnan equilibrium but also hornification, the extent of which decreases when the content of ionizable groups increases.

ACKNOWLEDGEMENTS

The authors thank Ms Ritva Kivelä and Ms Aila Siltala, laboratory technicians, for excellent laboratory assistance. This work was funded by grants from the Finnish Technology Development Centre (TEKES) and the industrial group supporting the program "Uudistuva paperi" (New generation paper technology) managed by TEKES.

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Transcription of Discussion

The Effect of Surface Chemical Composition and Charge on the Fibre and Paper Properties of Unbleached and Bleached Kraft Pulps

Professor Per Stenius, Helsinki University of Technology, Finland

Petri Kärenlampi, Champion International Corp, USA

One of the main results show that differences in fibre fibre bonding between pulps of similar origin but different pulping and bleaching treatments is mainly due to flexibility and the relative bond area. I got an impression that there were some observations in Lars Wågberg's presentation this morning which indicated that there had been significant differences in the so called specific bond strength. Was there a discrepancy between the two presentations?

Lars Wågberg, Research Manager, SCA Research AB, Sweden

If there is a discrepancy it might be that I was talking about the influence of external surface of different pulps on their bonding ability and that Professor Stenius is studying the same types of pulp all the time. Furthermore I think it is very dangerous to keep talking about studying bonding with light scattering measurements because we are talking about totally different length scales than we should talk about. There are no obvious methods available today but we should try to push ourselves to find these. To be honest I have myself used the RBA approach to determine bond strength but even though I believe in the conclusions in that paper I think the absolute value of the bond strength might be a bit misleading.

Per Stenius

I agree that light scattering is not a measure of bonding strength, but for want of something else that would measure bonding area we have tried to find some correlation to the light scattering properties. I fully agree that we need a better way of characterising the nature of the bond.

Dr Lennart Salmén, Head Fiber Physics, STFI, Sweden

You mainly related effects on swelling to changes of the total charge. However, there are two effects that can occur, as you are comparing different pulps - both that you change the charge and that you change the composition so that you may change the pore size distribution or the amount of amorphous gel material simultaneously with the change in charge. If you cancel out the effect of the charges by having them in the proton form I will expect that you will still see an increase in the swelling if plotted against the total charge.

Per Stenius

We added 0.5 mol/l NaCL in order to screen the electrostatic effects but this may actually not be quite sufficient to do so. I therefore cannot give a definite answer to that. However, our results for the highest ion strength (0.5 mol/l) still show a strong correlation with charge, but if we extrapolate to zero charge there is a considerable residual swelling which is independent of ionic strength and probably is due to hemicelluloses. The differences between hardwood or softwood pulps are systematic but all pulps are fully bleached industrial pulps of more or less of the same composition. So I would not expect radical differences in porosity.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

I have a comment. I think that what we have seen here resembles what was the old battle between sulphite pulp and kraft pulp. We see the strong fragile type bonding with the tensile testing, but for a real papermaker there are other strength properties besides the tensile strength.

Lars Ödberg, Vice President Basic Research, STFI, Sweden

I was thinking about your experiment with xylan, you lost strength but got the same scattering coefficient and the same relative bonded area. How do you interpret that?
Did you look at the density of the sheets?

Janne Laine, Research Scientist, STFI, Sweden

We checked the density of paper sheet and it did not increase a lot during the treatment. For the precipitation of xylans we adjusted the xylan solution to pH 11 and added different amounts to the pulp suspension (pH 6.5) and then prepared the sheets.

Ilkka Kartovaara, R&D Vice President, Enso Group, Finland

You showed that the total charge correlates very well with strength within a group of bleached pulps. The strongest pulp that we make is a 90 kappa unbleached high yield sulphate pulp with a lignin content of about 15% and probably a surface lignin content of about 40%. Do you think that this total charge would be a good indicator of the strength regardless of the surface composition and chemistry of the fibres.

Per Stenius

That is quite a different pulp and we can only speculate. But obviously the lignin content would affect the bonding strength of those fibres. If you could systematically vary the amount of charge without varying strongly the lignin content my guess is that you would see something similar.

Göran Annergren, SCA Research, Sweden

I would like to comment on this question. What you have shown is mainly bleached pulp with a low degree of beating. If you want to make a strong paper out of a 90 kappa pulp you have to beat like hell.