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## **Influence of Fiber Properties on the Network Strength of Softwood and Hardwood Kraft Pulp Fibers from Different Stages of a Bleaching Sequence**

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### **ABSTRACT**

During chemical pulping and bleaching operations, fiber properties are gradually changed due to mechanical and chemical treatment. The changes in fiber properties, in turn, influence network strength, i.e., the rigidity of fiber networks. In this study, the influence of fiber length, lignin content, specific surface area, total charge, and fiber flexibility on the network strength of commercial unbleached and totally chlorine free (TCF) bleached (ozone and hydrogen peroxide) softwood and hardwood kraft pulp suspensions have been investigated. The fiber length, total lignin content, and total charge decreased together with the network strength along the fiber line while the specific surface area and

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fiber flexibility increased. Correlations equal to or greater than 90% were found between network strength and fiber length, lignin content, specific surface area, and total charge. The interrelationship between the fiber properties indicated that for a given pulp, the total lignin content was the parameter that had the greatest influence on the network strength.

*Key Words:* Kraft pulps; Oxygen delignification; Bleaching; Hydrogen peroxide; Ozone; Fiber properties; Fiber length; Lignin content; Network strength.

## INTRODUCTION

In connection with closing the water loops of pulp mills, medium consistency (MC) and high consistency (HC) technologies have been introduced into the pulp and paper industry. MC refers to suspensions with a fiber concentration between 8% and 15% and HC to suspensions with a fiber concentration between 15% and 40%. Operations under MC and HC conditions reduce water and energy consumption within the pulp mill, as well as equipment dimensions. However, MC and HC technologies also result in increased fiber–fiber interaction, and thus, a change in the rheology of pulp suspensions. MC and HC pulp suspensions increase their resistance to motion, i.e., receive higher network strength (yield stress), and thus, processing in operations like screening, pumping, washing, and mixing become more difficult. Better knowledge of the mechanisms that cause fiber suspensions to form strong networks is needed in order to be able to optimize various process operations, with respect to energy efficiency, water and chemical consumption, as well as equipment dimensions.

As early as 1964, Meyer and Wahren<sup>[1]</sup> concluded that fiber networks are coherent mainly through physical bonding caused by entanglement of the fibers. They described a fiber network as a system of fibers in contact in which every fiber is locked in position in the network by contact with at least three other fibers in the network, and in such a way, as to be able to transmit forces. Normal forces arise between the fibers, and these in turn produce frictional forces that provide fiber network strength. Accordingly, the cohesion of fiber networks is strongly dependent upon the number of contact points per fiber (i.e., dependent on fiber length), fiber flexibility, and the coefficient of friction between fibers. Furthermore, other cohesive forces, such as colloidal, mechanical surface linkage, and surface tension, also contribute to the total strength of a fiber network.<sup>[2]</sup> Recently, Andersson et al.,<sup>[3]</sup> proposed a model for homogeneous suspensions, which postulates that network strength is the product of the number of affected contact points

and the average frictional force per contact point. Network strength has been shown to be very dependent on the concentration of fiber suspensions.<sup>[1–8]</sup> Concentration also enters indirectly into the model of Andersson et al.,<sup>[3]</sup> as higher concentration increases inter-fiber contact.

Different methods have been applied during the years, for measuring network strength (or yield stress). Several researchers have used a kind of viscometer in their work. Earlier, Thalén and Wharen<sup>[4]</sup> developed a technique for measurements of yield stresses in an elasto-viscometer. In the elasto-viscometer, used by Thalén and Wharen,<sup>[4]</sup> fiber network samples are subjected to simple shear deformation between two concentric cylinders. A sinusoidal movement is applied to the outer cylinder, and the yield stress on the surface of the inner cylinder can be measured. One drawback with the elasto-viscometer is that slippage, between the boundary layer of the fiber network and the inner cylinder, might occur. This drawback was overcome by Bennington et al.<sup>[8]</sup> They have measured yield stresses, in the range of 0.6–1230 Pa, in pulp suspensions, using a Haake RV12 Rotovisco concentric cylinder viscometer. The baffled housing of the instrument together with the use of lugged rotors ensured that shear was applied to the body of the suspension. Thus, the yield values represented the inter-fiber failure of the network rather than the failure between the suspension and a solid surface. Andersson et al.<sup>[3]</sup> have used a device for measuring network strength similar to that of Bennington et al.,<sup>[8]</sup> which has also been used in this work and will be described in more detail in the Experimental section.

As mentioned, fiber length, fiber flexibility, the coefficient of friction between fibers, and the concentration of fiber suspensions are the primary parameters influencing the network strength of pulp fiber suspensions. Other fiber properties that may contribute to the network strength as well, named secondary parameters, are lignin content, specific surface area, and fiber charge. Fiber flexibility is defined as the inverted fiber stiffness, which in turn is defined as the product of the elastic modulus of fibers and their moment of inertia.<sup>[9]</sup> The shear modulus of a pulp fiber network has been shown to be inversely proportional to the flexibility of individual fibers.<sup>[5,10]</sup> Both lignin content and fiber charge effect fiber flexibility. Fiber flexibility increases when pulp yield decreases.<sup>[10,11]</sup> According to measurements performed by Scallan and Tigerström,<sup>[11]</sup> the elastic modulus of kraft fiber cell walls drops from about 10 to about 3 MPa when the pulp yield decreases from 100% to 65%. They stated that this decrease is due to cleavage of chemical bonds in the cell wall matrix, occurring during lignin removal, which reduces the effectiveness of the ligno-hemicellulose as a cross-linking agent in the cell wall.

Recent studies have shown that carboxymethylation of commercial bleached softwood kraft fibers results in higher fiber flexibility.<sup>[12]</sup> This is in agreement with the results reported by Laine and Stenius,<sup>[13]</sup> i.e., the

flexibility of industrially produced elementary chlorine free (ECF) and totally chlorine free (TCF) bleached hardwood and softwood kraft fibers increases with increasing fiber charge. Beghelli and Lindström<sup>[12]</sup> have also shown that yield stress decreases with the increasing degree of carboxymethylation, i.e., the charge of the fibers. They have considered that an increase in surface charge leads to greater repulsion between the fibers, thus decreasing fiber–fiber friction and the yield stress of the fiber network. Andersson et al.<sup>[14]</sup> have described the fiber–fiber friction as a function of the normal force,  $N$ , times the coefficient of friction,  $\mu$ , plus an additional adhesive force,  $F_0$ , independent of the normal force.  $F_0$  is assumed to arise from the hooking of fibrils.<sup>[15]</sup> Hence,  $F_0$  is expected to be proportional to the contact area.

This study will provide knowledge of the influence of secondary parameters, i.e., fiber properties such as lignin content, specific surface area, and fiber charge on the network strength of pulp suspensions of different commercial unbleached and bleached softwood and hardwood kraft pulp fibers.

## EXPERIMENTAL

### Pulps

Pulp samples from one softwood kraft pulp line and one hardwood kraft pulp line were used for the studies in this investigation. The pulps were obtained from SCA (Svenska Cellulosa Aktiebolaget) Östrand in Sundsvall, Sweden. The pulps were oxygen delignified and TCF bleached according to the following sequence: Q(OP)(ZQ)(OP). Table 1 shows a summary of basic pulp properties.

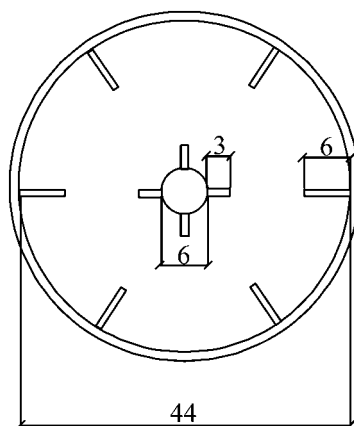
### Network Strength

The network strength of the pulp samples was measured according to a method developed by Andersson et al.<sup>[3]</sup> using a concentric cylinder rheometer (Viscolab LC1 manufactured by Physica). This rheometer enables the measurement of shaft torques of up to  $50 \times 10^{-3}$  Nm. The rotor can be run at a number of constant speeds. The slowest rotational speed of 1 rpm was used in order to avoid viscous effects. A rotor with a diameter,  $d_r$ , of 12 mm and a height,  $h_r$ , of 20 mm was used for all of the network strength measurements. This gave a gap between the rotor and housing of 10 mm in both the axial and the radial directions, which ensured that no fiber was able to bridge the gap. Both the rotor and the housing were baffled at  $90^\circ$  and  $60^\circ$ , respectively, in order to prevent fiber slippage at the walls as well

**Table 1.** Basic pulp properties of softwood and hardwood pulps studied.

Bleaching stage	Softwood			Hardwood		
	Kappa number	Intrinsic viscosity (dm <sup>3</sup> /kg)	Brightness (%)	Kappa number	Intrinsic viscosity (dm <sup>3</sup> /kg)	Brightness (%)
Unbleached	30	1,032	26.1	17	1,234	36.4
O	10	878	45.9	11	1,073	53.0
OQ(OP)	6.4	847	62.5	7.2	988	71.4
OQ(OP)(ZQ)	1.7	815	81.7	3.5	835	82.2
OQ(OP) (ZQ)(OP)	1.1	617	89.3	2.8	780	88.6

as to achieve a shearing surface within the suspension. The dimensions and configuration of the rotor and the housing, respectively, are given in Fig. 1. The lower part of the housing was covered with filter cloth, so that a highly diluted suspension, 0.125 wt%, could be drained directly into the apparatus with the rotor in place, producing a homogeneous, random, fiber network. Network strength was measured by deforming the fiber network in the rheometer described earlier. By using a simple momentum balance, assuming that the network ruptured at the cylindrical surface defined by the baffles of



**Figure 1.** The dimensions and configuration of the rotor and the housing. The dimensions are given in millimeters.

the rotor, the network strength was calculated from the maximum shaft torque noted. Three tests were performed for each sample, and average values were obtained. The mass concentration ( $C_m$ ) of the fibers, in the network, was held constant at around 4% for all samples. All measurements were carried out at room temperature and at pH 7.

### Analyses

Fiber flexibility was determined by using the Steadman method.<sup>[16]</sup> In the Steadman method, fibers are pressed against a glass plate on which there are thin metal wires. The fibers are attached to the glass plate, but are free around the wires. The stiffer the fiber, the longer the free span is. About 200 fibers per sample were measured. The specific surface of the pulp fibers was measured using a permeability–compressibility cell developed by Grén and Hedström.<sup>[17]</sup> Fiber length and coarseness measurements were performed with a Kajaani FS-100 fiber size analyzer. The kappa number and viscosity of the pulps were analyzed according to SCAN-C 1:77 and SCAN-C 15:62, respectively. The total lignin content, expressed as a percentage of the dry weight of the pulp, was measured as the sum of acid-insoluble (Klason) and acid-soluble lignin.<sup>[18]</sup> An absorptivity value of 110 L/g cm was used for calculating acid-soluble lignin. Brightness was measured using an Elrepho 2000 spectrophotometer (SCAN-C 11:75). The total charge of the pulps was determined according to Katz et al.<sup>[19]</sup> In this method, the sulfonate and carboxylate groups are converted to hydrogen form and are then titrated conductometrically with sodium hydroxide in the presence of 0.001 M sodium chloride. Inflexion points mark the end of titration of the strong acids and the total acids. Scanning electron microscopy (SEM) analyses were performed with a Jeol JSM-5200 scanning electron microscope. The specimens were sputter coated with gold–palladium. The procedure used for determining the water retention value (WRV) was as described in standard method SCAN-C 102 XE with the exception of a lower centrifugal force (2000g) and a longer centrifugal time (30 min).

### Statistical Evaluation

The correlations between the measured fiber properties and between network strength and each fiber property were evaluated with help from the Department of Mathematical Statistics, Chalmers University of Technology. The statistical data analysis software used was the SAS System for Windows V8.

## RESULTS AND DISCUSSION

When pulp fibers are processed in the fiber line, the fibers are successively subjected to both mechanical and chemical treatment, and thus, their properties are gradually changed. These changes, in turn, influence the network strength of fiber suspensions. It is well known that properties such as fiber length, fiber flexibility, fiber–fiber friction, and pulp consistency have a major influence on the network strength. Other fiber properties such as total lignin content, specific surface area, and total charge almost certainly influence both fiber flexibility and fiber–fiber friction. In this investigation, an analysis will be presented describing how these secondary fiber properties changes in a bleaching sequence and subsequently how these changes relate to the fiber network strength.

### Changes in Fiber Properties During Bleaching

The results from the measured fiber properties of both the softwood and the hardwood pulps are presented in Tables 2 and 3, respectively. As expected, the surface area increases during bleaching. This is due to the fact that the fiber cell wall is loosened, i.e., becomes more porous, when lignin and carbohydrates are removed. A more porous fiber will, in turn, lead to fiber surfaces being more easily fibrillated by process equipment. Furthermore, the hardwood fibers have greater specific surface area than the softwood fibers, throughout the whole bleaching sequence. This is because the hardwood fibers are much shorter, have thinner cell walls, and contains vessel elements. However, SEM analysis of the pulp fiber samples has shown that the softwood pulp fibers are more fibrillated than the hardwood pulp fibers.

The total charge gradually decreases for the investigated pulps, as bleaching proceeds, with the exception of a slight increase after oxygen delignification of the hardwood pulp. A decrease in lignin content will lead to a decrease in total charge, as carboxylic groups are removed with the lignin. Indeed, Laine<sup>[20]</sup> has found that carbohydrate losses and concomitant dissolution of lignin decreased the charge on bleached kraft fibers. As anticipated, the hardwood pulps have greater total charge than the softwood pulps. The higher charge of hardwood fibers have been shown to be due to their higher content of uronic acids, when compared with that of softwood fibers.<sup>[21]</sup>

Despite rather high experimental errors associated with the fiber flexibility analysis (Tables 2 and 3), the results can be discussed overall. From Tables 2 and 3, it can be noted that the fiber flexibility is higher for the hardwood pulp, in the beginning of the bleaching sequence, when compared



**Table 2.** Results of the measured fiber properties of softwood pulp samples.

Bleaching stage	Fiber length <sup>a</sup> (mm)	Total lignin content <sup>b</sup> (%)	Specific surface area (m <sup>2</sup> /kg)	Total charge (mmol/kg)	Fiber flexibility ( $\times 10^{12}$ ) (1/Nm <sup>2</sup> )	Water retention value (g/g)
Unbleached	2.29	5.3	1070 $\pm$ 52	113 $\pm$ 5	0.61 $\pm$ 0.3	1.63 $\pm$ 0.02
O	2.14	2.5	1238 $\pm$ 40	105 $\pm$ 4	0.75 $\pm$ 0.2	1.51 $\pm$ 0.02
OQ(OP)	2.13	2.3	1318 $\pm$ 40	80 $\pm$ 6	0.64 $\pm$ 0.3	1.48 $\pm$ 0.02
OQ(OP)(ZQ)	2.11	1.9	1455 $\pm$ 45	53 $\pm$ 5	1.4 $\pm$ 0.6	1.46 $\pm$ 0.02
OQ(OP)(ZQ)(OP)	2.11	1.5	1560 $\pm$ 51	57 $\pm$ 5	2.0 $\pm$ 1.0	1.47 $\pm$ 0.02

*Note:* The experimental error associated with the lignin analysis was maximum,  $\pm 0.2\%$ .

<sup>a</sup>Length weighted average fiber length (Kajaani FS-100).

<sup>b</sup>The sum of Klason lignin and acid-soluble lignin.

**Table 3.** Results of the measured fiber properties of hardwood pulp samples.

Bleaching stage	Fiber length <sup>a</sup> (mm)	Total lignin content <sup>b</sup> (%)	Specific surface area (m <sup>2</sup> /kg)	Total charge (mmol/kg)	Fiber flexibility ( $\times 10^{12}$ ) (1/Nm <sup>2</sup> )	Water retention value (g/g)
Unbleached	0.82	2.6	1277 $\pm$ 33	166 $\pm$ 7	1.4 $\pm$ 0.9	1.94 $\pm$ 0.01
O	0.79	2.2	1318 $\pm$ 50	181 $\pm$ 5	1.5 $\pm$ 1.0	1.73 $\pm$ 0.01
OQ(OP)	0.75	1.7	1407 $\pm$ 41	137 $\pm$ 7	1.2 $\pm$ 0.6	1.77 $\pm$ 0.04
OQ(OP)(ZQ)	0.70	1.1	1678 $\pm$ 64	119 $\pm$ 4	1.8 $\pm$ 0.9	1.67 $\pm$ 0.02
OQ(OP)(ZQ)(OP)	0.69	0.66	1966 $\pm$ 70	117 $\pm$ 5	1.8 $\pm$ 1.1	1.73 $\pm$ 0.02

*Note:* The experimental error associated with the lignin analysis was maximum,  $\pm 0.2\%$ .

<sup>a</sup>Length weighted average fiber length (Kajaani FS-100).

<sup>b</sup>The sum of Klason lignin and acid soluble lignin.

with that of the softwood pulp. This is explained by the lower total lignin content of hardwood. It has also been reported that fiber swelling is greater for hardwood than for softwood fibers because of their higher charge, and their thinner cell walls containing more hemicelluloses.<sup>[13]</sup> A more swollen fiber is known to have higher flexibility than a less swollen one. Indeed, the water retention values are higher for the hardwood pulps when compared with that of the softwood pulps (cf. Tables 2 and 3). Furthermore, the hardwood pulp fibers show lower coarseness values than the softwood pulp fibers (cf. Table 4). After the ozone bleaching stage, the fiber flexibility, especially of the softwood pulp, increases considerably. The reason for this sudden increase is not yet known. A possible explanation is that much lignin has been removed from the fiber walls at this stage, that lignin only has a minor function as a cross-linking agent within the wall (cf. the theory about fiber cell walls of Scallan and Tigerström<sup>[11]</sup>). Thus, fiber flexibility would increase significantly. Except for chemical, physical changes of the fibers in a fiber line occur, i.e., kinks and micro compression are introduced and these changes will also certainly influence the flexibility of the fibers. Indeed, in a study carried out by Samuelsson,<sup>[22]</sup> it was shown that mechanical treatment of both sulfate and sulfite pulps reduced the stiffness of individual fibers.

### Influence of Bleaching on Network Strength

During bleaching, the network strength decreases along the fiber line (cf. Table 5). In a previous study, the yield stress in different positions in a

**Table 4.** Coarseness and the number of contacts per fiber of the softwood and hardwood pulps.

Bleaching stage	Softwood		Hardwood	
	$\omega^a$ (mg/m)	$n_c^b$	$\omega^a$ (mg/m)	$n_c^b$
Unbleached	0.198	10.3	0.138	4.4
O	0.182	10.0	0.123	4.5
OQ(OP)	0.191	9.7	0.131	4.1
OQ(OP)(ZQ)	0.190	9.6	0.137	3.7
OQ(OP)(ZQ)(OP)	0.182	9.9	0.138	3.6

<sup>a</sup>Coarseness.

<sup>b</sup>Number of contact points per fiber (from Eq. (2), Appendix A).

softwood kraft pulp fiber line was measured with a similar system as in this investigation.<sup>[23]</sup> The values are difficult to compare, as the samples are taken at different positions in the fiber line and no lignin content of the samples is given. However, on the whole, the network strength in this investigation is somewhat lower in comparison with the values obtained by Wikström and Rasmuson,<sup>[23]</sup> but the trend in the results is similar. The relation between network strength and each fiber property, as well as the interrelationship between the fiber properties, can be found in the correlation matrixes (cf. Tables 6 and 7). Correlations equal to or greater than 90% are found between network strength and fiber length, lignin content, specific surface area, and total charge. The fiber length, total lignin content, and total charge decrease together with the network strength along the fiber line while the specific surface area increases.

The rather weak correlation found between network strength and fiber flexibility, for both the softwood pulp and the hardwood pulp, was not expected. According to earlier investigations,<sup>[5,10]</sup> the network strength is proportional to the elastic modulus of the fibers, i.e., inversely proportional to fiber flexibility. However, Bennington et al.<sup>[8]</sup> have found only a weak dependence between the elastic modulus and the network strength for both synthetic and pulp fiber suspensions. According to these authors, the result suggests that factors other than fiber bending, e.g., hooking forces, contribute to

**Table 5.** Network strength ( $\tau$ ) of the examined softwood and hardwood kraft pulp samples.

Bleaching stage	Softwood [ $C_m^a = 3.7 \pm 0.2$ (%)]				Hardwood [ $C_m^a = 4.3 \pm 0.1$ (%)]			
	$\tau^b$ (Pa)	$\tau_{max}^c$ (Pa)	$\tau_{min}^d$ (Pa)	$N^e$	$\tau^b$ (Pa)	$\tau_{max}^c$ (Pa)	$\tau_{min}^d$ (Pa)	$N^e$
Unbleached	564	608	508	3	232	243	221	3
O	468	497	442	3	206	221	199	3
OQ(OP)	405	420	387	3	170	177	166	3
OQ(OP)(ZQ)	383	409	365	3	144	155	133	3
OQ(OP) (ZQ)(OP)	357	387	332	3	133	144	122	3

<sup>a</sup>Mass concentration (%).

<sup>b</sup>Average network strength.

<sup>c</sup>Maximum network strength.

<sup>d</sup>Minimum network strength.

<sup>e</sup>Number of measurements.

**Table 6.** Correlation matrix for measured fiber properties of the examined softwood kraft pulps, including the correlation between network strength and each fiber property.

	Strength	Length	Lignin	Surface	Charge	Flex
Strength <sup>a</sup>	1					
Length <sup>b</sup>	0.93	1				
Lignin <sup>c</sup>	0.95	0.99	1			
Surface <sup>d</sup>	-0.96	-0.85	-0.89	1		
Charge <sup>e</sup>	0.92	0.76	0.79	-0.94	1	
Flex <sup>f</sup>	-0.73	-0.56	-0.63	0.89	-0.81	1

<sup>a</sup>Network strength.<sup>b</sup>Length weighted average fiber length (Kajaani FS-100).<sup>c</sup>Total lignin content.<sup>d</sup>Specific surface area.<sup>e</sup>Total charge.<sup>f</sup>Fiber flexibility.

the network strength. These forces can be assumed to increase with increasing fibrillation and surface area.

It can be noted from Tables 2 and 3 that the change in fiber length during bleaching is minor, for both the softwood and the hardwood fibers. Actually,

**Table 7.** Correlation matrix for measured fiber properties of the examined hardwood kraft pulps, including the correlation between network strength and each fiber property.

	Strength	Length	Lignin	Surface	Charge	Flex
Strength <sup>a</sup>	1					
Length <sup>b</sup>	0.99	1				
Lignin <sup>c</sup>	0.98	0.99	1			
Surface <sup>d</sup>	-0.9	-0.92	-0.96	1		
Charge <sup>e</sup>	0.91	0.92	0.89	-0.85	1	
Flex <sup>f</sup>	-0.61	-0.68	-0.71	0.79	-0.53	1

<sup>a</sup>Network strength.<sup>b</sup>Length weighted average fiber length (Kajaani FS-100).<sup>c</sup>Total lignin content.<sup>d</sup>Specific surface area.<sup>e</sup>Total charge.<sup>f</sup>Fiber flexibility.

the fiber length can be seen as constant in the two final bleaching stages. Thus, one can expect that some of the other fiber properties contribute to the strong correlation between network strength and fiber length. In Tables 6 and 7, it can be seen that the correlation between fiber length and total lignin content is 99%. Lignin and concomitant removal of carbohydrates weaken the fiber, which facilitate its shortening during processing in the mill. As already mentioned, lignin removal is probably the main reason for the observed increase in specific surface area and decrease in total fiber charge along the fiber line. This is supported by findings from Tables 6 and 7 where the correlation between total lignin content and specific surface area is good, almost  $\geq 90\%$ , for both the softwood and the hardwood pulps. Furthermore, good correlation is also found between the total lignin content and the total charge of the hardwood pulp.

The results obtained in this study thus indicate that the total lignin content is the secondary parameter that has the greatest influence on network strength. As pulp consistency is held constant, variation in fiber length is minor, and fiber flexibility does not seem to significantly affect network strength, the primary parameter exerting greatest influence on network strength, of the investigated suspensions, appears to be the fiber–fiber friction. Hence, lignin removal and fiber–fiber friction seem to be connected. Employing classical beam theory,<sup>[8]</sup> the network strength may be expressed as:

$$\tau_y = k \cdot \mu \cdot E \cdot A^2 \cdot C_v^3 \quad (1)$$

where  $\tau_y$  is the network strength (or yield stress),  $\mu$  is the coefficient of friction,  $E$  is the modulus of elasticity,  $A$  is the fiber aspect ratio (fiber length/fiber diameter), and  $C_v$  is the volume concentration of fibers, and  $k$  is a constant. According to Eq. (1), the network strength of a fiber suspension is proportional to the coefficient of friction. Andersson et al.<sup>[3]</sup> have proposed a model, for non-flocculated fibre suspensions, that postulates that the network strength is a product of the number of contact points per unit shearing surface,  $N_{SS}$ , and the average frictional force per contact point,  $F_f$ :

$$\tau_y = N_{SS} \cdot F_f \quad (2)$$

The number of contacts per fiber,  $n_c$ , that can be estimated as in Appendix A, are almost constant in the bleaching sequence (cf. Table 4). If the model of Andersson et al.<sup>[3]</sup> is assumed to be applicable, and the number of contacts per fiber does not change, the network strength of the investigated suspensions is very dependent on  $F_f$ . The average frictional force has been described to be dependent on both  $\mu$  and an additional

adhesive force  $F_0$ :

$$F_f = \mu N + F_0 \tag{3}$$

where  $N$  is the normal force. The coefficient of friction is most likely influenced by surface properties, e.g., charge, the amount of lignin and fiber morphology as well as the properties of the fiber bulk, whereas  $F_0$  is expected to be proportional to the contact area.<sup>[14,15]</sup> When lignin is removed, all these properties are changed. It has been shown by Andersson et al.<sup>[14]</sup> that  $\mu$  for wet pine kraft pulp fibers decreases as the kappa number decreases. One possible explanation for this decrease may be the removal of lignin and concomitant decrease in surface lignin content. This makes the fiber surfaces more hydrophilic. As a result, a decrease in  $\mu$  is found due to weakening of the cohesion between fibers.<sup>[24]</sup>

The same pulps studied in this work have been investigated in another work made by Risé et al.<sup>[25]</sup> In this work, the chemical composition of the fiber surfaces was studied. A linear correlation between total lignin content and surface coverage by lignin, greater than 99%, was found in both the softwood and the hardwood pulp samples (cf. Fig. 2). Furthermore,

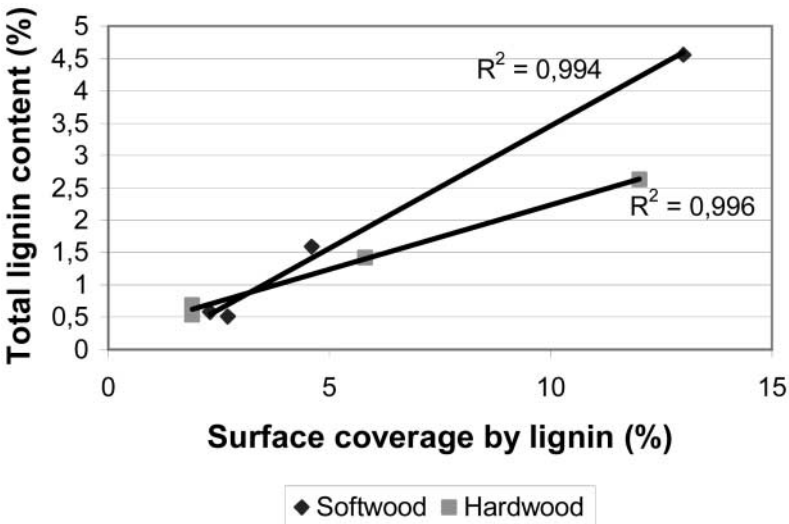


Figure 2. The surface coverage by lignin plotted vs. the total lignin content of the investigated pulp samples. The surface coverage by lignin is taken from Risé et al.,<sup>[25]</sup> and was obtained with the mercerization method.

the change in surface coverage by lignin correlates well to the change in network strength.

Towards the end of the bleaching process, the reduction of network strength is lower. A possible explanation for this is that towards the end of the bleaching sequence, further reduction of  $\mu$  is compensated for by an increase in  $F_0$ . SEM studies have shown that fibrillation increases along the bleaching sequence. Thus, hooking forces, contributing to network strength, will also increase.<sup>[8]</sup> In addition, loosening of the cell wall, due to lignin removal, will lead to outer cell wall swelling. Swelling is expected to increase fiber–fiber friction and hence network strength of a pulp suspension.

In summary, the change in network strength along the fiber line is, to a large extent, attributed to the change in fiber–fiber friction due to the removal of lignin and the concomitant decrease in surface lignin content during bleaching.

## CONCLUSIONS

During bleaching, lignin and carbohydrates are removed. Consequently, the fiber cell wall becomes more porous. This was seen as an increase in fiber flexibility and specific surface area of the studied pulps. The total charge gradually became lower for the investigated pulps, as bleaching proceeded, with the exception of a slight increase after oxygen delignification of the hardwood pulp. The change in fiber length during bleaching was minor for both the softwood and the hardwood fibers.

The network strength decreased along the fiber line. Correlations equal to or greater than 90% were found between network strength and fiber length, lignin content, specific surface area, and total charge. The interrelationship between the fiber properties indicated that for a given pulp, the total lignin content was the secondary parameter that had the greatest influence on network strength.

Lignin removal and fiber–fiber friction seemed to be connected. This supposition was supported by results from another work where the chemical composition of the fiber surfaces of the same pulps investigated in this work was studied. A linear correlation between total lignin content and surface coverage by lignin, greater than 99%, was found in both the softwood and the hardwood pulp samples. Furthermore, the change in surface coverage by lignin correlated well to the change in network strength. The change in network strength along the fiber line was thus, to a large extent, attributed the change in fiber–fiber friction due to the removal of lignin and the concomitant decrease in surface lignin content during bleaching.



## APPENDIX A

The concept of crowding factor ( $N_{\text{crowding}}$ ) has been developed as an indicator of inter-fiber contacts formed in a fiber network.<sup>[2,26]</sup> According to Kerekes and Schell,<sup>[26]</sup>  $N$  can be readily calculated from the mass consistency,  $C_m$ , fiber length,  $L$ , and fiber coarseness,  $\omega$ , using the following expression:

$$N_{\text{crowding}} = \frac{5C_m L^2}{\omega} \quad (\text{A1})$$

where  $C_m$  is expressed in %,  $L$  in m and  $\omega$  in kg/m.

By simplifying an expression of Meyer and Wahren<sup>[1]</sup> for the case of  $L/d \gg 1$ , where  $d$  equals the fiber diameter, Kerekes and Schell<sup>[26]</sup> have derived an expression linking  $N$  and the number of contacts per fiber ( $n_c$ ):

$$N_{\text{crowding}} \cong \frac{4\pi n_c^3}{3(n_c - 1)} \quad (\text{A2})$$

When  $n_c \cong 3$  ( $N \cong 60$ ), fibers may form a continuous network that has a mechanical strength resistable to rupture.<sup>[1]</sup>

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