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# Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption

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ABSTRACT

Xylan is known to adsorb irreversibly on cellulose and on bleached kraft pulp fibres. This investigation shows that adsorption of birch glucuronoxylan (GX) reduces the degree of drying-induced property changes of bleached softwood kraft pulp fibres. GX was adsorbed at different amounts on never-dried fibres, which provided pulps with xylan contents ranging from 67 to 126 mg/g. By fluorescent labelling of the GX, followed by adsorption and subsequent imaging using confocal laser scanning microscopy, it was concluded that GX adsorbs on fibril surfaces throughout the fibre wall with enrichment on the outer fibre surface. Adsorption of GX before drying preserved a considerable part of the fibre-swelling (water retention value and fibre saturation point), specific fibre surface area, and wet fibre flexibility observed in the never-dried state. It is therefore suggested that GX adsorption reduces the degree of drying-induced fibre wall cross-linking. The use of GX as a hornification inhibitor would provide once-dried pulps with increased tensile strength and beatability.



## 1. Introduction

The term "hornification" is widely used in different industrial papermaking situations, as well as in paper science literature, to describe structural changes in chemical pulp fibres caused by water removal or pulp fibre recycling (cf. Weise, 1998). Hornification was originally defined as the relative reduction in water holding capacity, i.e. the water retention value (WRV), of pulp after drying (Jayme, 1944). The loss in swelling ability of once-dried fibres is related to the closure of pore spaces in the fibre wall (e.g. Berthold & Salmén, 1997; Häggkvist, Li, & Ödberg, 1998; Stone & Scallan, 1968; Wang, Maloney, & Paulapuro, 2003). The change in fibre wall pore size distribution (PSD) is proposed to depend on an increase in the degree of cross-linking between cellulose fibrils when the fibre wall collapses during drying. It is commonly suggested that the bonds formed are hydrogen bonds (e.g. Laivins & Scallan, 1993; Mohlin, 1975). It has also been proposed that hornification is an effect of lactone formation (cf. Fernandes Diniz, Gil, & Castro, 2004). This fibre wall cross-linking not only affects swelling and PSD, but will also reduce the specific fibre surface area (e.g. Stone & Scallan, 1965; Wang et al., 2003), reduce fibre surface fibrillation (Klungness & Caulfield, 1982), and increase the elastic modulus of the wet fibre wall (Scallan & Tigerström, 1992).

A consequence of these drying-induced structural changes is the formation of a stiff fibre with a collapsed outer surface. In papermaking, a soft fibre wall, i.e. a fibre wall with a low transverse modulus, promotes larger molecular contact area between fibres and better mixing of the surface fibrils of adjacent fibres during consolidation and drying, which results in greater fibre/fibre joint strength. Consequently, sheets made of hornified fibres will have lower tensile strength than sheets prepared from never-dried fibres (e.g. Nazhad & Paszner, 1994; Paavilainen, 1993). Hornification is therefore important for pulp producers and papermakers, since market pulps are dried before being shipped and dry waste paper is used as raw material in the manufacture of recycled papers.

Due to the tendency for recycled kraft fibres to have reduced water retention, reduced flexibility and reduced bonding potential, a number of investigations have explored possible ways to restore the papermaking properties of such fibres, e.g. by refining, caustic treatments and various ways of fibre modification (cf. Hubbe, Venditti, & Rojas, 2007). Other investigations have focused on blocking hornification, i.e. treatment of pulp fibres before they are dried in order to inhibit the effects associated with drying. The main idea of this approach is to introduce "spacer" material or functional groups and by these means interrupt local formation of intra-fibre hydrogen bonding. This has been performed by

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drying pulps in the presence of different reagents, such as various salts, simple sugars, polysaccharides and detergents (e.g. Higgins & McKenzie, 1963; Laivins & Scallan, 1993; Zhang, Hubbe, Vanditti, & Heitmann, 2002; Zhang, Hubbe, Vanditti, & Heitmann, 2004), or by chemical derivatization of the fibres (e.g. Gruber & Weigert, 1998; Laivins & Scallan, 1993). Chemical derivatization by carboxymethylation appears to be effective in reducing the degree of hornification, as long as the acidic groups are in their sodium salt form (Laivins & Scallan, 1993; Lindström & Carlsson, 1982a).

It is well known that chemical pulps with a low content of hemicellulose (i.e. xylan and/or glucomannan) have an increased tendency to undergo drying-induced property changes (e.g. Cao, Tschirner, & Ramaswamy, 1998; Hult, Larsson, & Iversen, 2001; Oksanen, Buchert, & Viikari, 1997; Rebuzzi & Evtuguin, 2006; Spiegelberg, 1966). Thus, hemicelluloses located in interfibrillar spaces seem to hinder hornification and act as a "spacer" as described above. If native hemicelluloses can act as hornification inhibitors, one could assume that added hemicelluloses would do so as well.

Glucuronoxylan is the main hemicellulose component of hardwoods, where it can constitute up to 35% of the wood (Timell, 1967). The structure consists of a backbone of β-(1 → 4)-linked D-xylopyranosyl units, where every tenth unit, on average, is substituted with α-(1 → 2)-linked 4-*O*-methyl-D-glucopyranosyl uronic acid (Timell, 1967). Glucuronxylans are known to adsorb irreversibly on cellulose and on bleached kraft fibres (e.g. Hansson & Hartler, 1969; Kabel, van den Borne, Vincken, Voragen, & Schols, 2007; Linder, Bergman, Bodin, & Gatenholm, 2003; Paananen et al., 2004), hence they could be used as cellulose fibril stabilizers. Furthermore, glucuronoxylans are negatively charged due to uronic acid side groups, and the introduction of these groups into the fibre wall would additionally act against hornification. The idea was evaluated in a previous investigation (Köhnke & Gatenholm, 2007), in which glucuronoxylan was adsorbed on bleached softwood kraft pulp before drying. The effects of xylan adsorption were mainly evaluated by analyzing the strength properties of the pulps. Results showed that once-dried pulp behaved more like never-dried pulp if it was modified with xylan before drying, and it was proposed that adsorbed xylan had a stabilising effect on cellulose fibrils, preventing hornification upon drying.

The purpose of the present work is to further investigate the impact of xylan adsorption on drying-induced property changes of bleached kraft pulp. The analysis techniques applied are water retention value, fibre saturation point (FSP), specific fibre surface area (determined by nitrogen adsorption), and wet fibre flexibility. Two different sets of conditions for xylan adsorption are used and evaluated; the first one identical with the conditions used in the work by Köhnke and Gatenholm (2007) and the second one is under more moderate conditions. In addition, the distribution of adsorbed xylan within the fibre wall is investigated by confocal laser scanning microscopy after the adsorption of fluorescent labelled xylan.

## 2. Experimental

### 2.1. Starting materials

A never-dried, industrially produced, TCF-bleached (OO)Q(OP)Q(PO) (ISO Brightness 85%) Scandinavian softwood kraft pulp was used in the experiments.

A 4-*O*-methylglucuronoxylan (GX) separated from birch wood by alkaline extraction was purchased from Sigma Aldrich and used without any further purification. The same batch of xylan was analyzed by Köhnke and Gatenholm (2007) and reported to have the following contents: neutral carbohydrates 79.0%, ash 10.4% and Klason lignin 0.6%. The relative carbohydrate composition was Xyl 96.1%, Glc 2.4%, Gal 1.0%, Ara 0.4%, and Man 0.1%. $^1$H NMR spectroscopy showed an average 4-*O*-methyl-glucurono acid/Xyl ratio of 1/12 and a hexenuronic acid/Xyl ratio of 1/66. A weight average molar mass of 9600 g/mol was determined using size exclusion chromatography in DMSO:$H_2O$.

### 2.2. Pulp pre-treatment

The fines were removed using a Dynamic Drainage Jar with a screening diameter of 76 μm. The pulp was then converted to its $Na^+$ form according to a procedure described elsewhere (Köhnke, Brelid, & Westman, 2009).

### 2.3. Pulp modification

GX was adsorbed on never-dried pulp under two different conditions: (L) 80 °C, 0.1 M NaCl, 180 min, and (H) 120 °C, 0.5 M NaCl, 180 min. In order to obtain pulps with different xylan contents, three different additions were used (40, 80, 160 mg GX/g fibres). Samples without xylan addition were also prepared in the same way. The modifications were performed as follows: The specified amount of GX was dissolved in 0.5 $dm^3$ deionised water at 95 °C for 15 min. NaCl was added and the solution was allowed to cool to room temperature. The GX solution was added to a pulp fibre suspension (25 g pulp fibres in 0.5 $dm^3$ deionised water) under stirring. The suspension was placed in a steel autoclave and rotated in a preheated polyethylene glycol bath. After the treatment, the pulp was washed with deionised water until conductivity less than 5 μS/cm was reached. The washed pulp (approx. 20% dry content) was divided into two portions. The first portion was stored in the fridge until analyzed as never-dried pulp and the other part was granulated by hand and air-dried at room temperature to the equilibrated moisture content (approx. 8%).

### 2.4. Pulp characterization

The neutral carbohydrate composition was analyzed after acid hydrolysis (Theander & Westerlund, 1986) using ion chromatography with pulsed amperometric detection. The separation was performed isocratically in Milli-Q water on a CarboPac™ PA1 column (Dionex, Sunnyvale, CA, USA). The detection was enhanced by post column addition of a NaOH solution. The experimental error of the measurements of carbohydrate monomer content in the pulp samples was estimated to be less than ±1%, based on duplicate measurements. The hexenuronic acid content was analyzed after enzymatic hydrolysis (Dahlman, Rydlund, & Lindquist, 1997) using ion chromatography (CarboPac™ PA10 column, Dionex, Sunnyvale, CA, USA) with pulsed amperometric detection (cf. Hausalo, 1995). All samples were analyzed in duplicates. The standard deviation of the method is 0.9 μmol/g. The total charge was determined using conductometric titration according to SCAN-CM 65:02, based on Katz, Beatson, and Scallan (1984). All measurements were repeated twice. The pooled standard deviation of the measurements was 0.8 μmol/g.

### 2.5. Fluorescent labelling of GX

GX was labelled with fluorescein isothiocyanate (FITC) based on a method developed by de Belder and Granath (1973) for preparation of fluorescein-labelled dextrans. 1 g of oven-dried GX was dissolved in 10 mL of dimethyl sulfoxide containing a few drops of pyridine. FITC (45 mg) was added, giving a ratio of about 1 fluorescent label to 50 anhydroxylose units, followed by the addition of 20 mg of dibutyltin dilaurate. The solution was treated under nitrogen and constant stirring for 2 h at 95 °C. The solution was then cooled to ambient conditions, diluted with deionised water,

dialyzed (Spectra/Por 3, MWCO: 3,500 Da) against deionised water in order to remove any excess FITC, and finally freeze-dried.

### 2.6. Confocal laser scanning microscopy (CLSM)

160 mg fluorescein-labelled GX/g fibres was adsorbed according to the two different methods described above. After the washing step the fibres were immerged in liquid nitrogen, freeze-dried and put in immersion oil for 24 h in accordance with Horvath, Horvath, Lindström, and Wågberg (2008). Two cover slips (Menzel-Gläser, #1.5), instead of a glass slide and a cover slip, were used to improve optical resolution. The microscope was a LSM 510 META from Zeiss equipped with a Plan-Apochromatic oil immersion objective (63×, N.A. 1.4). The fibres were irradiated with an Ar laser at 488 nm and the emitted light passed through an LP 505 filter in order to remove wavelengths not of interest. Transverse dimensions of fibres were imaged with z-stacking with a step size of 0.30 μm.

### 2.7. Water retention value

The WRV was analyzed after centrifugation (3000 *g*, 15 min) according to SCAN-C 62:00 using deionised water. The once-dried samples were soaked in deionised water for 1 h before disintegration. All measurements were repeated twice. The pooled standard deviation of the measurements was 0.01 g/g.

### 2.8. Fibre saturation point

The FSP was measured with the solute exclusion technique according to Stone and Scallan (1968), using Dextran T2000 purchased from Pharamacosmos, Denmark. The once-dried samples were soaked in deionised water over night before the experiment. In order to estimate the precision of the method, one sample (never-dried reference fibres) was analyzed six times and the results gave a standard deviation of 0.02 g/g.

### 2.9. Fibre surface area

The fibre surface area measurements were carried out with a Micromeritics TriStar 3000. The pulp samples were prepared using a solvent exchange procedure (cf. Wang et al., 2003) in which water was replaced with acetone and then acetone with cyclohexane, followed by drying over night in a nitrogen stream at room temperature. The once-dried samples were soaked in deionised water over night before the solvent exchange procedure. In order to estimate the precision of the method, one sample (L0, once-dried) was analyzed four times and the results gave a standard deviation of 1.3 $m^2/g$.

### 2.10. Wet fibre flexibility

Wet fibre flexibility was measured according to Steadman and Luner (1985), with the exception that glass fibres were used as support instead of metal wires (cf. Yan & Li, 2008). The preparation of slides with deposited glass fibres and pulp fibres was performed as follows: Glass fibres ($d$ = 17 μm, $l$ = 3 mm; Owens Corning, USA) were suspended in a 10% detergent solution (deconex 11 UNIVERSAL) and treated in an ultrasonic bath for 1 h. The glass fibres were then further washed with distilled water and acetone. 0.025 g of glass fibres were suspended in 2 $dm^3$ of distilled water and disintegrated in a standard pulp disintegrator (50,000 revs., 3000 rpm). The suspension was diluted with 1 $dm^3$ of distilled water and drained on a filter paper (Munktell no. 5) placed in a TAPPI standard sheet former. The suspension was swirled before draining in order to impart a tangential orientation to the fibres. Then the glass fibres were transferred to four carefully cleaned microscope slides by placing and gently tapping the filter paper onto the slides. 2 g (dry-weight) of a pre-soaked pulp sample was suspended in 1 $dm^3$ of distilled water and disintegrated in a standard pulp disintegrator (50,000 revs, 3000 rpm). The suspension was diluted with distilled water to a consistency of 0.03%. 20 mL of the suspension was further diluted with distilled water to about 8 $dm^3$ and drained on a filter paper as described above. The filter paper and the slides were then pressed against each other between two sets of water-saturated blotters in a regular hand sheet press. After 2.5 min pressing at 400 kPa, the glass slides were separated from the filter paper and viewed in a microscope under incident light. Around 100 fibres were analyzed in each sample. Fibre flexibility is presented as the geometric mean of the logarithms, according to Zhang et al. (2004).

## 3. Results and discussion

### 3.1. Pulp modification

Glucuronoxylan (GX) from birch was adsorbed on never-dried pulp fibres under two different conditions; at a high temperature and high ionic strength (H) and at a lower temperature and lower ionic strength (L), cf. Table 1. Conditions H are identical with the ones used in the work by Köhnke and Gatenholm (2007) and L would be more preferable in an industrial application. In order to obtain pulps with altered xylan contents, three different additions were used (40, 80, 160 mg GX/g fibres). The detected amounts of neutral anhydro sugars, hexenuronic acid and the total anionic charge of the starting material and the treated samples are shown in Table 1.

The neutral anhydro sugar composition of the starting material (Ref), L0 and H0 are more or less identical. This fact indicates that no degradation or dissolution of neutral polysaccharide components occurs during the treatments. However, the total anionic charge is lower for the H0 sample. As seen in Table 1, this is, at least partly, a result of the partial degradation of hexenuronic acids at 120 °C (cf. Granström, Eriksson, Gellerstedt, Rööst, & Larsson, 2001). Hexenuronic acid is a β-elimination product of 4-*O*-methyl-D-glucopyranosyl uronic acid, formed during the alkaline pulping process (Teleman et al., 1995).

The pulp was clearly modified with adsorbed glucuronoxylan as seen in the distinctive increase in xylan content and the anionic charge of the pulps. The H conditions seem to be more effective in respect of xylan retention than the L conditions. This is most probably due to the lower solubility of xylan at higher ionic strength (cf. Köhnke et al., 2009). On the other hand, the impact of higher temperature could not be ruled out. It is known that higher temperatures increase the degree of xylan adsorption, but the mechanism is not fully understood (cf. Hartler & Lund, 1962; Köhnke, Pujolras, Roubroeks, & Gatenholm, 2008).

### 3.2. Location of adsorbed xylan

The location of the adsorbed xylan is of great importance in this study, since the accessibility of xylan to fibril surfaces inside the fibre wall is essential for its mode of action as a possible hornification inhibitor. In order to study whether the used xylan can penetrate the porous fibre wall or not, fibres modified with fluorescent-labelled GX were analyzed with confocal laser scanning microscopy. From the CLSM images shown in Fig. 1 it is evident that GX adsorbs throughout the fibre wall, but enrichment on the outer surface can clearly be observed. The concentration (i.e. fluorescent intensity) profile is more uniform for H160 (Fig. 1b) than for L160 (Fig. 1a). Since H160 has a higher content of adsorbed xylan, it seems likely that GX primarily adsorbs on the available surfaces at the exterior of the fibre, and that further adsorption

**Table 1**
Detected amounts of neutral anhydro sugars, hexenuronic acid groups (HexA) and total anionic charge of the starting material (Ref) and samples treated under the specified conditions for 180 min using a fibre concentration of 25 g/dm$^3$. The content of adsorbed Xyl is estimated by assuming the ratio of Glc and originally attached Xyl to be constant.

| Sample | Treatment conditions | | Added GX [mg/g] | Neutral anhydro sugars [mg/g] | | | | | HexA [μmol/g] | Total charge [μmol/g] | Content of adsorbed Xyl [mg/g] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Temperature [°C] | NaCl concentration [M] | | Ara | Gal | Glc | Xyl | Man | | | |
| Ref | – | – | – | 6 | 2 | 788 | 67 | 58 | 26 | 73 | – |
| L0 | 80 | 0.1 | 0 | 6 | 2 | 786 | 68 | 60 | 26 | 73 | – |
| L40 | 80 | 0.1 | 40 | 6 | 2 | 770 | 82 | 57 | n.a. | 77 | 16 |
| L80 | 80 | 0.1 | 80 | 6 | 2 | 751 | 94 | 58 | n.a. | 81 | 29 |
| L160 | 80 | 0.1 | 160 | 5 | 2 | 733 | 103 | 59 | n.a. | 87 | 40 |
| H0 | 120 | 0.5 | 0 | 6 | 2 | 789 | 69 | 60 | 24 | 65 | – |
| H40 | 120 | 0.5 | 40 | 6 | 2 | 758 | 91 | 59 | n.a. | 73 | 24 |
| H80 | 120 | 0.5 | 80 | 5 | 2 | 734 | 106 | 57 | n.a. | 80 | 42 |
| H160 | 120 | 0.5 | 160 | 5 | 2 | 730 | 126 | 55 | n.a. | 91 | 62 |

n.a. = not analyzed.

occurs on internal surfaces after diffusion into the porous fibre wall. The same conclusion was drawn by Köhnke and Gatenholm (2007) based on interpretations of total and surface charge measurements of fibres modified with GX. As the transport of GX into the fibre pores would be kinetically limited by, e.g. the molecular conformation of GX and electrostatic interactions, it seems possible to, at least partly, control the concentration profile in the fibre wall by choice of modification conditions.

### 3.3. Fibre swelling

The most commonly used method to measure fibre swelling is the so-called water retention value. The basic principle is that a pulp pad is centrifuged under controlled conditions to remove the water between the fibres and from lumen. The ratio of water to dry fibres after centrifugation is a measure of fibre swelling. WRV has been criticized to be an incorrect measure of actual fibre swelling,

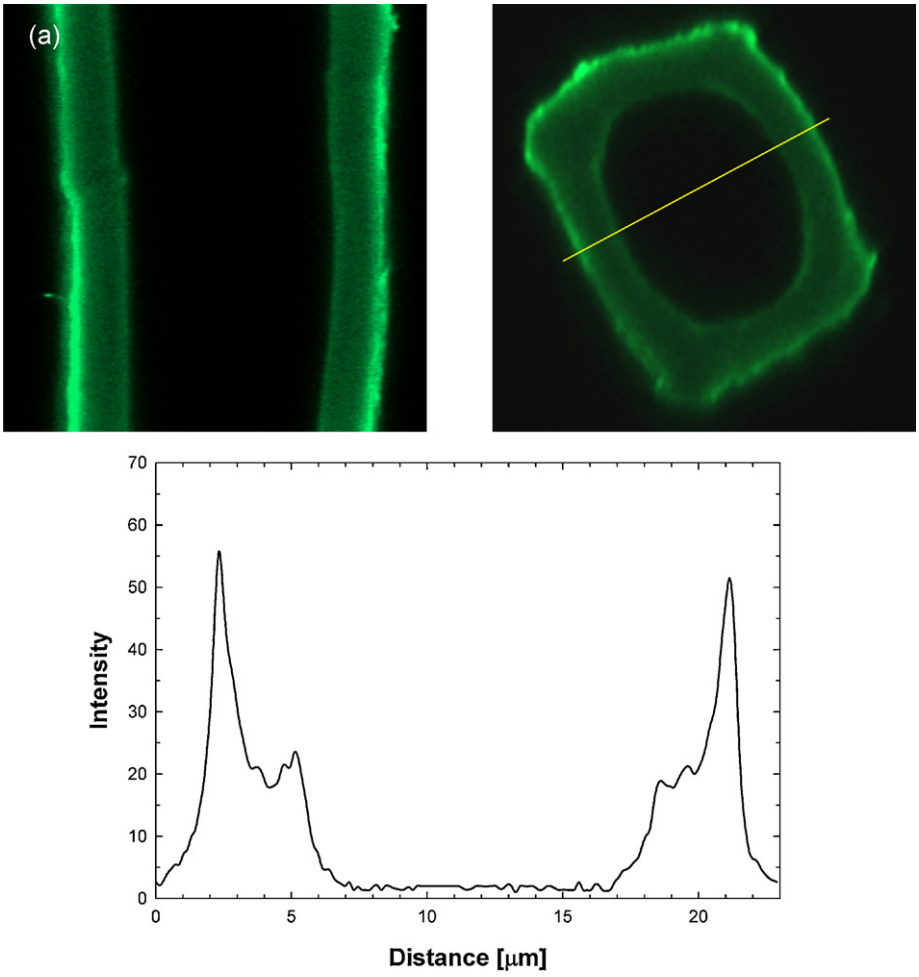


**Fig. 1.** Confocal laser scanning microscopy images of the fibre length-section and the fibre cross-section, and the corresponding intensity profile for the marked intersection, depicting the adsorption of fluorescein-labelled glucuronoxylan (FITC-GX) in the fibre wall. The images illustrate a representative fibre treated according to (a) L160 (80 °C, 0.1 M NaCl, 160 mg FITC-GX/g fibre) and (b) H160 (120 °C, 0.5 M NaCl, 160 mg FITC-GX/g fibre), cf. Table 1.

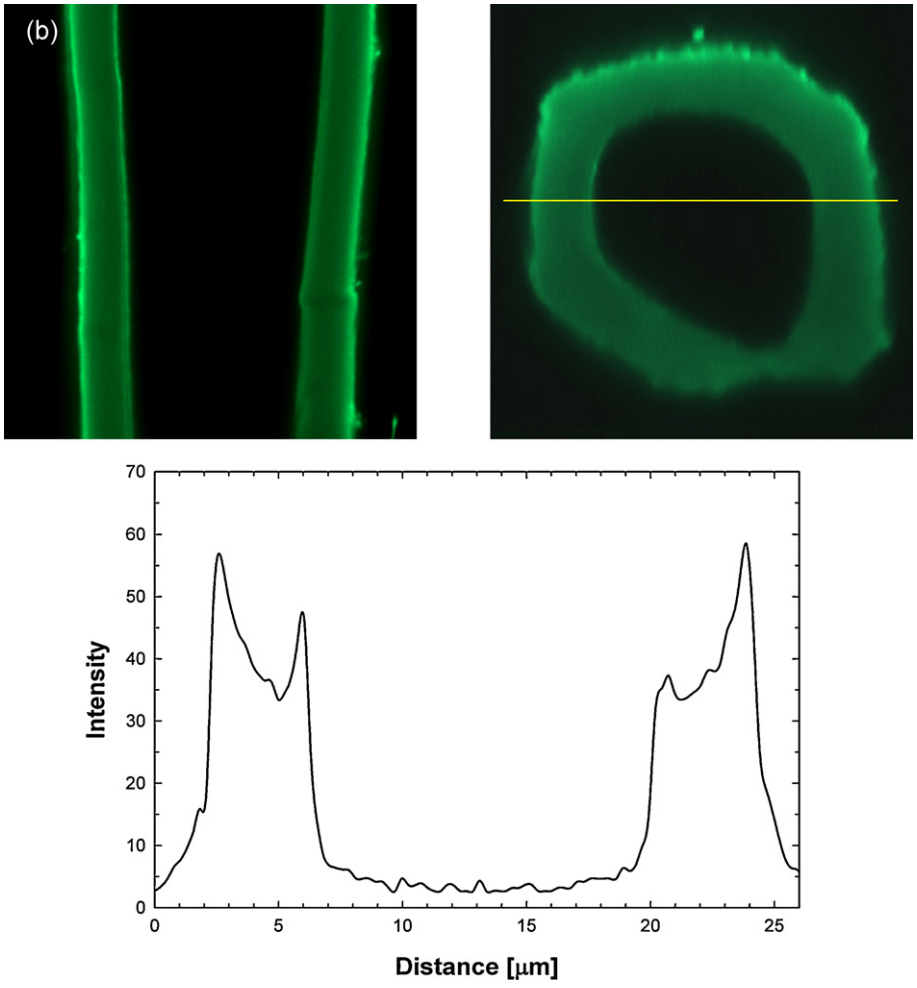


**Fig. 1.** (*Continued*).

because water is always, to some extent, retained between fibres (Maloney, Laine, & Paulapuro, 1999), and some water may be pressed from the fibre wall (Maloney & Paulapuro, 1999). Furthermore, it is suggested that WRV is sensitive to changes in the surface properties of the fibre wall (e.g. Forsström, Andreasson, & Wågberg, 2005; Laine, Lindström, Bremberg, & Glad-Nordmark, 2003), which affects the amount of externally held fibre water. The fibre saturation point is a more reliable method of evaluating the amount of water held within the fibre wall. It is usually determined by mixing wet pulp fibres with large non-interacting probe molecules (typically 2000 kDa dextran polymers), after which the change in probe molecule concentration is used to calculate the inaccessible amount of water (cf. Stone & Scallan, 1968). Consequently, WRV and FSP will give different results, and a combination of the two is necessary to give as complete a picture as possible of changes that occur in the fibre wall upon modification and drying. WRV and FSP were measured for all samples, both in the never-dried and in the once-dried state (Table 2).

The response in fibre swelling for the never-dried fibres due to the modification deviates between the WRV and FSP methods. Only a small change was observed in WRV, while a significant increase in FSP was obtained with the increased content of adsorbed xylan (Table 2, Fig. 2). The increase in FSP is probably due to the increased amount of charged groups in the modified fibres (cf. Table 1).

**Table 2**
Fibre swelling detected as water retention value (WRV) and fibre saturation point (FSP) for never-dried and once-dried samples; and the degree of hornification, defined as the relative decrease in fibre swelling due to drying. The samples were dried after the adsorption of glucuronoxylan.

| Sample | WRV [g/g] | | FSP [g/g] | | Hornification* (WRV) | Hornification* (FSP) |
|---|---|---|---|---|---|---|
| | Never-dried | Once-dried | Never-dried | Once-dried | | |
| Ref | 1.49 | 1.10 | 1.42 | 0.87 | 26 | 39 |
| L0 | 1.50 | 1.11 | 1.42 | 0.84 | 26 | 41 |
| L40 | 1.54 | 1.22 | 1.53 | 0.98 | 18 | 31 |
| L80 | 1.55 | 1.26 | 1.70 | 1.07 | 15 | 24 |
| L160 | 1.52 | 1.29 | 1.80 | 1.16 | 13 | 18 |
| H0 | 1.46 | 1.11 | 1.41 | 0.87 | 26 | 39 |
| H40 | 1.52 | 1.22 | 1.61 | 0.98 | 18 | 31 |
| H80 | 1.51 | 1.26 | 1.68 | 1.07 | 15 | 25 |
| H160 | 1.49 | 1.29 | 1.79 | 1.14 | 13 | 20 |

* Hornification = (Ref never-dried − Sample once-dried)/Ref never-dried [%].

The degree of fibre swelling is to a high extent determined by the balance between osmotic pressure and the elastic restraining force of the fibre wall (Scallan & Tigerström, 1992). The former has been recognized to be the more critical factor with regards to swelling of kraft pulp fibres (cf. Lindström & Carlsson, 1982b). Thus, it is the content of ionisable groups that determines the swelling of the never-dried fibres, which explains the increase in FSP with increased amount of adsorbed GX. The small change in WRV can be explained by the fact that the water associated with the increase in FSP is pressed out from the fibre wall during centrifugation. One could assume that increased swelling at these levels opens up the inter-lamellae structures of cellulose fibrils to such an extent that the force developed during centrifuging becomes large enough to overcome the capillary action that keeps the water in the largest pores. Additionally, increased swelling lowers the transverse modulus of the fibre wall, increasing the tendency of the fibre to deform during centrifuging, which would affect the compressive resistance of the pulp fibre pad. In any case, these results are in accordance with the findings of Maloney et al. (1999), who showed that the WRV method could underestimate fibre swelling of highly swollen fibres due to the loss of intra-fibre water during centrifugation.

Drying generates inter-fibrillar bonding, which closes pore spaces and decreases the elasticity of the fibre wall, both resulting in lower fibre swelling. Drying and rewetting of the reference fibres reduced the WRV by 26%, which can be seen as a measure of the degree of hornification (cf. Weise, 1998). The FSP is reduced by 39%. The once-dried modified fibres show an increase in both WRV and FSP with increased amounts of adsorbed xylan (Table 2). Furthermore, the difference between the WRV and FSP decreases with increasing xylan content. As seen in Fig. 2, this means that the swelling properties of the modified fibres approach those of the never-dried reference fibres. In the range studied, the degree of hornification can be reduced by 50% by GX adsorption. It has often been assumed that variations in the swelling of pulp fibres are due to the content of hemicelluloses. The presence of strongly hydrated polymers in the fibre wall is certainly a factor governing the amount of water that penetrates into the fibre when dry pulps are immersed in water. However, it has been shown that the content of hemicelluloses is of minor importance compared to the content of charged groups for the swelling of rewetted kraft pulp fibres (Laine & Stenius, 1997). It has been suggested that ionised carboxyl groups interfere with hydrogen bonding between the lamellae in the fibre wall during drying, or that when fibres are rewetted, osmotic pressure ruptures the cross-links formed during drying (Laivins & Scallan, 1993; Lindström & Carlsson, 1982a). Hence, it is plausible to assume that the decreased degree of hornification owing to GX adsorption is due to the introduction of uronic acid groups in the fibre wall, but the additional role of xylan as a sterical spacer cannot be ruled out.

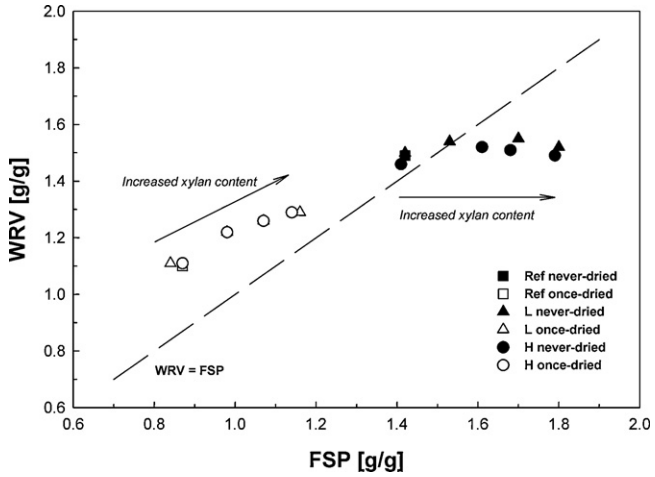


**Fig. 2.** Comparison between WRV and FSP measurements for never-dried and once-dried fibres. The variable in this figure is xylan content, which is varied by GX adsorption. L and H refer to conditions used during modification, cf. Table 1.

The fibre swelling after a certain level of GX addition is generally greater or about the same for fibres modified under L conditions compared to H (cf. Table 2). Since the adsorbed amount of GX is higher under the H conditions (cf. Table 1), this means that the response in fibre swelling to the adsorbed amount of GX is larger in the L case. Given that treatment under H conditions results in a decrease in the content of carboxylic acid groups originally attached to the fibres (cf. Table 1), one would expect to find the explanation in the total charge of the fibres. However, the swelling of the samples does not correlate with the total charge alone, but is also dependent on the conditions used during the adsorption. It could not be determined from this study whether this is due to conformational changes between GX adsorbed under the different conditions, or a matter of the GX/anionic charge location in the fibre wall.

### 3.4. Fibre surface area

The specific fibre surface area is closely associated with the pores in the fibre wall, especially the fraction of the small pores (cf. Stone & Scallan, 1965). Using the nitrogen adsorption technique to determine the surface area of fibres, sample preparation is crucial, since the method requires samples in the dry state. Drying of bleached pulp fibres from water gives a surface area of about 1 $m^2/g$, a couple of hundred times smaller than the area in the never-dried water swollen state. The dramatic loss of surface area is due to the fact that drying pulps from polar liquids, such as water, causes collapse of pores and loss of internal surface. The use of different solvent exchange systems has shown to be an effective way to remove water in a manner that prevents the collapse of fibre wall pores during drying (e.g. Haselton, 1955; Stone & Scallan, 1965; Wang et al., 2003). In the present work, a solvent exchange procedure was applied in which water is first replaced with acetone, a water-miscible organic solvent, and then acetone with cyclohexane, a non-polar solvent. Wang et al. (2003) have shown that the specific fibre surface area, measured on solvent exchanged fibres as described above, correlates well with the amount of non-freezing cyclohexane obtained from differential scanning calorimetry (DSC) thermoporosimetry measurements. Furthermore, the amount of non-freezing cyclohexane was shown to be related to the pores most affected by drying. Thus, measurement of surface area after water–acetone–cyclohexane solvent exchange is a useful approach for studying effects related to hornification.

The specific surface area for never-dried and once-dried samples, with and without adsorbed GX, treated under the two different conditions used during the modification (L and H), is presented in Fig. 3. An increase in surface area for the never-dried samples containing adsorbed xylan is observed. This could be a result of the increased swelling (cf. Table 2). The greater penetration of water into the fibre wall of these samples than in the never-dried non-modified samples causes additional de-bonding and the separation of solid elements (fibrils/lamellae), which may result in increased internal surface.

Drying of the non-modified samples (L0 and H0) reduces the surface area by about 30%, as a consequence of hornification. As seen in Fig. 3, adsorbing GX before drying the fibres preserves a considerable amount of the original surface area. This indicates that adsorbed xylan to a high extent prevents the collapse of fibre wall pores during drying.

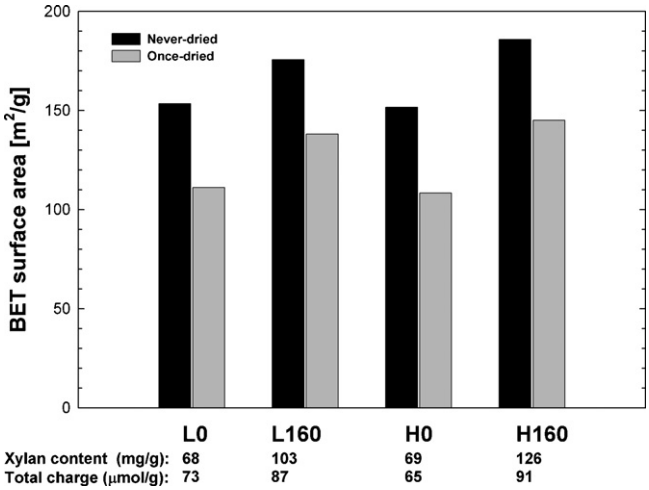


**Fig. 3.** BET surface area for never-dried and once-dried samples.

### 3.5. Wet fibre flexibility

The flexibility ($F$) of individual fibres is defined as the reciprocal of the bending stiffness, $F = 1/EI$, where $E$ is the elastic modulus of the fibre wall, and $I$ is the moment of inertia of a fibre cross-section (cf. Steadman & Luner, 1985). Drying bleached pulp fibres increases $E$ due to the internal cross-linking of the fibre wall (Scallan & Tigerström, 1992). Consequently, drying and recycling of bleached pulp fibres is associated with a great loss in fibre flexibility, which is also shown in this study where about 70% of the original fibre flexibility is lost upon drying (Fig. 4). Xylan adsorption has a significant effect on the drying-induced loss in fibre flexibility. It is evident that adsorbed GX prevents hornification (i.e. prevents reduction in the elastic modulus of the cell wall upon drying), which results in more flexible once-dried fibres. Since wet fibre flexibility has a decisive impact on the tensile strength and apparent sheet density of softwood fibres (Paavilainen, 1993), this means that a modified once-dried pulp would behave more like never-dried pulp. These results are in line with, and confirm, the observations of Köhnke and Gatenholm (2007).

### 3.6. Implications of the results on the relationship between GX adsorption and tensile strength

Based on the observations made in this study and in Köhnke and Gatenholm (2007), the relationship between GX adsorption and the tensile strength of rewetted pulp can be explained as follows: The swelling of the once-dried fibres increases with increasing content of adsorbed GX, due to the reduced degree of drying-induced fibre wall cross-linking. This results in increased wet fibre flexibility which promotes the conformability of the fibres and thus the formation of a denser paper sheet with higher tensile strength. Since the swelling/softening properties of the fibre are retained to a high degree, the beatability of the once-dried pulp fibres can be expected to increase (cf. Seth, 2001).

Finally, some comments have to be made concerning the importance of the location of adsorbed GX for tensile strength development. It has been shown that ionised groups located at the external part of the fibre surface are important for fibre/fibre joint strength, due to softening of the fibre surface (cf. Barzyk, Page, & Ragauskas, 1997; Torgnysdotter & Wågberg, 2003). In analogy with this, one could assume that GX adsorbed on the outer fibre surface is more effective than the GX adsorbed inside the fibre wall for the development of fibre/fibre joint strength, because of reduced surface hornification. It should also be mentioned that there are some reports in the literature about the correlation between pulp strength and xylan content on the fibre surface layer (e.g. Dahlman, Sjöberg, Jansson, & Larsson, 2003; Schönberg, Oksanen, Suurnäkki, Kettunen, & Buchert, 2001; Sjöberg, Kleen, Dahlman, Agnemo, & Sundvall, 2004). From the confocal experiments in this study, it has been concluded that GX adsorbs throughout the fibre wall, but enrichment on the outer surface can clearly be observed. The importance of GX adsorbed on the outer fibre surface contra inside the fibre wall for tensile strength development is not clear, and must be further studied.

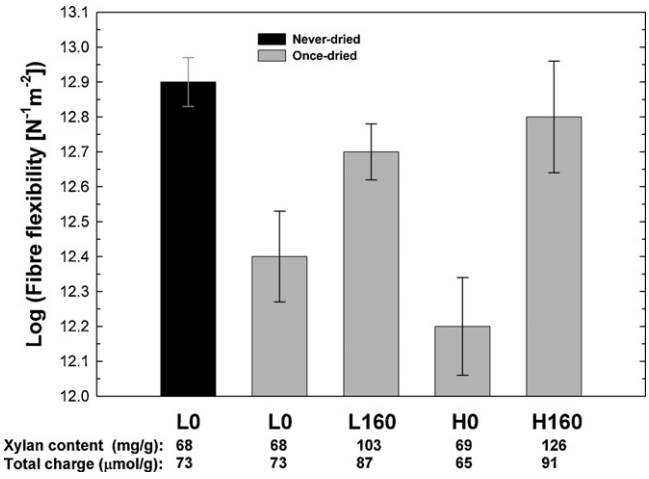


**Fig. 4.** Wet fibre flexibility for never-dried and once-dried samples. The limit bars in the figure represent 99% confidence intervals for the mean.

## 4. Conclusions

Adsorption of glucuronoxylan was enhanced by high temperature and/or high ionic strength. Xylan adsorbed on fibril surfaces inside the fibre wall, but the enrichment of adsorbed xylan could be seen on the outer fibre surface. Adsorption of GX on never-dried fibres increased fibre-swelling, specific fibre surface area, and wet fibre flexibility in the once-dried rewetted state, probably due to a reduced degree of drying-induced fibre wall cross-linking. Increased wet fibre flexibility promotes the conformability of the fibres and thus the formation of a denser paper sheet with higher tensile strength. Findings show that adsorbed GX can reduce the degree of hornification which is important for pulp producers and papermakers since market pulps are dried before being shipped and dry waste paper is used as raw material in the manufacture of recycled papers.

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## References

Barzyk, D., Page, D. H., & Ragauskas, A. (1997). Acidic group topochemistry and fibre-to-fibre specific bond strength. *Journal of Pulp and Paper Science*, *23*, J59–J61.

Berthold, J., & Salmén, L. (1997). Effects of mechanical and chemical treatments on the pore-size distribution in wood pulps examined by inverse size-exclusion chromatography. *Journal of Pulp and Paper Science*, *23*, J245–J253.

Cao, B., Tschirner, U., & Ramaswamy, S. (1998). Impact of pulp chemical composition on recycling. *Tappi Journal*, *81*, 119–127.
Dahlman, O., Rydlund, A., & Lindquist, A. (1997). Characterization of carbohydrates from chemical pulps using capillary electrophoresis and MALDI-TOF-MS. In *Proceedings from the 9th international symposium on wood and pulping chemistry* Montreal, Canada, L5-1–L5-4.
Dahlman, O., Sjöberg, J., Jansson, U. B., & Larsson, P. O. (2003). Effects of surface hardwood xylan on the quality of softwood pulps. *Nordic Pulp and Paper Research Journal*, *18*, 310–315.
de Belder, A. N., & Granath, K. (1973). Preparation and properties of fluorescein-labelled dextrans. *Carbohydrate Research*, *30*, 375–378.
Fernandes Diniz, J. M. B., Gil, M. H., & Castro, J. A. A. M. (2004). Hornification—its origin and interpretation in wood pulps. *Wood Science and Technology*, *37*, 489–494.
Forsström, J., Andreasson, B., & Wågberg, L. (2005). Influence of pore structure and water retaining ability of fibres on the strength of papers from unbleached kraft fibres. *Nordic Pulp and Paper Research Journal*, *20*, 176–185.
Granström, A., Eriksson, T., Gellerstedt, G., Rööst, C., & Larsson, P. (2001). Variables affecting the thermal yellowing of TCF-bleached birch kraft pulps. *Nordic Pulp and Paper Research Journal*, *16*, 18–23.
Gruber, E., & Weigert, J. (1998). Chemische Modifizierung von Zellstoffen zur Verminderung ihrer Verhornungsneigung. *Das Papier*, *52*, V20–V26.
Häggkvist, M., Li, T.-Q., & Ödberg, L. (1998). Effects of drying and pressing on the pore structure in the cellulose fibre wall studied by $^{1}H$ and $^{2}H$ NMR relaxation. *Cellulose*, *5*, 33–49.
Hansson, J.-Å., & Hartler, N. (1969). Sorption of hemicelluloses on cellulose fibres. Part 1. Sorption of xylans. *Svensk Papperstidning*, *72*, 521–530.
Hartler, N., & Lund, A. (1962). Sorption of xylans on cotton. *Svensk Papperstidning*, *65*, 951–955.
Haselton, W. R. (1955). Gas adsorption by wood, pulp and paper. II. The application of gas adsorption techniques to the study of the area and structure of pulps and the unbonded and bonded area of paper. *Tappi*, *38*, 716–723.
Hausalo, T. (1995). Analysis of wood and pulp carbohydrates by anion exchange chromatography with pulsed amperometric detection. In *Proceedings from the 8th international symposium on wood and pulping chemistry, Vol. 3* Helsinki, Finland, (pp. 131–136).
Higgins, H. G., & McKenzie, A. W. (1963). The structure and properties of paper. XIV. Effects of drying on cellulose fibres and the problem of maintaining pulp strength. *Appita*, *16*, 145–164.
Horvath, A. T., Horvath, A. E., Lindström, T., & Wågberg, L. (2008). Adsorption of low charge density polyelectrolytes to an oppositely charged porous substrate. *Langmuir*, *24*, 6585–6594.
Hubbe, M. A., Venditti, R. A., & Rojas, O. J. (2007). What happens to cellulosic fibers during papermaking and recycling? A review. *BioResources*, *2*, 739–788.
Hult, E. L., Larsson, P. T., & Iversen, T. (2001). Cellulose fibril aggregation—an inherent property of kraft pulps. *Polymer*, *42*, 3309–3314.
Jayme, G. (1944). Mikro-Quellungsmessungen an Zellstoffen. *Papierfabrikant/Wochenblatt für Papierfabrikation*, *6*, 187–194.
Kabel, M. A., van den Borne, H., Vincken, J.-P., Voragen, A. G. G., & Schols, H. A. (2007). Structural differences of xylans affect their interaction with cellulose. *Carbohydrate Polymers*, *69*, 94–105.
Katz, S., Beatson, R. P., & Scallan, A. M. (1984). The determination of strong and weak acidic groups in sulfite pulps. *Svensk Papperstidning*, *87*, R48–R53.
Klungness, J. H., & Caulfield, D. F. (1982). Mechanisms affecting fibre bonding during drying and aging of pulps. *Tappi Journal*, *12*, 94–97.
Köhnke, T., Brelid, H., & Westman, G. (2009). Adsorption of cationized barley husk xylan on kraft pulp fibres: Influence of degree of cationization on adsorption characteristics. *Cellulose*, *16*, 1109–1121.
Köhnke, T., & Gatenholm, P. (2007). The effect of controlled glucuronoxylan adsorption on drying-induced strength loss of bleached softwood pulp. *Nordic Pulp and Paper Research Journal*, *22*, 508–515.
Köhnke, T., Pujolras, C., Roubroeks, J. P., & Gatenholm, P. (2008). The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres. *Cellulose*, *15*, 537–546.
Laine, J., Lindström, T., Bremberg, C., & Glad-Nordmark, G. (2003). Studies on topochemical modification of cellulosic fibres. Part 4. Toposelectivity of carboxymethylation and its effects on the swelling of fibres. *Nordic Pulp and Paper Research Journal*, *18*, 316–324.
Laine, J., & Stenius, P. (1997). Effect of charge on the fibre and paper properties of bleached industrial kraft pulps. *Paperi ja Puu*, *79*, 257–266.
Laivins, G. V., & Scallan, A. M. (1993). The mechanism of hornification of wood pulps. In C. F. Baker (Ed.), *Products of papermaking, Trans-actions of the 10th fundamental research symposium, Vol. 2* Oxford, UK, (pp. 1235–1260).
Linder, Å., Bergman, R., Bodin, A., & Gatenholm, P. (2003). Mechanism of assembly of xylan onto cellulose surfaces. *Langmuir*, *19*, 5072–5077.
Lindström, T., & Carlsson, G. (1982a). The effect of carboxyl groups and their ionic form during drying on the hornification of cellulose fibers. *Svensk Papperstidning*, *85*, R146–R151.
Lindström, T., & Carlsson, G. (1982b). The effect of chemical environment on fiber swelling. *Svensk Papperstidning*, *85*, R14–R20.
Maloney, T. C., Laine, J. E., & Paulapuro, H. (1999). Comments on the measurement of cell wall water. *Tappi Journal*, *82*, 125–127.
Maloney, T. C., & Paulapuro, H. (1999). The centrifugal compression value. *Tappi Journal*, *82*, 150–154.
Mohlin, U.-B. (1975). Cellulose fiber bonding. 3. Effect of beating and drying on interfiber bonding. *Svensk Papperstidning*, *78*, 338–341.
Nazhad, M. M., & Paszner, L. (1994). Fundamentals of strength loss in recycled papers. *Tappi Journal*, *77*, 171–179.
Oksanen, T., Buchert, J., & Viikari, L. (1997). The role of hemicelluloses in the hornification of bleached kraft pulps. *Holzforschung*, *51*, 355–360.
Paananen, A., Österberg, M., Rutland, M., Tammelin, T., Saarinen, T., Tappura, K., et al. (2004). Interaction between cellulose and xylan: An atomic force microscope and quartz crystal microbalance study. In P. Gatenholm, & M. Tenkanen (Eds.), *Hemicelluloses: Science and technology. ACS Symposium Series, Vol. 864* American Chemical Society, (pp. 269–290).
Paavilainen, L. (1993). Conformability – flexibility and collapsibility – of sulphate pulp fibres. *Paperi ja Puu*, *75*, 689–702.
Rebuzzi, F., & Evtuguin, D. V. (2006). Effect of glucuronoxylan on the hornification of Eucalyptus globulus bleached pulp. In K. Fischer, & T. Heinze (Eds.), *Hemicelluloses. Macromolecular Symposia* (pp. 121–128). Weinheim: WILEY-VCH Verlag GmbH & Co.
Scallan, A. M., & Tigerström, A. C. (1992). Swelling and elasticity of the cell walls of pulp fibres. *Journal of Pulp and Paper Science*, *18*, J188–J192.
Schönberg, C., Oksanen, T., Suurnäkki, A., Kettunen, H., & Buchert, J. (2001). The importance of xylan for the strength properties of spruce kraft fibres. *Holzforschung*, *55*, 639–644.
Seth, R. S. (2001). The difference between never-dried and dried chemical pulps. *Tappi Solutions*, *1*, 95–110.
Sjöberg, J., Kleen, M., Dahlman, O., Agnemo, R., & Sundvall, H. (2004). Fiber surface composition and its relations to papermaking properties of soda-anthraquinone and kraft pulp. *Nordic Pulp and Paper Research Journal*, *19*, 392–396.
Spiegelberg, H. L. (1966). The effect of hemicelluloses on the mechanical properties of individual pulp fibres. *Tappi*, *49*, 388–396.
Steadman, R., & Luner, P. (1985). The effect of wet fibre flexibility on sheet apparent density. In C. V. Punton (Ed.), *Papermaking Raw Materials, Trans-actions of the 8th fundamental research symposium, Vol. 1* Oxford, UK, (pp. 311–337).
Stone, J. E., & Scallan, A. M. (1965). A study of cell wall structure by nitrogen adsorption. *Pulp and Paper Magazine of Canada*, *66*, T407–T414.
Stone, J. E., & Scallan, A. M. (1968). A structural model for the cell wall of water-swollen wood pulp fibres based on their accessibility to macromolecules. *Cellulose Chemistry and Technology*, *2*, 343–358.
Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., et al. (1995). Characterisation of 4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by $^{1}H$ and $^{13}C$ NMR spectroscopy. *Carbohydrate Research*, *272*, 55–71.
Theander, O., & Westerlund, E. A. (1986). Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber. *Journal of Agricultural and Food Chemistry*, *34*, 330–336.
Timell, T. E. (1967). Recent progress in the chemistry of wood hemicelluloses. *Wood Science and Technology*, *1*, 45–70.
Torgnysdotter, A., & Wågberg, L. (2003). Study of the joint strength between regenerated cellulose fibres and its influence on the sheet strength. *Nordic Pulp and Paper Research Journal*, *18*, 455–459.
Wang, X., Maloney, T. C., & Paulapuro, H. (2003). Internal fibrillation in never-dried and once-dried chemical pulps. *Appita Journal*, *56*, 455–459.
Weise, U. (1998). Hornification—mechanisms and terminology. *Paperi ja Puu*, *80*, 110–115.
Yan, D., & Li, K. (2008). Measurement of wet fibre flexibility by confocal laser scanning microscopy. *Journal of Materials Science*, *43*, 2869–2878.
Zhang, M., Hubbe, M. A., Vanditti, R. A., & Heitmann, J. A. (2002). Can recycled kraft fibres benefit from chemical addition before they are first dried? *Appita Journal*, *55*, 135–144.
Zhang, M., Hubbe, M. A., Vanditti, R. A., & Heitmann, J. A. (2004). Effects of sugar addition before drying on the wet flexibility of redispersed kraft fibres. *Journal of Pulp and Paper Science*, *30*, 29–34.