THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Adsorption of xylans on cellulosic fibres

Influence of xylan composition on adsorption characteristics and kraft pulp properties

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Xylans are not only present in wood, but also in various other plants such as grasses, cereals and herbs; where they can constitute a major fraction of the cell wall polysaccharides. One part of this thesis work investigates the possibility of utilizing xylans from agricultural residues, i.e. xylan isolated from barley husks, in softwood kraft pulp fibre modification.

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ABSTRACT

Xylans are polysaccharides present in large amounts in cell walls of vascular plants. They possess an inherent affinity to cellulose and will thus adsorb irreversibly on cellulose surfaces. This propensity, along with the great abundance in nature, provides great opportunities for the use of xylans as renewable and biodegradable cellulose fibre modifying agents. The research presented in this thesis provides further knowledge of how the composition of xylan fractions influences solution properties and characteristics of xylan adsorption on cellulosic fibres. The study also describes how xylan adsorption can be used to improve the strength properties of bleached softwood kraft pulp. Furthermore, the work investigates the potential of utilizing xylan isolated from agricultural waste materials in cellulose fibre modification.

Results show that lignin has a great influence on the aggregation behaviour of glucuronoxylan (GX) from birch. As lignin affects the solubility of xylan, it most likely also influences the driving force for xylan adsorption and deposition on cellulosic surfaces.

Adsorption of GX on bleached softwood kraft pulp before drying is shown to preserve a considerable part of the fibre-swelling, fibre wall porosity, 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 provides once-dried fibres with increased tensile strength and beatability.

Water-soluble (glucurono)arabinoxylan (GAX) isolated from barley husks is shown to interact with cellulose fibres. GAX with a low degree of substitution has an enhanced propensity to form aggregates in aqueous solutions and adsorb on cellulosic surfaces. In order to increase the driving force of adsorption of the more highly substituted xylan, GAX was cationized. This chemical modification increases the rate and magnitude of GAX adsorption extensively, due to the induced electrostatic interaction between anionic pulp fibres and cationic xylan. Furthermore, it is shown that adsorption of GAX on never-dried fibres may be beneficial in the production of market pulps with increased tensile strength and beatability.

Keywords: Adsorption, Cationization, Extraction, Hornification, Isolation, Lignin-carbohydrate complexes, Softwood kraft pulp, Xylan

List of publications

This thesis is mainly based on results presented in the following papers, referred to by Roman numerals in the text. The papers are appended at the end of the thesis.

I Fractionation and characterization of xylan rich extracts from birch
Westbye P, Köhnke T, Gatenholm P
Holzforschung 62(1), 31-37, 2008

II The influence of lignin on the self-assembly behaviour of xylan rich fractions from birch (*Betula pendula*)
Westbye P, Köhnke T, Glasser W, Gatenholm P
Cellulose 14(6), 603-613, 2007

III The effect of controlled glucuronoxylan adsorption on drying-induced strength loss of bleached softwood pulp
Köhnke T, Gatenholm P
Nordic Pulp and Paper Research Journal 22(4), 508-515, 2007

IV Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption
Köhnke T, Brelid H, Westman G
Submitted to Carbohydrate Polymers

V NMR cryoporometry to study the fiber wall structure and the effect of drying
Östlund Å, Köhnke T, Nordstierna L, Nydén M
Cellulose (in press)

VI The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres
Köhnke T, Pujolras C, Roubroeks JP, Gatenholm P
Cellulose 15(4), 537-546, 2008

VII Adsorption of cationized barley husk xylan on kraft pulp fibres: influence of degree of cationization on adsorption characteristics
Köhnke T, Brelid H, Westman G
Cellulose 16(6), 1109-1121, 2009

The progress of this work has also been presented at the following conferences:

i Reassembly of xylans as a tool for modification of lignocellulosic fibers from surface to bulk
Köhnke T, Westbye P, Linder Å, Roubroeks JP, Gatenholm P
In: Abstracts of papers. 231st ACS National Meeting, Atlanta, USA, March 26-30, 2006, CELL-126

ii Modification of cellulose fibres by controlled xylan adsorption and its effect on softwood pulp properties
Köhnke T, Gatenholm P
In: Conference proceedings. 14th International Symposium on Wood, Fibre and Pulping Chemistry, Durban, South Africa, June 25-28, 2007, O-62

iii The effect of xylan adsorption on pulp and paper properties
Köhnke T, Gatenholm P
In: Abstracts. 3rd Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives, Karlstad, Sweden, November 13-14, 2007, pp 62-64

iv The effect of xylan adsorption on hornification
Köhnke T
Ekmandagarna, Stockholm, Sweden, January 29-30, 2008

v Modification of cellulose fibers by controlled adsorption of xylans with various molecular structures
Köhnke T, Gatenholm P
In: Abstracts of papers. 235th ACS National Meeting, New Orleans, USA, April 6-10, 2008, CELL-261

vi Adsorption of cationized barley husk xylan on kraft pulp fibres
Köhnke T, Brelid H, Westman G
In: Conference proceedings. 10th European Workshop on Lignocellulosics and Pulp, Stockholm, Sweden, August 25-28, 2008, pp 181-184

vii Modification of kraft pulp fibres by adsorption of cationized (glucurono)arabinoxylan
Köhnke T, Brelid H, Westman G
In: Conference proceedings. 15th International Symposium on Wood, Fibre and Pulping Chemistry, Oslo, Norway, June 15-18, 2009, P-111

Contribution report

The author's contributions to the papers in this thesis:

I Active in planning the experimental outline and interpretation of results. Performed the xylan fractionation. Minor contribution to writing the article.

II Active in planning the experimental outline and interpretation of results. Shared experimental work with Peter Westbye. Minor contribution to writing the article.

III Main author. Responsible for experimental outline, experimental work, interpretation of results and writing the article. The pulp/fibre property analyses were performed by Södra Innovation.

IV Main author. Responsible for experimental outline, experimental work, interpretation of results and writing the article. The confocal laser scanning microscopy imaging was performed with the assistance of Kristoffer Lund.

V Active in planning the experimental outline and minor contribution to writing the article. Performed the sample modifications.

VI Main author. Responsible for experimental outline, interpretation of results and writing the article. Shared experimental work with Carla Pujolras.

VII Main author. Responsible for experimental outline, experimental work, interpretation of results and writing the article. The NMR spectra were obtained with assistance of staff at the Swedish NMR Centre, Göteborg, Sweden.

Contents

1 Introduction

1.1 Background

Hemicelluloses, e.g. xylans, mannans and xyloglucans are, together with cellulose and pectins, polysaccharides that build up the cell walls of vascular plants. Xylans are the most common hemicelluloses, and are considered to be the second most abundant biopolymers in the plant kingdom. Xylans have an inherent affinity to cellulose and will thus adsorb irreversibly on cellulose surfaces. This propensity, along with the great abundance in nature, provides great opportunities for the use of xylans as cellulose fibre modifying agents.

Hemicelluloses have a positive effect on the tensile strength of manufactured pulp. An increase in the content of hemicelluloses in a pulp can be achieved by adsorption of xylan, which is a potential approach to pulp strength property enhancement. Furthermore, in the development of new cellulose-based materials, cellulose fibres may be chemically functionalized in order to modify interactions between fibres or to adjust compatibility with other materials. Since xylans adsorb irreversibly on cellulosic fibres, great potential is to be found in xylan functionalization before assembly on cellulose. However, the influence of xylan composition on interaction with cellulose surfaces is not fully understood, and needs to be investigated further.

Due to the lack of a commercial supply, xylans have found little industrial utility, and interest in xylan modification has been rather low compared to that of commercially available polysaccharides. Nevertheless, in the current trend for a more effective utilization of biomass, increasing attention has been paid to the exploitation of xylans as biopolymer resources. A feasible procedure for xylan isolation in the pulp and paper industry would be extraction from wood chips prior to cooking. Another option is isolation, or more efficient use, of xylan dissolved in cooking liquors. A third alternative would be distribution of xylan between pulps, and in this way produce pulps with different properties and qualities. However, these procedures have to be more or less integrated with the pulping process, which places great demands on compatibility and efficiency. Even though there is an emerging interest in integrating the concept of biorefinery and pulp production, the isolation of xylans from annual plants may be closer to practical application. Residues from agriculture represent a potentially low cost source of material with high xylan content that could be used for such an application.

1.2 Objectives and thesis outline

The work of this thesis has been divided into four main parts. The aim of the first part was to investigate the influence of lignin on birch xylan solubility and agglomeration in aqueous systems, since this phenomenon is expected to influence the adsorption and deposition of xylan on cellulose surfaces. The aim of the second part was to study the effect of birch xylan adsorption on drying-induced property changes in bleached softwood kraft pulp, and the potential of using birch xylan as a hornification inhibitor. The aim of the third part was to investigate the possibility of utilizing xylans from agricultural residues, i.e. xylan isolated from barley husks, in cellulose fibre modification. The aim of the last part was to study how the interaction between barley husk xylan and bleached pulp fibres could be increased by chemical modification of the isolated xylan, i.e. the introduction of electrostatic interactions by xylan cationization.

In order to introduce the reader to the topic, Chapter 2 presents findings in the literature about xylans and xylan properties in general, and xylan adsorption on cellulosic surfaces/fibres in particular. Chapter 3 contains information on how the different materials in this study were obtained, i.e. methods of isolation, fractionation and modification of the xylans used. Results are presented and discussed in Chapter 4. This chapter is divided into four parts, representing the four main objectives of the work. Each part starts with an introduction, including background information relevant to the investigation, and ends with concluding remarks of the section. Chapter 5 presents the overall conclusions of this work.

2 Xylans

2.1 Classification of xylans

Hemicelluloses (e.g. xylans, mannans and xyloglucans) are, together with cellulose and pectins, polysaccharides that build up the cell walls of higher plants. The term “hemicellulose” was originally proposed for polysaccharides extractable by aqueous alkaline solutions. The name was based on the early belief that they were intermediates in the biosynthesis of cellulose, which later turned out to be incorrect (Sjöström 1993). Hemicelluloses are heteropolysaccharides built up from relatively few sugar units, where the most common are D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-*O*-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid (Timell 1967). Xylans are the most common hemicelluloses and are considered to be the second most abundant biopolymers in the plant kingdom (Ebringerová, Heinze 2000). Depending on the plant species and cell wall function, xylan content might differ greatly. There is also large variation in the structural features of the xylan molecule. Xylans may be grouped into the following structural subclasses (Ebringerová et al. 2005; Ebringerová 2006):

(*i*) *Homoxylans* (X), common in some seaweeds, are linear polysaccharides composed of D-xylopyranosyl (Xyl*p*) units linked by β-(1→3) (X3), or β-(1→4) (X4) or mixed β-(1→3, 1→4)-glycosidic linkages (X_m).

(*ii*) *Glucuronoxylans* (GX), common in hardwoods, generally consist of a backbone of β-(1→4)-linked D-Xyl*p* units substituted with α-(1→2)-linked 4-*O*-methyl-D-glucopyranosyl uronic acid (MeGlcA). The Xyl*p* units are partly acetylated at *O*-2 and/or *O*-3.

(*iii*) *(Arabino)glucuronoxylans* (AGX), common in softwoods, consist of a backbone of β-(1→4)-linked D-Xyl*p* units substituted with α-(1→2)-linked MeGlcA and α-(1→3)-linked L-arabinofuranosyl (Ara*f*) units.

(*iv*) *Arabinoxylans* (AX), common in cell walls of the starchy endosperm (flour) and outer layers of cereal grains (bran), consist of a backbone of β-(1→4)-linked D-Xyl*p* units substituted with α-L-Ara*f* at position 2 and/or 3. A particular feature of AX is the presence of phenolic acids (mainly ferulic acid (FA) and *p*-coumaric acid (PCA)) esterified to *O*-5 of some Ara*f* units.

(*v*) *(Glucurono)arabinoxylans* (GAX), are the dominant hemicelluloses in the lignified tissues of grasses and cereals (straw, stems, stalks and outer pericarp of grains). In contrast to AGX, the GAX backbone may be disubstituted with Ara*f* units, partly acetylated and esterified with FA.

(*vi*) *Heteroxylans* (HX), present in cereal bran, seeds and gum exudates, have the β-(1→4)-linked D-Xyl*p* backbone heavily substituted with a variety of mono- and oligosaccharide side groups.

2.2 Xylans in wood

Glucuronoxylan (GX) is the main hemicellulose component of hardwoods, where it can constitute up to 35% of the wood (Timell 1967). Every tenth Xyl*p* residue, on average, is substituted with MeGlcA (Timell 1967). Irregular distribution of MeGlcA in hardwood xylan has been suggested, and confirmed (Havlicek, Samuelson 1972; Rosell, Svensson 1975; Jacobs et al. 2001). Consequently, fractional precipitation (e.g. Wikström 1967) or fractional extraction (e.g. Sjöström, Enström 1967) of xylan usually yield preparations with great variations in the Xyl:MeGlcA ratio. GX is acetylated in the native state with about four to seven acetyl residues per ten Xyl*p* units (Lindberg et al. 1973, Teleman et al. 2002). The end group configuration consists of a special structure (Johansson, Samuelson 1977); the unit next to the reducing Xyl*p* end group is D-galacturonic acid, which is linked to an L-rhamnosyl unit through the C-2 position. The rhamnosyl unit, in turn, is connected through its C-3 position to the xylan chain. A broad range of different average molar masses have been reported for hardwood xylans over the years, probably due to different wood species, mode of isolation and analytical method used. A recent study based on SEC/MALDI mass spectrometry of xylan isolated from birch and aspen wood (holocellulose) by alkaline extraction suggests that the average number of xylose units per xylan molecule, DP_n, is 84-108 (DP_w=101-122); with a rather narrow polydispersity index M_w/M_n of 1.1 (Jacobs, Dahlman 2001).

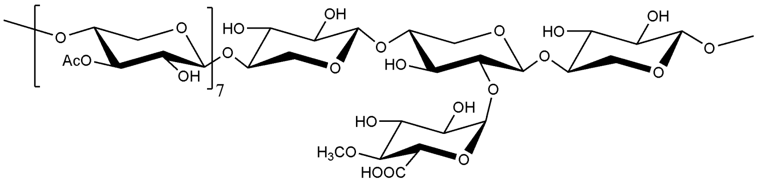

Fig. 1 Principal structure of birch xylan (*O*-acetyl-4-*O*-methylglucuronoxylan). (cf. Timell 1967)

Softwoods contain 5-10% (arabino)glucuronoxylan (AGX) with an average Xyl:MeGlcA:Ara ratio of 10:2:1.3 (Timell 1967). Unlike hardwood xylan, regular distribution of MeGlcA groups has been suggested (Jacobs et al. 2001), and no acetyl groups have been found. The average molar masses of softwood xylans are somewhat higher than the values for hardwood xylans, with DP_n and DP_w determined to 89-120 and 107-145, respectively (Jacobs, Dahlman 2001).

The existence of covalent linkages between lignin and polysaccharides in native wood, traditionally known as lignin-carbohydrate complexes (LCC) (Björkman 1957), has been debated for a long time (cf. Lai, Sarkanen 1971). However, evidence for covalent bonds between them has been increasing gradually (cf. Koshijima, Watanabe 2003; Lawoko et al. 2006). Three main types of native lignin-carbohydrate bonds have been suggested in the literature, viz. benzyl esters, benzyl ethers and phenyl glycosides. The formation of these linkages has been proposed to be closely related to the biosynthesis of lignin (Freudenberg, Grion 1959). As judged from model experiments involving reactions between quinone methide intermediates and carbohydrates, it is reasonable to believe that lignin may be linked to xylan preferably by ester bonds to MeGlcA (Tanaka et al. 1979) and by ether bonds to the primary alcohol at C-5 in Ara*f* (Leary et al. 1983). The former are labile under mild alkaline conditions, whereas the latter are not (Lundquist et al. 1983).

2.3 Xylans in annual plants

Xylans are not only present in wood, but also in various other plants such as grasses, cereals and herbs; where they can constitute a major fraction of the cell wall polysaccharides. Mixtures of xylans with different structures are normally present in annual plant tissue. Variations in xylan structure from different parts of a plant, from plants grown under various conditions or seasons may be as significant as interspecies variations (Stephen 1983). Cereal arabinoxylans, for example, exhibit great structural heterogeneity with respect to the ratio of Ara/Xyl, substitution pattern, content of phenolic acids and uronic acids, as well as molecular size distribution (Izydorczyk, Biliaderis 1995). Phenolic acids have been proposed as bridging molecules between xylans and between xylan and other cell wall polysaccharides, as well as lignin and proteins (cf. Ebringerová et al. 2005). Molecular weights up to several hundreds of kDa have been reported for arabinoxylans, but substantial variations occur depending on species, mode of isolation, and analytical method.

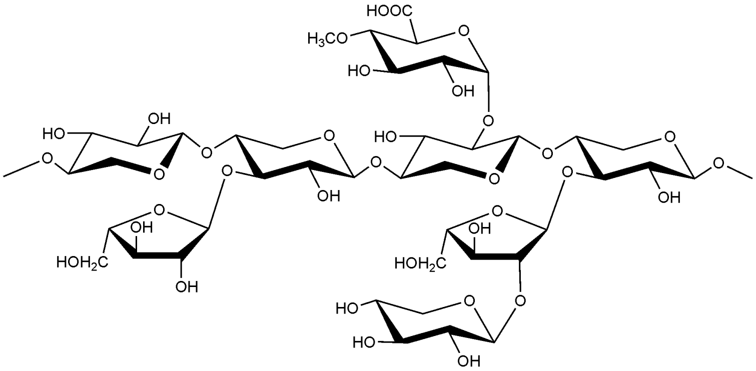

Fig. 2 Principal structure of barley husk xylan (4-*O*-methylglucuronoarabinoxylan). (cf. Höije et al. 2006)

2.4 Xylan in the plant cell wall

In the biosynthesis of the plant cell wall, cellulose fibrils are produced by cellulose synthase proteins (CESA) which are embedded in the plasma membrane in hexameric arrays called particle rosettes (cf. Cosgrove 2005). Non-cellulosic polysaccharides (e.g. hemicelluloses) are considered to be synthesized in the Golgi apparatus, packed into vesicles and targeted to the plasma membrane, where they become integrated with the newly synthesized cellulose fibrils that are extruded into the extracellular environment (cf. Carpita, McCann 2000). Xylans have been suggested to play an important role in the aggregation pattern of cellulose, which affects the crystalline structure and changes the dimensions of cellulose fibrils (e.g. Hackney et al. 1994; Tokoh et al. 2002; Reis, Vian 2004).

Several models describing the molecular arrangement in cell walls have been proposed throughout the years, where two of the most cited models for wood cells have been proposed by Fengel (1970) and by Kerr and Goring (1975). Both models describe cellulose fibrils surrounded by hemicellulose in a matrix of hemicellulose and lignin. It has later been suggested that xylan is associated with lignin and glucomannan with cellulose (Salmén, Olsson 1998). A recent study, however, shows that the ultrastructural arrangement, including the covalent bonding between polysaccharides and lignin, must have a more complex pattern (Lawoko et al. 2005). The size of cellulose fibrils in wood and pulp have been estimated using different microscopy techniques (cf. Duchesne, Daniel 1999) and CP/MAS ^{13}C NMR (e.g. Wickholm et al. 1998; Hult et al. 2000), reporting an elementary fibril size of about 3-5 nm in diameter, which in turn is aggregated into larger features called fibril aggregates of about 15 nm in diameter. It has been shown that the ultrastructure of kraft pulp fibres, i.e. the average fibril aggregate width, varies with varying hemicellulose content, and removal of large proportions of hemicelluloses allows cellulosic fibrils to associate more closely in larger fibril aggregates (Duchesne et al. 2001).

2.5 Xylans in solid state

Examination of naturally occurring 1→4-linked xylans in plant cell walls and gums shows that xylan chains form extended conformations, with the xylose ring in the $^4C_1$ chair and the glycosidic linkage diequatorial, and with a preference for a chain twist in a three-fold left-handed helical structure (Atkins 1992). Xylans are generally considered to be amorphous in the native state (i.e. in the cell wall) but can crystallize *in situ* after chemical modification, e.g. deacetylation (Marchessault et al. 1967), or after separation and isolation (e.g. Gröndahl, Gatenholm 2005). The degree of crystallinity is a function of relative humidity. When water content is reduced crystallinity drops, but the basic three-fold structure of the molecule persists. Xylans thus seem to be dependent on the presence of water to stabilise their structure (Nieduszynski, Marchessault 1971; Almond, Sheehan 2003). Xylan hydrate has been proposed to crystallize in a hexagonal unit cell structure, which contains two anti-parallel xylan chains stabilized in this conformation by their interaction with chains of water molecules (Nieduszynski, Marchessault 1972). The lattice spacing containing the stabilising water molecules is also able to accommodate xylan side groups. The basic conformation remains intact even after extensive substitution of the backbone (Atkins 1992). However, it has been shown that the tendency of xylan to crystallize is dependent on the degree of substitution, where crystallinity increases with decreasing amount of substituents (e.g. Höije et al. 2008).

2.6 Solution behaviour of xylans

The solubility of xylans is affected by the presence of substituents, substitution pattern and hydrogen bonding pattern. For example, arabinoxylans have been shown to become less soluble in water as the amount of Ara*f* side groups decreases (Andrewartha et al. 1979). Intra- and inter-molecular hydrogen bonds may be created during drying of extracted xylan, and also during storage. Complexing solvents, such as cuoxam, cadoxen and FeTNa have been used for breaking these hydrogen bonded networks (Ebringerová et al. 1994). Several researchers have reported that xylans have a strong tendency to form associated structures in aqueous solutions. Two basic mechanisms of the aggregation have been suggested: hydrogen bonds between linear portions of polysaccharide chains (e.g. Blake, Richards 1971; Dea et al. 1973; Linder et al. 2003), and association between hydrophobic substituents, i.e. lignin linked to the polysaccharide chain (e.g. Saake et al. 2001; Linder et al. 2003; Roubroeks et al. 2004). By analogy with the latter suggestion, LCCs have been shown to exhibit a strong tendency to form micelles or aggregates in aqueous solutions (e.g. Yaku et al. 1979; Uraki et al. 2006; Barakat et al. 2007).

Light scattering measurements of xylan in water or aqueous NaOH mostly give extremely high molar masses and radii of gyration, in contrast to measurements performed with osmosis, ultracentrifugation and SEC in combination with viscosity (LeBel et al 1963). This discrepancy can be explained by the presence of xylan aggregates. Even though only a very small number of large aggregates are present, this small fraction of particles dominates the scattering behaviour (Burchard 2005). Molar mass determination of xylans has been shown to best be analysed using a mobile phase of DMSO:H_2O (90:10) with the addition of 0.05 M LiBr, a system offering good solubilisation of the polymers and proper chromatographic separation (Saake et al. 2001).

2.7 Isolation of hemicelluloses

A standard procedure for isolation of hemicelluloses from wood is the extraction of chlorite holocellulose with aqueous alkaline solutions (Wise et al. 1946). Glucomannans are considered to be more effectively extracted by sodium hydroxide than by potassium hydroxide (Sjöström 1993). However, potassium hydroxide is preferred if the alkali extract is neutralized with acetic acid prior to precipitation in alcohol, because of the higher solubility of potassium acetate (Fengel, Wegener 1989). The addition of borate to the alkali facilitates the dissolution of glucomannans (Timell 1967). Hemicelluloses can be precipitated from the alkaline extract by acidification and the addition of e.g. methanol, ethanol or acetone. Some more specific precipitation agents are also known, for instance barium hydroxide for glucomannan and cetyltrimethylammonium bromide or hydroxide for glucuronoxylan (Sjöström 1993). Alkaline extraction deacetylates the hemicelluloses almost completely. If deacetylation is to be avoided, DMSO may be used (cf. Timell 1967). Steam pre-treatment/explosion (e.g. Glasser et al. 2000; Puls, Saake 2004; Krawczyk et al. 2008; Roos et al. 2009) and/or mild acid hydrolysis (e.g. Gustavsson et al 2004) prior to extraction may give relatively good purity and an adequate yield of xylan. The degree of polymerisation (DP) of the xylan may, however, drop considerably due to acid hydrolysis. Alternative approaches for hemicellulose extraction may be organosolv fractionation and the use of supercritical carbon dioxide, ($scCO_2$), near critical water or ionic liquids (cf. Ragauskas et al. 2006).

Compared to wood, the extractability of xylan from lignified annual plant fibres is easier, probably due to the lower amounts and different structure of the lignin component, as well as different cell wall architecture (Ebringerová, Heinze 2000). The isolation of xylan might, however, be complicated because of the presence of proteins, starch and β-glucans. The problem with co-extracted β-glucans can be avoided by the use of barium hydroxide (e.g. Gruppen et al. 1991).

Potential sources for xylan isolation in the kraft pulp industry may be wood chips (cf. van Heiningen et al. 2008), cooking liquors (e.g. Axelsson et al. 1962; Simonson 1963; Dahlman et al. 2008) and pulp (e.g Sjöström, Enström 1967; Janzon et al. 2006, 2008; Krogerus, Fuhrmann 2009).

2.8 Sorption of xylans on cellulosic surfaces

Hemicellulose reactions are comprehensive during kraft delignification and result in a large yield loss. The level of the alkaline degradation of hemicelluloses is determined, to a large extent, by their propensity to undergo peeling reactions (endwise degradation). Glucomannan is degraded more extensively than xylan (Aurell, Hartler 1965). The higher stability of xylan is the result of its end group configuration (Johansson, Samuelson 1977) and its substituents, which suppress peeling reactions (Sjöström 1977). A considerable part of the lost xylan is not degraded, but dissolved from the wood into the pulping liquor in the early part of the cook (Simonson 1963). It was early suggested, and is now generally accepted, that a part of this dissolved xylan will readsorb/precipitate on the pulp fibres as the cook proceeds. The idea of xylan sorption during pulping was raised based on the observations that xylan adsorbs on cotton fibres exposed to pulping liquor (Yllner, Enström 1956), that the xylan content of pulps may be varied by using a continuous flow method (Yllner et al. 1957), and that added tritium-labelled xylan can be traced to the fibres (Clayton, Stone 1963). Several methods to optimize the use of xylan-enriched cooking liquors have been published (e.g. Aurell 1965; Dillén, Noréus 1968) and patented (e.g. Aurell, Hartler 1964; Snekkenes et al. 2000).

In order to understand the mechanism of xylan retake during alkaline pulping, most studies dealing with xylan adsorption on cellulose fibres are conducted under alkaline conditions and at high temperatures. Adsorption has been shown to be dependent on the structure and concentration of xylan, the pH of the solution, time and temperature, and the nature of the cellulose fibres (see early review of Meller (1965)).

2.8.1 Effect of xylan composition

Xylan-cellulose interactions have been shown to depend on the molecular structure of xylan, and consequently the botanical origin and the choice of isolation method of the extracted xylan (e.g. Kabel et al. 2007). Several studies show favoured sorption of low substituted xylans, especially with a low content of uronic acids. This has been explained by a decrease in xylan solubility (Axelsson et al. 1962; Walker 1965; Mitikka-Eklund 1996), a decrease in xylan-cellulose steric repulsion (Mitikka-Eklund 1996), a decrease in the hydration of xylan (Hartler, Lund 1962; Hansson, Hartler 1969), and greater xylan-xylan interaction (Linder et al. 2003; Kabel et al. 2007).

Lignin fragments linked to xylan by covalent bonds have been suggested both to facilitate (e.g. Linder et al. 2003; Winter et al. 2006) and inhibit (Simonson 1971) adsorption on cellulose surfaces. Studies of polysaccharide model substances representing lignin-carbohydrate complexes have demonstrated a self-association which promotes adsorption on cellulose surfaces (Esker et al. 2004; Gradwell et al. 2004).

The effect of molecular weight is not fully understood. The reason for this is probably the fact that the preparation of low molecular weight xylan usually affects the degree of substitution, which makes it difficult to study these two properties independent of each other (cf. Hartler, Lund 1962). However, recent published investigations, based on enzymatic hydrolysis of the xylan backbone, suggest that reduced xylan molar mass results in lower adsorption (Winter et al. 2006; Kabel et al. 2007). Furthermore, it is indicated that a minimal backbone length of at least 15 xylose residues is needed for xylan adsorption (Kabel et al. 2007). Considering thermodynamics, longer polymers have a stronger driving force for adsorption, because they lose less entropy (per unit mass) upon adsorption (cf. Fleer et al. 1993; Stenius 2000). However, since pulp fibres are porous it is obvious that the molecular weight of an adsorbing molecule, i.e. the molecular size, has an impact on the accessible surface area, and thus the adsorbed amount.

2.8.2 Effect of cellulosic substrate

The nature and structure of the cellulose substrate have a great influence on the extent of xylan adsorption, already demonstrated in 1956 by Yllner and Enström. Almost all features of the cellulose fibre, such as porous structure, surface area, swelling capacity, crystallinity and chemical composition, have been shown to influence the adsorption of xylan.

An extensive study by Hansson and Hartler (1969) shows that disintegration of a cotton fibre structure by beating results in an increase in adsorption, which correlates with the swelling of the fibres and the fibre surface area. A decrease in the DP of the cotton cellulose performed with acid hydrolysis also increased the adsorption, indicating a positive effect of increasing the crystallinity of the sorbent and/or opening of the fibre structure. It was thus concluded that a vital factor during adsorption seems to be the possibility for xylan to get into the fibre structure. The effect of surface area and crystallinity has also been studied by Linder and Gatenholm (2004), and their results are in line with the earlier observation that a large accessible surface area facilitates xylan adsorption. The study also shows that xylan adsorbs on regenerated cellulose.

A trial performed by Mitikka-Eklund (1996) shows that xylan adsorption on kraft pulp occurs more extensively than adsorption on cotton fibres. This was explained by the difference in accessible surface area and degree of crystallinity. Additionally, bleached pulp seemed to adsorb more xylan than unbleached pulp. This was partly explained by the difference in chemical composition, where low lignin content and low amounts of negatively charged groups favour adsorption. The importance of the chemical composition of the substrate has also been illustrated by the finding that the amount of xylan adsorbed on cotton fibres is reduced if the cotton already contains glucomannan (Hansson, Hartler 1969).

2.8.3 Effect of temperature

Adsorption of xylan is strongly influenced by temperature; generally the rate of adsorption increases with an increase in temperature (e.g. Yllner, Enström 1957; Hartler, Lund 1962; Eriksson et al. 1963; Clayton, Phelps 1965; Hansson 1970; Henriksson, Gatenholm 2001; Ribe et al. 2009). It has been proposed that increased adsorption at higher temperatures is due to the dehydration of xylan (Hartler, Lund 1962; Hansson 1970). However, many of these studies have been performed under alkaline conditions, and an increase in temperature will consequently affect the alkaline degradation of the xylan side groups. Such degradation will decrease xylan solubility and may consequently induce xylan precipitation. It has also been suggested that degradation of xylan side groups increases xylan aggregation and thus the driving force for xylan assembly on cellulose surfaces (Linder et al. 2003).

2.8.4 Effect of xylan concentration

Hansson and Hartler (1969) have shown that the adsorption of birch xylan on cotton fibres under pulping conditions is greatly influenced by hemicellulose concentration, whereas the adsorption of pine xylan is only slightly influenced. The difference was explained by the higher degree of substitution of pine xylan, affecting the hydration of the polysaccharide molecule. The observation that the degree of substitution clearly affects the xylan adsorption isotherm has also been demonstrated by Kabel et al. (2007).

2.8.5 Effect of pH and ionic strength

Within the pH-interval 2-11, pH has been shown to only slightly influence the adsorption of xylan on cellulose fibres (Eriksson et al. 1963; Henriksson, Gatenholm 2001). Increasing pH from 11 has been shown to decrease adsorption (Hansson, Hartler 1969; Mitikka-Eklund 1996; Danielsson, Lindström 2005; Ribe et al. 2009). Results from these studies are in line with the fact that xylan redeposition at the end of the kraft cook is favoured if the pH of the cooking liquor is low (Yllner, Enström 1957; Aurell 1963). The increase in sorption of xylan by decreasing the pH level of the solution in the alkaline regime is explained by a decrease in xylan solubility (Yllner, Enström 1957; Hansson, Hartler 1969; Mitikka-Eklund 1996) and a decrease in electrostatic repulsion (Mitikka-Eklund 1996), due to a pKa value of about 14 (25°C) (Sjöström 1989) for the most acidic hydroxyl groups in polysaccharides.

Adsorption of negatively charged xylan is found to be more extensive at high ionic strength (Ström et al. 1982; Mitikka-Eklund 1996; Ribe et al. 2009). This has been explained to be a consequence of a decrease in repulsive forces between negatively charged xylans and pulp fibres (Ström et al. 1982; Mitikka-Eklund 1996), as well as a decrease in the molecular extension of xylan which favours penetration of xylan molecules in the pores of the fibre wall (Ström et al. 1982). It has also been shown that the presence of an electrolyte decreases the stability of high concentrated glucuronoxylan solutions, which induces phase separation and precipitation (Linder et al. 2003). Such precipitation would result in xylan deposition and assembly on cellulose surfaces.

2.9 Mechanism for xylan adsorption and desorption

The adsorption of xylan on cellulose fibres has been characterized as a relatively slow process, probably due to hindered molecular diffusion into the porous fibre wall (Clayton, Phelps 1965; Hansson 1970; Ström et al. 1982). However, a slow adsorption equilibration also occurs on non-porous silica surfaces (Neuman et al. 1993; Claesson et al. 1995; Österberg et al. 2001). This behaviour has been suggested to be an effect of xylan polydispersity and the fact that the xylan and the surface have the same sign of charge; thus, a depletion layer probably occurs outside the surface and reduces the adsorption rate. By studying the energy of activation for xylan adsorption on cellulose and kraft pulp fibres, the process has been suggested to involve forces of the van der Waals-type or hydrogen bonds (Clayton, Phelps 1965; Hansson 1970; Danielsson, Lindström 2005; Ribe et al. 2009). Mora et al. (1986) demonstrated the role of strong hydrogen bonding in the retention of xylan on microfibril surfaces in association-dissociation experiments involving hydrogen bond-rupting reagents. The formation of hydrogen bonds between xylan and cellulose as the driving force of adsorption has, however, been questioned. Paananen et al. (2004) claim that if the formation of hydrogen bonds was the case, the adsorbed layer of xylan on cellulose surfaces would be flat and not swollen with water as their results, based on the QCM-D technique, indicate. Instead, they suggest, that the driving force is a combination of the inherent entropy increase associated with the release of solvent molecules when polymers are adsorbed, and weak van der Waals attraction. Since the solubility of xylan in water is relatively low, even weak attraction could promote substantial adsorption. Furthermore, they state that their conclusions do not eliminate the possibility that hydrogen bonds may be of great importance in dry systems, such as dried fibre networks (paper).

The backbone of xylan in crystalline form or in aqueous solution has a three-fold conformation, whereas plant cellulose possesses a two-fold axis conformation (e.g. Nieduszynski, Marchessault 1971; Rees 1977; Teleman et al. 1995; Almond, Sheehan 2003). CP/MAS ^{13}C NMR spectroscopy studies show that the chain conformation of adsorbed xylan on bleached pulp fibres and on cellulose clearly differs from its conformation in solution (cf. Mitikka-Eklund 1996; Larsson et al. 1999; Tenkanen et al. 2000; Teleman et al. 2001; Liitiä et al. 2003). It seems possible that in the interaction with cellulose, xylan tends to adopt the same two-fold axis conformation as cellulose, which has also been demonstrated using molecular dynamic modelling (Leeflang et al. 2006). With hydrogen substituted to the carbon at position 5 instead of a hydroxymethyl group as in cellulose, the intra- and inter-chain cooperative hydrogen bonding pattern is suppressed. This makes the xylan molecule more flexible and stereochemically capable of forming a flat ribbon-like structure similar to cellulose (Atkins 1992).

A mechanism for xylan sorption on cellulose surfaces based on the tendency of xylan to self-associate has been proposed by Linder et al. (2003). They suggest that xylan exists in aqueous solution both as dissolved single molecules and as aggregated structures in the colloidal size range. The formation of aggregates is promoted by interactions between unsubstituted regions of the xylan chains, as well as by hydrophobic interaction due to lignin residues covalently attached to the xylan. Consequently, adsorption on cellulose surfaces occurs both in the case of single molecules and in the case of aggregates. This mechanism, which includes polymer adsorption and deposition of xylan aggregates, is probably highly relevant in systems where the solubility of xylan is low. The effect of low xylan solubility on the adsorption of birch xylan on cellulose has been observed by Tammelin et al. (2009). They studied xylan adsorption on cellulose using the QCM-D technique in combination with a Voigt-based model for a viscoelastic solid. The Voigt model estimated a relatively weakly bound xylan film on cellulose at low ionic strength, but at high ionic strength the model failed. The reason for this behaviour was suggested to be a consequence of the moderately limited solubility of the xylan molecules. At high ionic strength, when solubility is impaired, the xylan chains formed soluble clusters which adsorbed on cellulose forming patches. The formation of unevenly distributed xylan globular structures on the cellulose surface was explained to be the reason why the Voigh model could not estimate xylan layer properties.

The adsorption of xylan is considered to be irreversible and only very small amounts are removed upon dilution (Paananen et al. 2004), or when washed with water (Eriksson et al. 1963). Treatment under alkaline conditions at high temperature increases the extent and rate of desorption (Hansson, Hartler 1969). Adsorbed xylan is more resistant than native xylan towards degradation/dissolution in acidic and alkaline media, which has been explained by assuming the adsorbed molecules to be more physically well-ordered than their native counterparts (Yllner, Enström 1957; Hartler, Lund 1962). Xylanase can act on adsorbed xylan (e.g. Schönberg et al. 2001). However, it has been shown that only part of the adsorbed xylan can be liberated from pulp fibres by xylanase treatment. This observation has been explained to either be a consequence of the restricted accessibility of the enzyme to the porous structure of the fibre wall, or a result of crystallization of the adsorbed xylan (Mitikka-Eklund 1996). Xylan adsorbed from black liquors on softwood kraft fibres has been found to remain on the fibre surface even after subsequent oxygen delignification and ECF bleaching, as well as after laboratory beating (Dahlman et al. 2003).

2.10 Location of adsorbed xylan

As mentioned earlier, the adsorption of xylan on pulp fibres has been characterized as a relatively slow process, probably due to hindered molecular diffusion into the porous fibre wall (Clayton, Phelps 1965; Ström et al. 1982), indicating that xylan may adsorb on internal fibre wall surfaces. Linder and Gatenholm (2004) visualized glucuronoxylan adsorbed on dissolving pulp by immunolabeling in combination with confocal laser microscopy. They suggested that the adsorbed xylan was located not only on the external surface of the fibre but also on the internal surfaces and/or in the pores. Mitikka–Eklund (1996) analyzed the topological distribution of adsorbed xylan on bleached softwood kraft pulp fibres by studying the ratio between anomeric and non-anomeric carbons using ESCA. The outcome of the study was that the adsorbed xylan was enriched, but only slightly, on the outer fibre surface; suggesting that adsorption occurs quite evenly throughout the fibre wall. This interpretation of the results agrees with the finding that only part of the adsorbed xylan was liberated by xylanase treatment, which is assumed to act predominantly on the outer fibre surface.

The analyses described above were conducted after adsorption of xylan on bleached pulp fibres. The location of xylan adsorbed from black liquor during a kraft cook has been studied using mechanical peeling (Dahlman et al. 2003), showing that xylan is adsorbed primarily on the outer fibre surface. The location has, however, been suggested to be dependent on the molecular weight of the xylan present in the cooking liquor. Danielsson and Lindström (2005) observed that the addition of high molecular weight glucuronoxylan induces more surface charges on the produced pulp than low molecular weight xylan.

2.11 Effect of hemicellulose retention on pulp properties

It is generally agreed that retention of hemicelluloses during chemical pulping has an improving effect on the tensile strength of the pulp. The effect of hemicelluloses on the properties of the pulp has traditionally been interpreted as a contribution to the swelling tendency of the fibre, which facilitates the beating action and gives wet flexibility to the fibres during paper formation and/or a direct strengthening effect of the fibre/fibre bond (cf. Rydholm 1965).

Another interesting characteristic of pulps with a high content of hemicelluloses is their reduced tendency to undergo drying-induced property changes. Delignified pulp fibres subjected to a drying-rewetting cycle show an irreversible loss in swelling capacity, a phenomenon denoted as “hornification” (cf. Weise 1998). Hornification is proposed to depend on an increase in the degree of cross-linking between cellulose fibrils when the fibre wall collapses during drying (Laivins, Scallan 1993). However, the magnitude of hornification has been shown to be related to the content of hemicelluloses in the pulp (e.g. Spiegelberg 1966; Oksanen et al. 1997; Cao et al. 1998; Hult et al. 2001; Rebuzzi, Evtuguin 2006;

Moss, Pere 2006). Thus, hemicelluloses located in interfibrillar spaces seem to prevent the formation of irreversible bonds during drying.

2.12 Effect of hemicellulose adsorption on pulp properties

The effect of xylan readsorption during the kraft cook not only affects the total yield, but has also been shown to improve the tensile strength and beatability of the pulp (Dahlman et al. 2003; Danielsson, Lindström 2005). Schönberg et al. (2001) have shown that the same trend is observed when bleached pulp is treated with hardwood xylan. There are a few published observations that adsorbed arabinoxylan increases the strength properties of bleached pulp, and even indications that arabinoxylans are superior to glucuronoxylan as dry strengthening agents (e.g. Saake et al. 2005; Ramirez et al. 2008).

Henriksson and Gatenholm (2002) have shown that surface modification of CTMP with xylan significantly decreases the advancing contact angle of single fibres, which improves the water sorption of fibre networks.

Due to the lack of a commercial supply, as well as their usually low molecular weight and poor solubility, xylans have found little industrial utility and interest in their modification has been rather low in comparison to commercially available polysaccharides (Ebringerová et al. 2005). However, adsorption of cationized xylans seems to have the potential to improve strength properties of bleached pulp, as indicated by Antal et al. (1991, 1997) and Ren et al. (2009).

It should also be mentioned that utilization of hemicelluloses other than xylans in cellulose fibre modification has gained lot of attention in recent years. Adsorption of pre-isolated mannans (e.g. Suurnakki et al. 2003; Hannuksela et al. 2004) and xyloglucans (e.g. Lima et al. 2003; Christiernin et al. 2003) has been shown to increase strength properties of bleached pulps. Moreover, great potential is to be found in hemicellulose functionalization before assembly on cellulose, as demonstrated by Brumer et al. (2004) using chemoenzymatic modification of xyloglucans.

3 Materials and Methods

3.1 Xylans

3.1.1 Papers I and II

Xylan was isolated by mild hydrolysis of birch wood chips using 0.01 M acetic acid at 140°C for 1 h followed by sodium hydroxide (1 M) extraction at room temperature for 16 h. The extract was removed by filtration and the pH was adjusted to 7 using concentrated hydrochloric acid. Non-soluble material was removed by centrifugation and the supernatant was dialysed (molecular cut-off (MWCO): 12-14 kDa) against deionised water, rota-evaporated and finally freeze-dried. For details, see Karlsson et al. (2006).

In order to reduce the lignin content of the crude xylan fraction, an extraction was performed essentially according to Roubroeks et al. (2004), who adopted the method from Lundquist et al. (1977). The xylan fraction was suspended in a pyridine:acetic acid:water (9:1:4) mixture. After extraction under continuous stirring at room temperature, the sample was centrifuged and the supernatant decanted. The supernatant was then extracted with chloroform. The organic phase was treated with repeated addition and removal (rota-evaporation) of ethanol before drying. The water phase was mixed with ethanol (1:4) and the precipitate was isolated by centrifugation. The solid material was washed with ethanol and then dissolved in deionised water and freeze-dried. A more detailed description of the fractionation and characterisation of all sub-fractions can be found in *Paper I*.

3.1.2 Papers III, IV and V

A 4-*O*-methylglucuronoxylan (GX) separated from birch wood by alkaline extraction was purchased from Sigma Aldrich and used without any further purification. Analysis of the xylan showed the following contents: neutral carbohydrates 79.0%, ash 10.4%, acid-soluble lignin 2.1% and Klason lignin 0.6%. The relative carbohydrate composition was determined to Xyl 96.1%, Glc 2.4%, Gal 1.0%, Ara 0.4% and Man 0.1%. ^1H NMR spectroscopy showed an average MeGlcA/Xyl ratio of 1/12 and a HexA/Xyl ratio of 1/66. A weight average molar mass of 9,600 g/mol and a polydispersity index (M_w/M_n) of 2.6 was determined using size exclusion chromatography (SEC) in DMSO:H_2O.

3.1.3 Papers VI and VII

Xylan was separated from chlorite delignified barley husks by sodium hydroxide (1 M) extraction at room temperature for 16 h. The extract was recovered by filtration and the pH was adjusted to 7 using concentrated hydrochloric acid. Non-soluble material was removed by centrifugation and the supernatant was precipitated in ethanol (1:4). The solid material was collected by filtration and thoroughly washed with ethanol before it was dissolved in deionised water and freeze-dried. In order to reduce the starch content, the isolated fraction was purified using amylases. For details, see *Paper VI*.

3.2 Chemical modification of xylan

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

3.2.2 GAX cationization

In a typical synthesis, GAX was suspended in deionized water and treated at 95°C for 15 min in order to activate the xylan (cf. Ebringerová et al. 1994). The solution was cooled to room temperature and sodium hydroxide was added. A specified volume of 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) was then added and the reaction mixture was stirred for 24 h at 25°C. After neutralization with concentrated hydrochloric acid, the product, 2-hydroxypropyltrimethyl-ammonium-GAX (HPTMA-GAX), was dialyzed (MWCO: 3,500 Da) against deionised water and finally freeze-dried. For details, see *Paper VII*.

3.3 Cellulosic substrates

A never-dried, industrially produced, TCF-bleached (peroxide-based sequence) Scandinavian softwood kraft pulp was used in all adsorption experiments involving pulp fibres (*Papers III-VII*).

In *Paper VI* cotton linters (Munktell, Sweden) and Lyocell fibres (Lenzing, Austria) were used without further purification.

3.4 Analytical methods

A number of different analytical methods were used in the presented studies. For information about the equipment and how the analyses were performed, please confer the attached papers.

4 Results and Discussion

4.1 Influence of lignin on the solution properties of birch xylan

(*Papers I* and *II*)

4.1.1 Background

Linder et al. (2003) proposed a mechanism for xylan adsorption on cellulose fibres based on the tendency of xylan to self-associate, where the self-association was suggested to be promoted by hydrophobic interaction due to covalently bounded lignin residues. This mechanism is supported by studies where polysaccharide model substances, representing lignin-carbohydrate complexes, have been shown to self-associate and adsorb on cellulose surfaces in a similar pattern (Esker et al. 2004; Gradwell et al. 2004). In order to investigate the influence of lignin on xylan solubility, i.e. aggregation in aqueous systems, xylan fractions with different contents of lignin were isolated and analysed.

4.1.2 Extraction of xylan from lignin containing fractions

A crude, lignin containing, xylan fraction (XL) was isolated by pre-hydrolysis and mild alkaline extraction of birch chips. Material with high lignin content was removed using a method developed by Lundquist et al. (1977), involving solid-liquid (pyridine/ acetic acid /water) extraction and subsequent liquid-liquid (chloroform) extraction. This method was originally developed in order to purify milled wood lignin, i.e. to remove carbohydrate residues. In the present investigation the aim was to purify carbohydrates, i.e. to remove lignin residues from xylan. A purified xylan fraction (X) is found in the water phase and a material with a high content of lignin (C) is found in the organic phase. The composition of the different fractions is presented in Table 1. The purification method yielded a xylan fraction with ~75% reduced Klason and acid-soluble lignin content, or ~90% reduced lignin content as detected with UV at 280 nm.

Table 1 Composition of the original xylan fraction (XL), the purified xylan fraction (X) and the fraction dissolved in the organic phase (C). Values are given as weight percentage of dry sample.

Fraction	**Ara**	**Gal**	**Glc**	**Xyl**	**Man**	**Lignin**			**MeGlcA**	**Yield [%]**
						Klason	**Acid-soluble**	**UV (280 nm)**		
XL	3.2	4.2	1.4	66.9	1.3	7.6	4.2	6.9	11.3	100
X	3.2	5.9	3.0	70.0	2.4	2.0	1.0	0.6	12.5	23
C	n.d.	n.d.	0.4	1.4	n.d.	81.5	16.7	n.a.	n.d.	10

n.d. = not detected
n.a. = not analysed

The carbohydrate analysis, along with NMR and IR analyses, revealed that the lignin removed contained only a very small amount of carbohydrate residues (cf. *Paper I*). The lignin was apparently water-soluble in the presence of xylan (as part of the original xylan fraction), but not in the isolated form. The remaining lignin in the purified xylan fraction obviously interacts more closely with the xylan, and thereby its separation by liquid-liquid extraction is more difficult.

4.1.3 Influence of lignin on aggregation of xylan

The two xylan fractions (XL and X) were studied using dynamic light scattering in order to examine their agglomeration behaviour caused by the presence of lignin. Fig. 3 shows the diffusion coefficient as a function of concentration. The hydrodynamic radius (R_h) for the two fractions, calculated with the Stoke-Einstein relationship from the diffusion coefficient at zero concentration (D_0), was 93 nm for XL and 42 nm for X. Consequently, the aggregates are larger in size when lignin is present. Furthermore, the dependency of the diffusion coefficient due to a change in concentration followed different trends, implying that the two fractions have different aggregation behaviours.

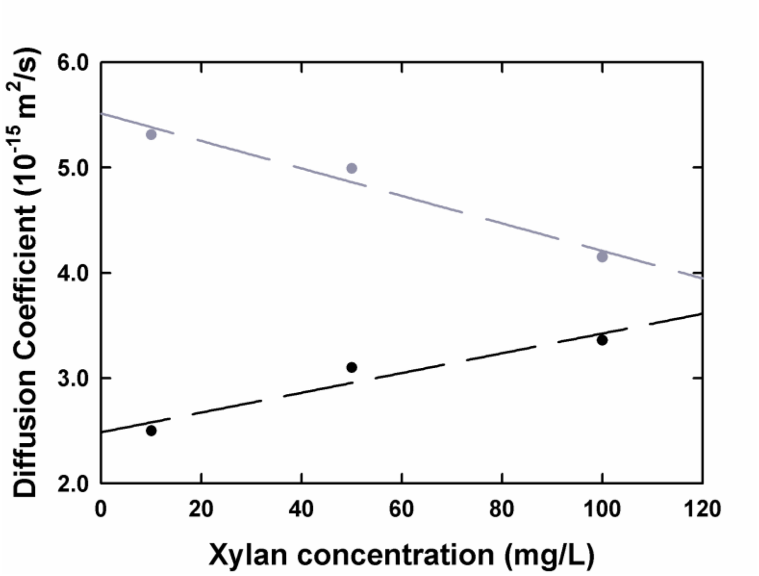

Fig. 3 Dependency of diffusion coefficient due to change in concentration of XL (black lower line) and X (grey upper line) fraction.

In order to visualise the aggregates, the two fractions were subjected to cryo-TEM analysis. The agglomerates in the XL fraction were larger and built up of two kinds of aggregates; one that is perfectly spherical and one that is looser in its structure (Fig. 4). The radius of the spherical particles is in the same size range as calculated from the dynamic light scattering data, while the looser structures are much larger. Spherical particles of lignin in the range of 10–100 nm have been reported by Košiková et al. (1978), who also observed that constituents of hemicelluloses appeared as fibril structures associated with the spherical lignin agglomerates. The more loosely bound structures in the cryo-TEM images could, in this sense, be composed of xylan.

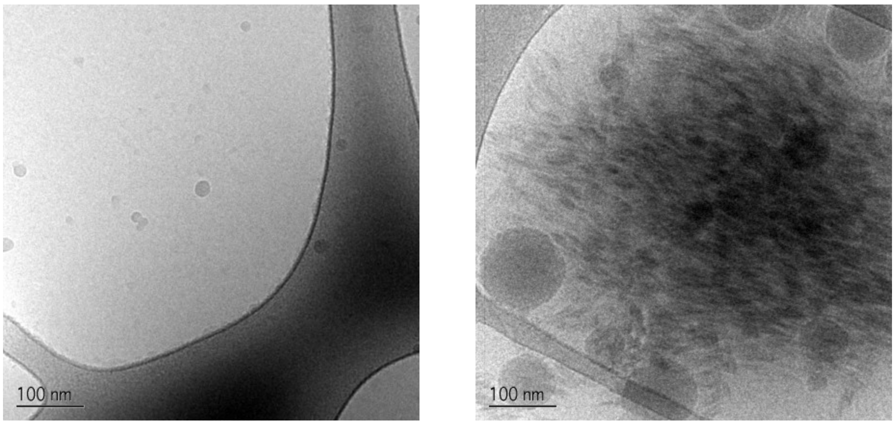

Fig. 4 Cryo-TEM images of X (left) and XL (right) fractions, both at concentration 2 g/dm^3. For pictures with lower magnification, cf. *Paper II*.

Lignin extraction of the crude xylan fraction showed that it was possible to remove lignin not covalently attached to xylan. While this lignin was not soluble in water in its isolated form, it was apparently water-soluble in the presence of xylan. This behaviour suggests that xylan is capable of forming inclusion complexes with lignin. This hypothesis was tested by the addition of lignin (obtained from yellow poplar by steam explosion and alkaline extraction, cf. *Paper II*) to the purified xylan fraction (X) under alkaline conditions, followed by neutralisation and subsequent turbidity measurements. As seen in Fig 5, the turbidity increased linearly with xylan concentration, but measured values of the lignin-X combination had a 20 times steeper gradient than the line representing the theoretical summation. This indicates that X promotes the formation of colloidal aggregates with lignin that results in increased turbidity.

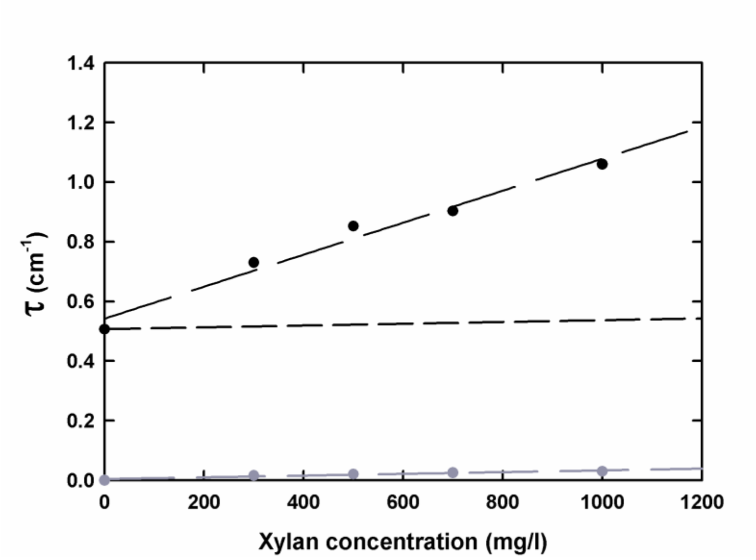

Fig. 5 Turbidity (τ) measurements using UV-VIS at 500 nm. Turbidity of X (lower line) and lignin (single data point at X=0) is contrasted by mixture of X and lignin (upper line) and by theoretical (summative) relationship between lignin and X (middle line). The concentration of lignin is 300 mg/dm^3.

4.1.4 Concluding remarks

The data presented show that xylan rich fractions will form aggregates in neutral aqueous solutions. Lignin induces agglomeration of xylan upon neutralization of alkaline aqueous solutions, where xylan concentration plays an active role in the aggregation phenomenon. This agglomeration probably starts with the nucleation of lignin polymer molecules that are complexed with xylan molecules, due to hydrophobic interactions between lignin and phenolic substituents attached to the xylan chain. These results are in line with the observations done by Uraki et al. (2006) who studied the amphiphility of lignin-carbohydrate complexes. They proposed a core-corona structure of the formed LCCs, with lignin moieties in the hydrophobic cores and hydrophilic polysaccharides in the corona.

The fact that xylan shows a tendency to self-association would promote accumulation on cellulose surfaces, and the presence of “free lignin” would increase the driving force. Lignin by itself is known to self-aggregate when solubility becomes poor (e.g. Lindström 1979, Norgren et al. 2001, 2002) and accumulate on cellulose surfaces (Maximova et al. 2004). However, most of the deposited lignin associates with fibres loosely and can easily be removed by washing with water (cf. Maximova et al. 2001; Notley, Norgren 2006). It is plausible to assume, that if lignin is associated with xylan, the structures would be more irreversibly deposited, due to the interaction between xylan and cellulose. In other words, lignin would work as a “xylan deliverer” for both chemically and physically bonded xylans to a cellulose surface, where xylan has an active role in the anchoring of the adsorbate to the surface. The tendency of xylan fractions containing different amounts of lignin to adsorb on model cellulose surfaces was later studied by Westbye (2008), and it was observed that lignin enhanced the adsorption process.

4.2 The effect of glucuronoxylan adsorption on drying-induced property changes of bleached softwood kraft pulp

(*Papers III, IV* and *V*)

4.2.1 Background

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 (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. Stone, Scallan 1968; Berthold, Salmén 1997; Häggkvist et al. 1998; Wang et al. 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. Mohlin 1975; Laivins, Scallan 1993), but other mechanisms have been proposed as well (cf. Back 1967; Fernandez Diniz et al. 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. Paavilainen 1993; Nazhad, Paszner 1994). 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 et al. 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 formations of intra-fibre hydrogen bonding. This has been performed by 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 et al. 2002, 2004), or by chemical derivatization of the fibres (e.g. Laivins, Scallan 1993; Gruber, Weigert 1998). 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 (Lindström, Carlsson 1982a; Laivins, Scallan 1993).

It is well known that chemical pulps with a low content of hemicellulose have an increased tendency to undergo drying-induced property changes (e.g. Spiegelberg 1966; Oksanen et al. 1997; Cao et al. 1998; Hult et al. 2001; Rebuzzi, Evtuguin 2006). 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. Glucuronoxylans are known to adsorb irreversibly on cellulose and on bleached kraft fibres (e.g. Hansson, Hartler 1969; Linder et al. 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. In order to investigate if glucuronoxylan would work as a hornification inhibitor, bleached softwood kraft fibres were treated with birch xylan before drying, and changes in fibre and pulp properties were analyzed.

4.2.2 Adsorption of GX on bleached softwood kraft pulp fibres

Glucuronoxylan (GX) from birch was adsorbed on never-dried softwood kraft 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 2. 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 and the total anionic charge of the starting material and the treated samples are shown in Table 2.

Table 2 Detected amounts of neutral anhydro sugars and total anionic charge of the starting material (Ref) and samples treated under the specified conditions at neutral pH for 180 min using a fibre concentration of 25 g/dm^3.

Sample	Conditions (Temp [°C], NaCl [M])	Added GX [mg/g]	Neutral anhydro sugars [mg/g]					Total charge [µmol/g]
			Ara	Gal	Glc	Xyl	Man	
Ref	-	-	6	2	788	67	58	73
L0	80, 0.1	0	6	2	786	68	60	73
L40	80, 0.1	40	6	2	770	82	57	77
L80	80, 0.1	80	6	2	751	94	58	81
L160	80, 0.1	160	5	2	733	103	59	87
H0	120, 0.5	0	6	2	789	69	60	65
H40	120, 0.5	40	6	2	758	91	59	73
H80	120, 0.5	80	5	2	734	106	57	80
H160	120, 0.5	160	5	2	730	126	55	91

The neutral anhydro sugar compositions 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, which is probably due to the partial degradation of hexenuronic acids at 120°C (cf. Granström et al. 2001), as indicated by the slightly brownish colour of the filtrate after the treatment. 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. Additionally, the impact of higher temperature cannot 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).

4.2.3 Location of adsorbed GX

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 analysed with confocal laser scanning microscopy (CLSM). From the CLSM images shown in Figs. 6 and 7 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. 7) than for L160 (Fig. 6). 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 occurs on internal surfaces after diffusion into the porous fibre wall. The same conclusion can be drawn based on interpretations of total and surface charge measurements of fibres modified with GX (Table 3).

Table 3 Charge distributions of never-dried bleached softwood kraft pulp fibres modified by GX adsorption under H conditions (cf. Table 2). S = surface charge [μeq/g pulp], T = total charge [μmol/g pulp]

Added GX [mg/g]	Content of adsorbed xylan [%]	S/T	(S-Sref)/(T-Tref)
0	0 (ref)	0.08	-
40	2.4	0.10	0.19
80	4.5	0.10	0.14
160	7.0	0.09	0.10
320	13.3	0.08	0.09

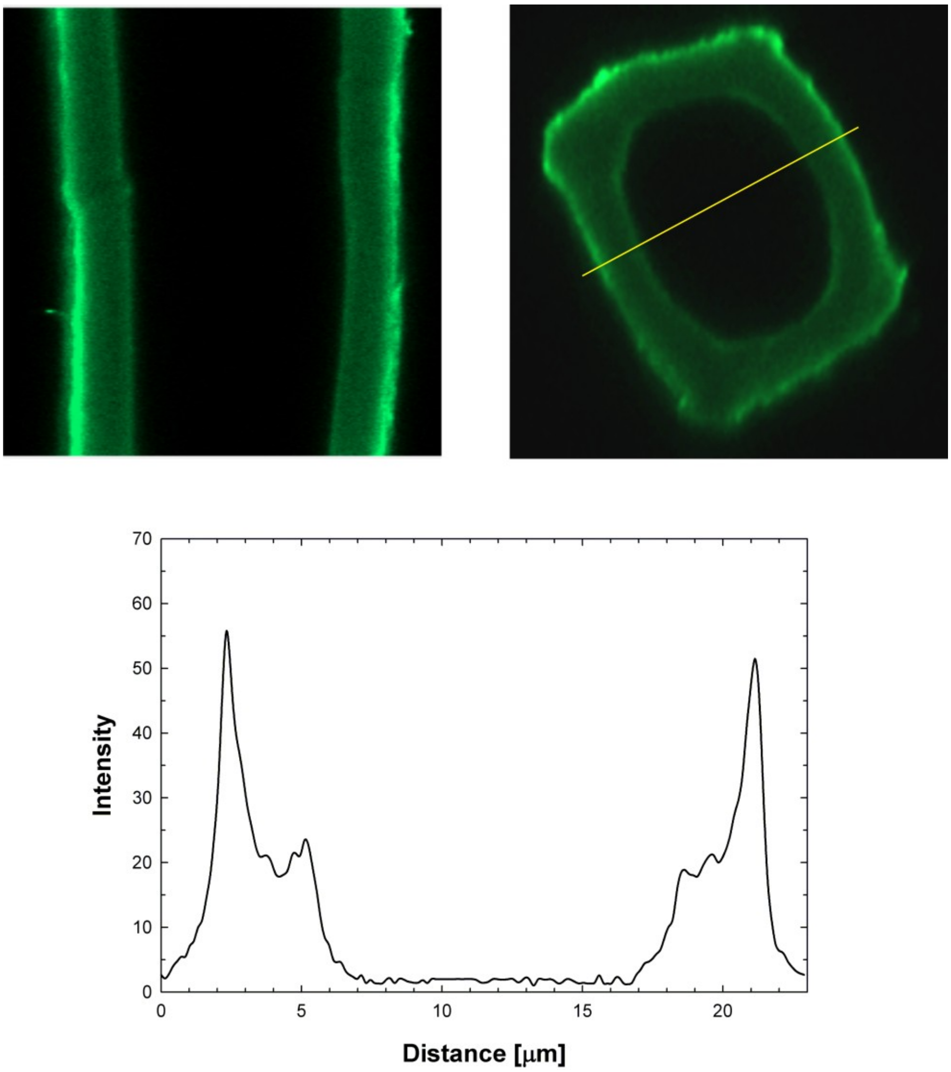

Fig. 6 CLSM image of the fibre length-section and the fibre cross-section, and the corresponding intensity profile for the marked intersection, depicting the adsorption of fluorescent labelled GX in the fibre wall. The images illustrate a representative fibre treated according to L160, cf. Table 2.

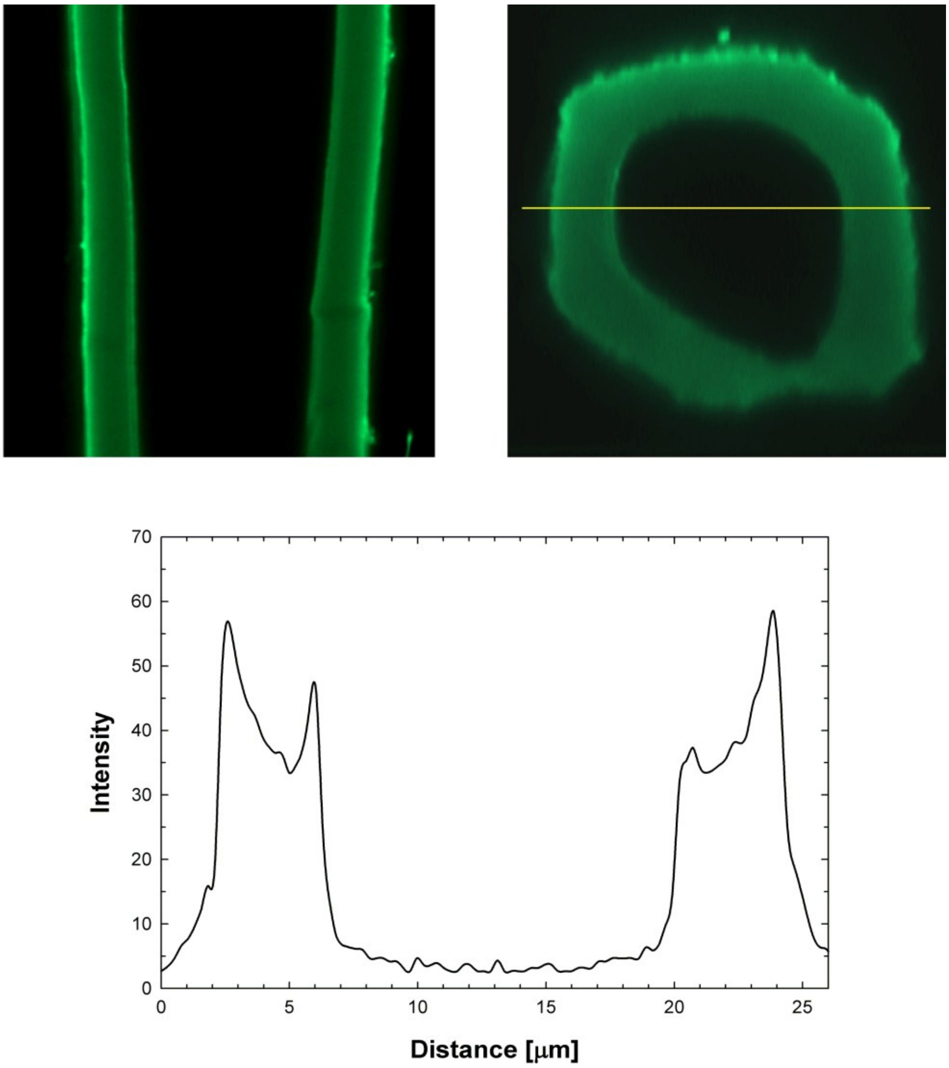

Fig. 7 CLSM image of the fibre length-section and the fibre cross-section, and the corresponding intensity profile for the marked intersection, depicting the adsorption of fluorescent labelled GX in the fibre wall. The images illustrate a representative fibre treated according to H160, cf. Table 2.

4.2.4 Swelling properties

Water retention value (WRV) and fibre saturation point (FSP) were measured for all samples, both in the never-dried and in the once-dried state. 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 4, Fig. 8). The increase in FSP is probably due to the increased amount of charged groups in the modified fibres (cf. Table 2). 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 applied 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.

Table 4 Fibre swelling detected as WRV and FSP for never-dried and once-dried samples; and the degree of hornification, defined as the relative decrease in fibre swelling due to drying.

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 [%]

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 4). As seen in Fig. 8, 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 ionized 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 (Lindström, Carlsson 1982a; Laivins, Scallan 1993). 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.

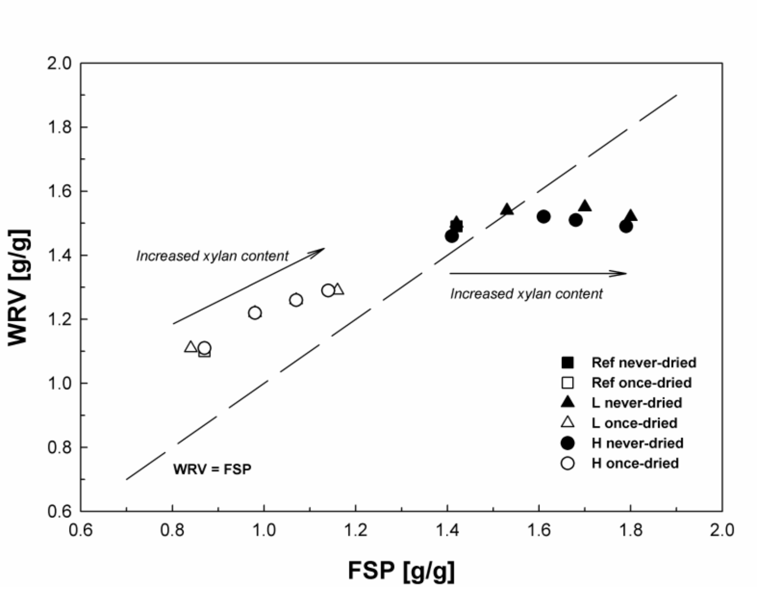

Fig. 8 Comparison between WRV and FSP measurements for never-dried and once-dried fibres. The variable in this figure is xylan content, which is varied by GX adsorption. L and H refer to conditions used during modification, cf. Table 2.

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 4). Since the adsorbed amount of GX is higher under the H conditions (cf. Table 2), 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 2), 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.

4.2.5 Ultra-structural fibre changes

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 (cf. Wang et al. 2003). 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. 9. 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 4). 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. However, it is also possible that adsorbed xylan in itself contributes to increased surface area, as indicated by the somewhat greater surface area in H160 than in L160.

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. 9, adsorbing GX before drying the fibres preserves a considerable amount of the original surface area, especially in the H160 case. This indicates that adsorbed xylan to a high extent prevents the collapse of fibre wall pores during drying.

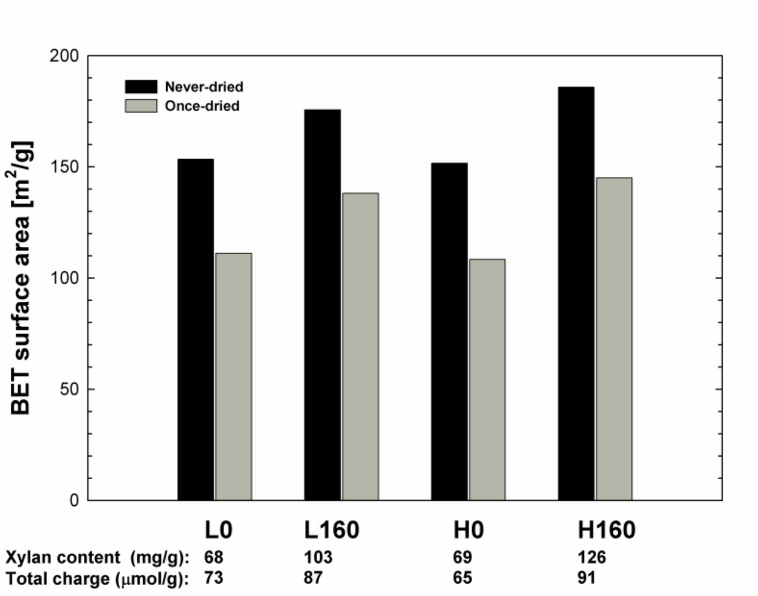

Fig. 9 BET surface area for never-dried and once-dried samples. The sample names refer to conditions used during the modification, cf. Table 2.

In order to investigate the influence of adsorbed GX on the collapse of fibre wall pores during drying, pore size distribution (PSD) was analysed with NMR cryoporometry (Fig. 10). The overall conclusion from these analyses is that the PSD of the fibres is less affected by drying if adsorbed GX is present. Results from the study also indicate that GX adsorption hinders the collapse of small pores upon drying, and even that the number of small pores increases, probably due to the fact that larger pores have collapsed to form smaller ones. Nevertheless, the results are in line with the interpretation that adsorbed GX inhibits hornification, which would preserve much of the original (never-dried) porosity.

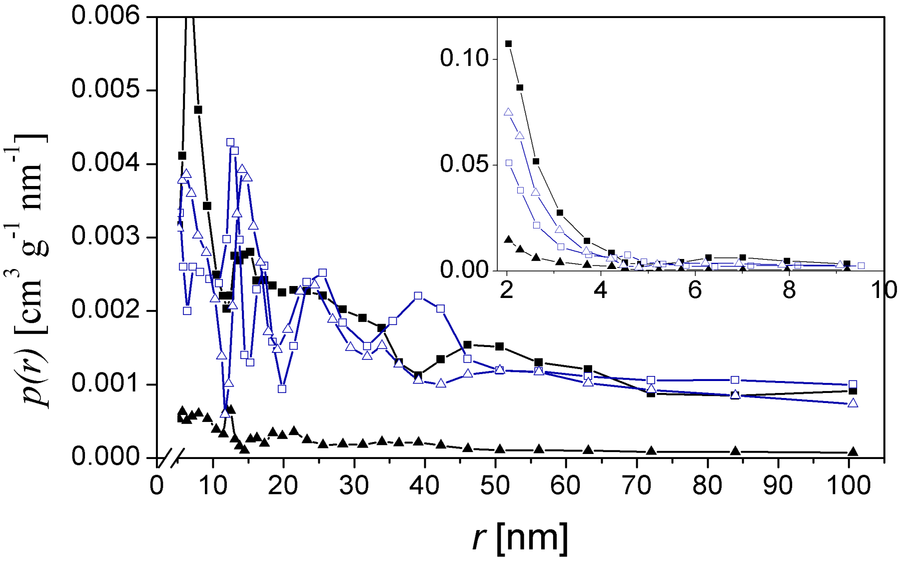

Fig. 10 PSD of GX modified pulp fibres never-dried (unfilled blue squares) and oven-dried (105°C, 24 h)(unfilled blue triangles) in comparison with a reference pulp; never-dried (filled black squares) and oven-dried (filled black triangles). The radii between 2 and 10 nm are shown in the upper right graph on a larger scale. The fibres were treated according to H160 (cf. Table 2).

4.2.6 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. 11). GX 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. These results show the same trend as measurements of "apparent wet fibre flexibility" performed using the STFI FiberMaster technique (cf. *Paper III*).

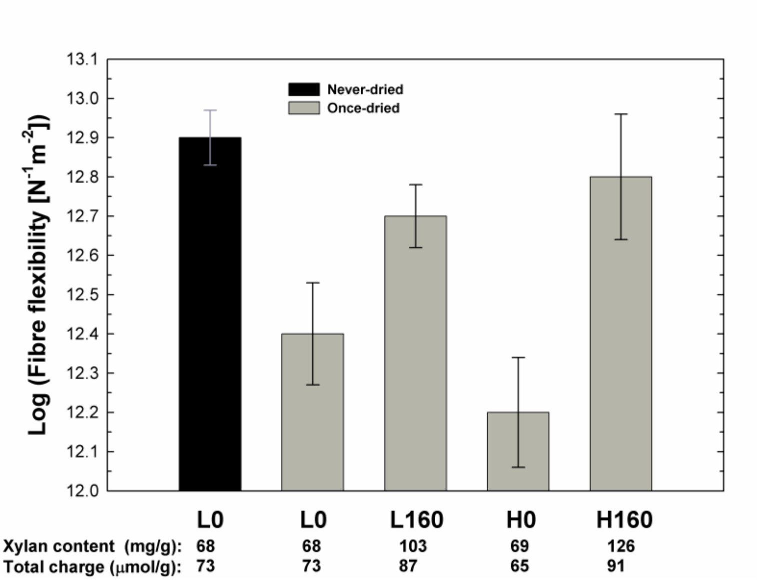

Fig. 11 Wet fibre flexibility for never-dried and once-dried samples. The limit bars in the figure represent 99% confidence intervals for the mean. The sample names refer to conditions used during modification, cf. Table 2.

4.2.7 Effect of GX adsorption on pulp properties

Wet fibre flexibility has a decisive impact on the tensile strength and apparent sheet density of softwood fibres (e.g. Paavilainen 1993). Since once-dried fibres show an increase in flexibility if they are modified with GX before drying (cf. Fig. 11), one would expect an increase in the tensile strength index and in sheet density compared to the once-dried reference. Furthermore, since the degree of hornification seems to be dependent on the amount of adsorbed xylan (cf. Table 4), one would also expect the increase in tensile strength and sheet density to be a function of GX content. As seen in Figs. 12 and 13, these interpretations are correct. The dry strengthening effect (at a specific number of PFI revolutions) is also present after beating. However, at a given sheet density the tensile strength is more or less unaffected by the amount of adsorbed xylan. The same trend is seen if tensile strength is evaluated as a function of the light scattering coefficient or °SR (cf. Paper III). These observations are consistent with the hypothesis that the increase in tensile strength is a matter of reduced hornification; where fibre modification by GX adsorption affects the energy required to attain a certain degree of flexibility by beating.

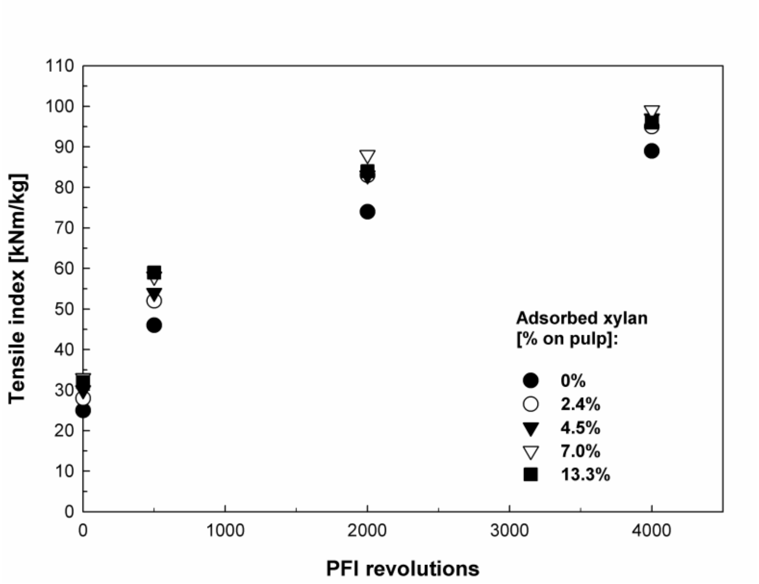

Fig. 12 Tensile index as a function of PFI revolutions for once-dried pulps with different amounts of adsorbed xylan. Modifications were performed under H conditions (cf. Table 2).

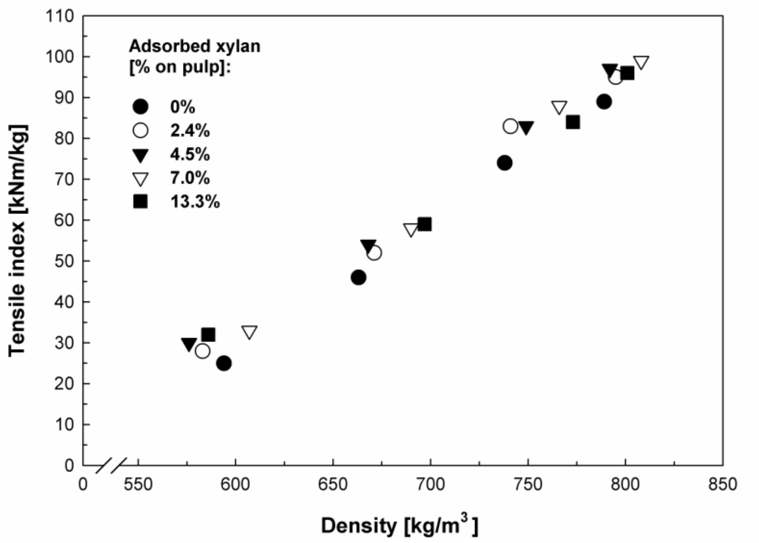

Fig. 13 Tensile index as a function of sheet density, at different degrees of beating (0, 500, 2000, 4000 PFI revs.), for once-dried pulps with different amounts of adsorbed xylan. Modifications were performed under H conditions (cf. Table 2).

An improvement in tensile strength with xylan adsorption was also seen for the never-dried pulps, but the effect was not as pronounced as for the once-dried pulps. The tensile strength development, as a function of sheet density and xylan content, caused by beating followed the same trend line as in the case of once-dried pulps (Fig. 14). The data presented show that once-dried pulp behaves more like never-dried pulp if it is modified with xylan before drying.

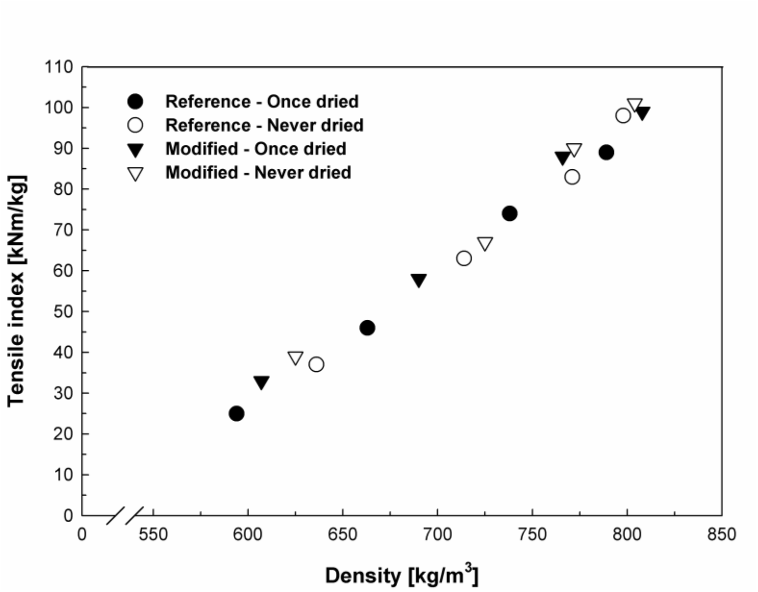

Fig. 14 Tensile index as function of sheet density, at different degrees of beating (0, 500, 2000, 4000 PFI revs.), for pulps with/without modification and drying. Modifications were performed under H conditions (cf. Table 2). Content of adsorbed xylan is ~7%.

4.2.8 Concluding remarks

Based on the observations made, 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 fibres are retained to a high degree, the beatability of the once-dried pulp fibres will increase. Consequently, once-dried fibres will behave more like never-dried fibres if they are modified with GX before drying.

Finally, some comments have to be made concerning the importance of the location of adsorbed GX for tensile strength development. The increase in tensile strength for the modified non-beaten once-dried pulp in the present investigation is more or less linearly dependent on the adsorbed amount of xylan, up to a content of about 7%. It is thus tempting to stress the importance of the total amount of adsorbed xylan for the observed tensile strength development. However, the increase in tensile strength as well as the surface charge show a tendency to level out at higher contents of adsorbed xylan (>7 %), implying the importance of xylan located at the outermost fibre surfaces. It has been shown that ionized groups located on the external part of the fibre surface are important for fibre/fibre joint strength, due to softening of the fibre surface (cf. Barzyk et al. 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 outer fibre surface layer (e.g. Schönberg et al. 2001; Dahlman et al. 2003; Sjöberg et al. 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.

4.3 Modification of cellulose fibres using xylan isolated from barley husks

(*Papers VI* and *VII*)

4.3.1 Background

Adsorption of pre-isolated hardwood xylan has been shown to improve pulp properties, such as tensile strength, beatability and resistance to hornification (e.g. Schönberg et al. 2001; Paper III, IV, V). An important issue when discussing the potential of using xylans as additives in the pulp and paper industry is the accessibility of large quantities of isolated material. Residues from agriculture represent a potential low cost source of material with high xylan content that could be used for such utilization. An example of such a potential residue is barley husk (cf. Glasser et al. 2000; Höije et al. 2005; Krawczyk et al. 2008; Pitkänen et al. 2008; Roos et al. 2009), a side-stream waste material from the manufacture of starch and ethanol. The main structural features of barley husk xylan were early identified (Aspinall, Ferrier 1957) and further knowledge of the structure was recently obtained by means of NMR (Höije et al. 2006). The xylan structure of barley husk is shown to consist of a β-D-(1→4)-linked xylopyranosyl backbone, which is randomly substituted at O-3 with α-L-arabinofuranosyl groups and to some extent at O-2 with 4-*O*-methylglucuronic acid. In addition to these substituents, disaccharide side-chains, 2-*O*-β-D-xylopyranosyl-α-L-arabinofuranose, are present at position O-3 of the main chain (cf. Fig. 2). In order to investigate the possibility of using xylan from agriculture residues in cellulose fibre modification, a xylan fraction was extracted from barley husk and its interaction characteristics with cellulose were studied.

4.3.2 Characterization of the isolated barley husk xylan

The total yield of water-soluble GAX after extraction and enzymatic purification, as a weight percentage of the starting material, i.e. dry barley husks, was 12.8%. Analysis of the isolated GAX fraction showed the following contents: neutral carbohydrates 69.2%, uronic acids 4.9%, Klason lignin 4.1%, protein 5.1% and ash 2.9%. The relative neutral carbohydrate composition was Xyl 74.0%, Ara 19.2%, Glc 4.3% and Gal 2.5%. The relative uronic acid composition was MeGlcA 68%, GlcA 22% and GalA 10%. It should be mentioned that proteins may contribute to the measured Klason lignin value (Lai, Sarkanen 1971; Theander et al. 1995), and consequently a part of the protein content will be found in this fraction as well. The data presented corresponds to the material extracted in *Paper VII*, which slightly differs to the yield and composition obtained for the isolated GAX in *Paper VI*. A weight average molar mass of 20,200 g/mol was determined using size exclusion chromatography in DMSO:H_2O. ^1H NMR data of the isolated fraction correlated with chemical shifts reported for barley husk xylan by Höije et al. (2006) and Pitkänen et al. (2008) (cf. *Paper VII*).

4.3.3 Adsorption characteristics of GAX on cellulose fibres

The isolated GAX fraction was found to interact with cellulose (cotton) fibres. A relatively slow adsorption equilibration was observed, especially at high concentrations of GAX. Temperature was shown to increase the rate of adsorption and, in the studied range of time, also the adsorbed amount (Fig 15).

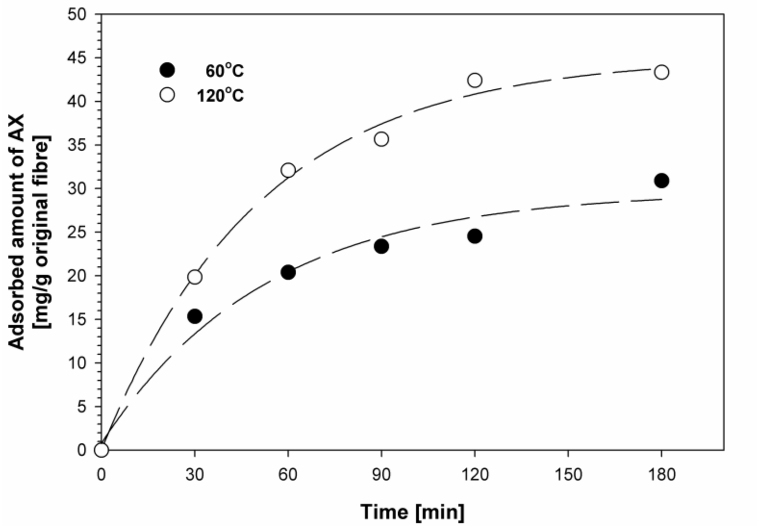

Fig. 15 Adsorbed amount of AX (content of anhydro arabinose and anhydro xylose) on cotton linters as function of time at initial GAX concentration of 320 mg/g fibre and different temperatures. Modifications were performed at neutral pH using a fibre concentration of 25 g/dm^3. Trend lines are used to guide the eye.

The treated cellulose fibres were analysed for their Ara/Xyl relationship. A relative low Ara/Xyl ratio was found for the modified fibres, around 0.10 compared with 0.22 for the isolated GAX fraction. This indicates preferential adsorption of low substituted xylans. The low Ara/Xyl ratio remained at a low level independent of adsorption time, temperature and added amount of GAX (cf. *Paper VI*). An increase in the Ara/Xyl ratio of the non-adsorbed GAX fraction present in the solution was observed, which was especially evident in *Paper VII* where a relatively low addition of GAX was used (Fig. 16).

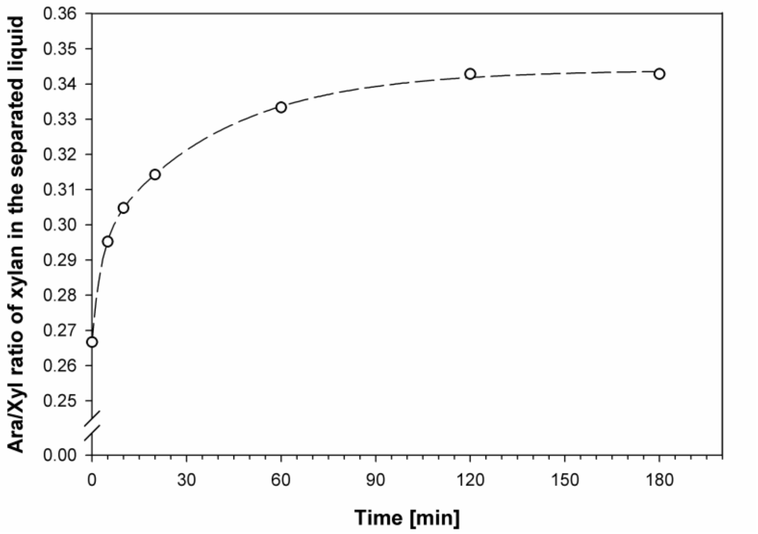

Fig. 16 Ara/Xyl ratio of non-adsorbed GAX as a function of adsorption time, detected by neutral carbohydrate analysis of the separated liquid. Adsorption studies were performed at 80°C using an initial GAX concentration of 40 mg/g fibres, a pulp fibre concentration of 25 g/dm^3 and a NaCl concentration of 10 mM. Trend line is used to guide the eye.

The distribution of substituents in barley husk xylan has been suggested to be random (Höije et al. 2006), and the degree of substitution of different xylan molecules in an isolated xylan preparation varies. Arabinoxylan has been shown to become less water soluble as the amount of Ara*f* side groups decreases (Andrewartha et al. 1979). Consequently, a fraction of the isolated barley husk xylan may have a lower degree of Ara*f* substitution, and hence reduced water solubility. The lower solubility would promote adsorption, but factors such as sterical hindrance and/or conformational changes due to the Ara*f* side groups may also influence adsorption. Nevertheless, the result that the frequency of Ara*f* side groups controls the adsorption of arabinoxylan on cellulose is in agreement with observations made by McNeil et al. (1975), studying the structure of barley aleurone cells.

Non-adsorbed xylan was also subjected to size exclusion chromatography (SEC) analysis in a water system. An evident decrease in light scattering (LS) (cf. *Paper VI*) and refractive index (RI) (Fig. 17) signals was registered with adsorption time for the fraction eluting first, implying a decrease in aggregated/associated material as the adsorption process proceeded. This indicates that xylan with a strong tendency towards self-association is preferentially adsorbed on cellulose fibres. It has been shown that xylans with few substituents tend to self-associate in aqueous solutions (e.g. Blake, Richards 1971; Dea et al. 1973), forming aggregates with lower solubility (Andrewartha et al. 1979). Such aggregates would have an increased tendency for adsorption/deposition on cellulose surfaces.

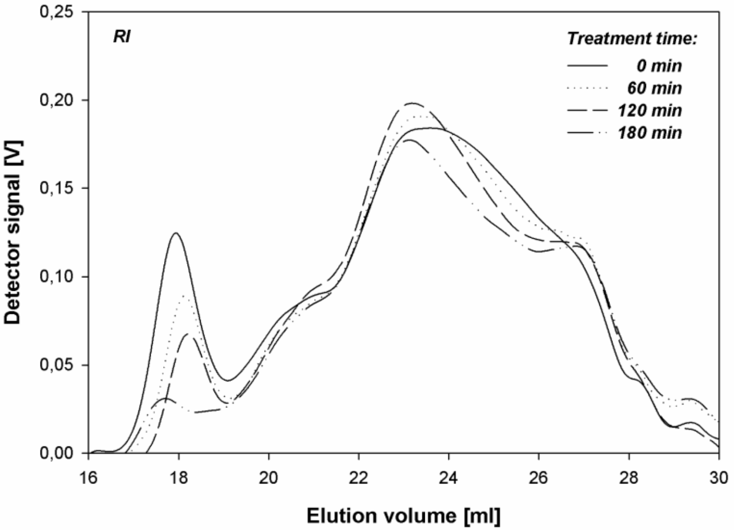

Fig. 17 SEC analysis in a water system. Reflective index (RI) signals from non-adsorbed GAX fractions, obtained after different times of adsorption at 120°C with an initial GAX concentration of 80 mg/g fibre and a cotton linters concentration of 25g/dm^3.

In order to investigate if aggregated xylan had been accumulated on the cellulose surfaces, the fibres were analysed with atomic force microscopy (AFM) in the tapping mode. Because of the fibrillar structure, the surface topography of natural cellulose fibres, e.g. cotton linters, is heterogeneous. Small changes in surface structure, such as macromolecular adsorption, are consequently difficult to visualize. However, analysis of the treated cotton fibres showed randomly distributed areas with changes in the phase and, to some extent, also in the height image (results not presented). These observations indicate heterogeneous adsorption of xylan structures on the fibre surface.

In order to confirm this observation, Lyocell fibres were treated with a GAX solution under the same conditions used for the analysed cotton fibres (320 mg GAX/g fibre at 120°C for 180 min using a fibre concentration of 25 g/dm^3). Lyocell fibres are composed of regenerated cellulose with a relatively smooth surface in comparison with natural cellulose fibres. Although Lyocell fibres possess a different type of crystallinity, they have been shown to adsorb xylan (Linder, Gatenholm 2004). The surface modified fibres showed considerable alterations in height amplitudes and phase shifts (Fig 18). Associated structures, ranging from tens of nanometres to the micrometre-scale, were seen randomly distributed over the fibre surfaces. It would be plausible to assume that there is a relation between the assembly of aggregates on the fibres and the aggregation of xylan in solution, which is supported by the SEC and light scattering results. It should be pointed out that these findings do not rule out the possibility of additional molecular GAX adsorption.

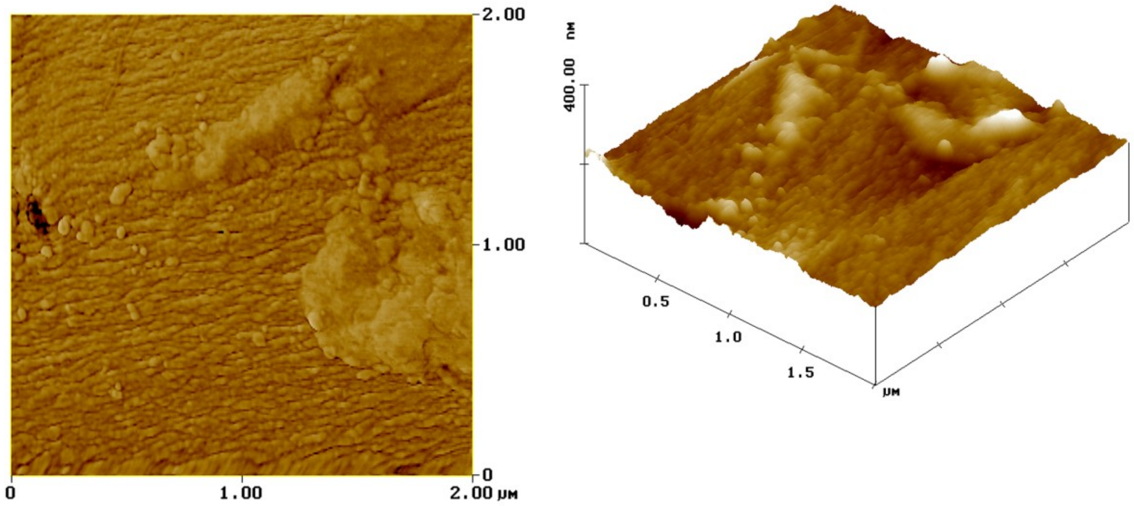

Fig. 18 AFM analysis of a modified Lyocell fibre; (left) phase image (right) height image. Cf. *Paper VI* for images of the reference fibre.

4.3.4 Effect of GAX adsorption on pulp properties

In order to study the effect of adsorbed barley husk xylan on pulp properties, never-dried bleached softwood kraft fibres were treated with GAX, yielding a modified pulp containing 2.6% adsorbed GAX. As seen in Fig. 19, the adsorption of GAX on bleached softwood pulp increases pulp strength in the once-dried state. The modified pulp also shows an increase in beatability, i.e. the response in tensile strength upon beating. The increase in tensile strength by GAX adsorption is associated with an increase in density and a decrease in light scattering of the produced hand sheets (cf. *Paper VI*), which implies an increase in the conformability and fibre-fibre bond capacity of the modified fibres.

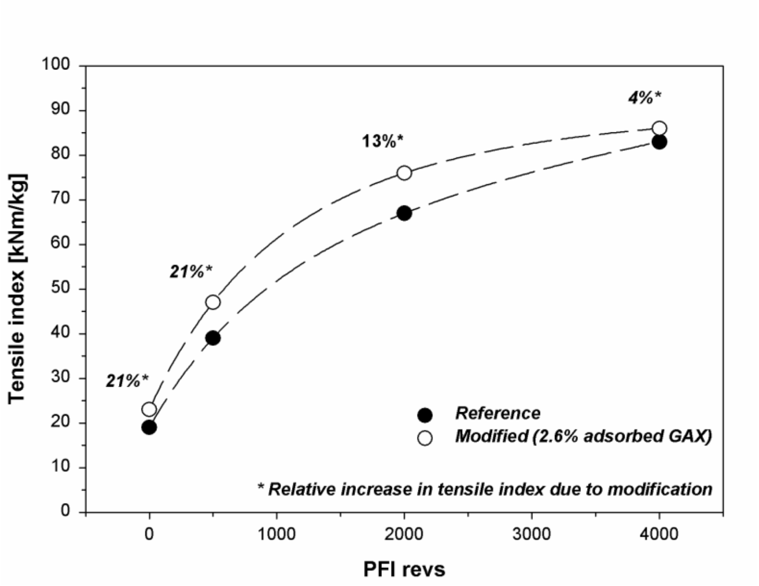

Fig. 19 Tensile index as a function of beating for a reference and a GAX modified once-dried bleached softwood kraft pulp. Modification was performed on never-dried pulp at 120°C using a GAX addition of 80 mg/g fibres, a pulp fibre concentration of 25 g/dm^3 and a treatment time of 180 min. Trend lines are used to guide the eye.

4.3.5 Concluding remarks

The data presented show that temperature and initial concentration of GAX are important parameters in controlling the level of adsorption on cellulose fibres, but the adsorption appears to largely depend on xylan molecular structure. GAX with a low degree of substitution has an enhanced propensity to form aggregates in aqueous solutions and to adsorb on cellulose surfaces. Results also indicate that GAX adsorption on never-dried fibres has the potential to improve tensile strength and beatability of market pulps.

4.4 Adsorption of cationized barley husk xylan on bleached softwood kraft pulp fibres

(*Paper VII*)

4.4.1 Background

One major advantage of using xylan in pulp fibre modification is the inherent affinity of xylan to cellulose, yielding an irreversible adsorption (e.g. Paananen et al. 2004). However, the level of xylan-cellulose interaction has been shown to depend on xylan molecular structure (e.g. Hansson, Hartler 1969; Kabel et al. 2007; *Paper III* and *VI*), which is dependent on botanical origin and the isolation procedure. If a high degree of xylan adsorption is desired, the xylan polymer may be chemically modified to improve interaction with anionic pulp fibres. In analogy with the addition of starch in the paper making process, this improvement can be achieved by cationization of the adsorbing biopolymer. Cationic groups are usually introduced into xylan, similar to cellulose or starch, either by reaction in an alkaline medium with various haloalkanes or epoxides containing quaternary amines, or by reaction with epichlorohydrin yielding a chlorohydroxypropyl group which can be quarternized subsequently by reaction with a tertiary amine (cf. Ebringerová et al. 2005). Preparation of cationic xylan can be performed by cationization of xylan-rich lignocellulosic material followed by water/alkaline extraction and isolation of the modified xylan (e.g. Antal et al. 1984; Šimkovic et al. 1990), or it can be done directly by cationization of pre-isolated and purified xylan (e.g. Ebringerová et al. 1994; Schwikal et al. 2006). The aim of this part of the thesis work was to isolate a water-soluble, relatively pure xylan from barley husks, and to investigate how cationization of the xylan, performed by reaction in an aqueous alkaline medium with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC), affects adsorption on bleached softwood kraft pulp fibres. Earlier studies concerning adsorption of cationic xylans on pulp fibres have focused on changes in pulp properties, rather than on the actual adsorption step; all of these studies lack quantification of the adsorbed amounts (e.g. Antal et al. 1991, 1997; Ren et al. 2009). Three methods for adsorption yield quantification were applied in the present study. Evaluation of the information gained from the different methods was expected to give more knowledge of xylan adsorption kinetics and xylan-fibre interaction mechanisms.

4.4.2 GAX cationization

The isolated GAX was cationized through a reaction in an aqueous alkaline medium with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC). In order to quantify the degree of substitution of the 2-hydroxypropyltrimethylammonium (glucurono)arabinoxylan (HPTMA-GAX), the increase in the nitrogen content of the xylan samples due to modification (representing the content of quaternary ammonium groups), was determined using elemental analysis. Chemical modification was confirmed by HSQC-NMR analysis (cf. *Paper VII*), based on ^{13}C data reported by Ebringerová et al. (1994) and Schwikal et al. (2006). The HSQC spectrum of HPTMA-GAX also revealed new signals, which may be attributed to C-6 (cf. Fig. 20 for carbon numbering) substituted to different hydroxyl groups of the GAX. The TOCSY spectrum of HPTMA-GAX showed three cross-peak correlations between the protons on C-7 and C-6 (Fig. 21). They may reflect different positions of the HPTMA substituent in the xylan molecule, but can also be a result of diastereotopicity and/or regioselectivity of the nucleophilic attack. Attempts were made, using the NOSEY experiment, to determine whether or not the observed cross-peaks were due to different reaction sites in the GAX molecule. Unfortunately, no such information could be obtained.

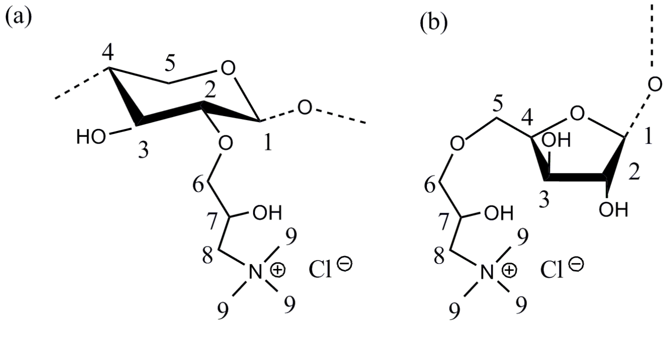

Fig. 20 (a) HPTMA- Xyl*p* **(b)** HPTMA- Ara*f*

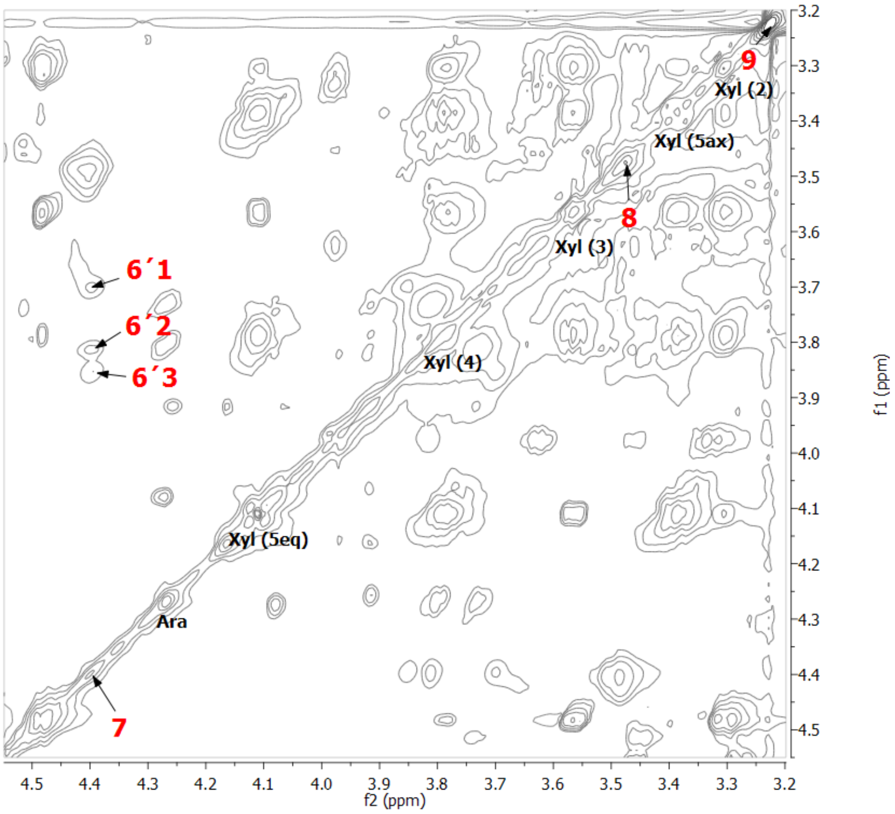

Fig. 21 TOCSY spectrum of HPTMA-GAX (charge density (CD) of 740 µeq/g, representing a DS of ~ 0.2). Xylans were dissolved in D_2O at 95°C and then cooled to 45°C. Spectra were recorded at 45°C on a Varian Inova 600 spectrometer equipped with a cold probe, operating at 599.76 MHz. Chemical shifts are referenced to internal acetone (δ_H 2.225 ppm).

To be able to determine the reaction selectivity between Xyl*p* units and Ara*f* units, an indirect method was used instead, based on analysis of neutral carbohydrates in the HPTMA-GAX fractions (Fig. 22). The method showed that both Xyl*p* and Ara*f* were modified. Furthermore, the Ara/Xyl ratio decreased as the degree of substitution (DS) of the HPTMA-GAX increased, which indicates that the Ara*f* units are preferentially modified.

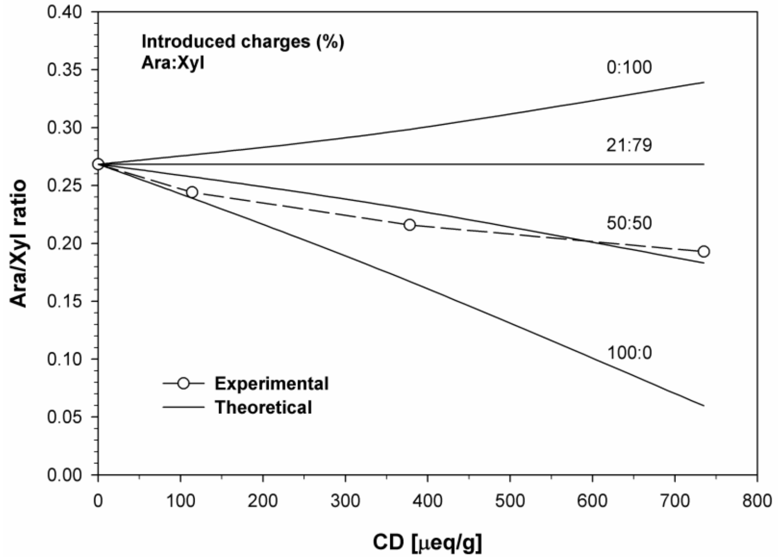

Fig. 22 Ara/Xyl ratio of HPTMA-GAX hydrolysates as a function of cationic charge density (CD). The four theoretical trend-lines represent the following cases: 0:100, only Xyl*p* is substituted; 21:79, equal probability of Xyl*p* and Ara*f* substitution; 50:50, Ara*f* is preferentially substituted and equal amounts of substituents are introduced to Ara*f* as to Xyl*p*; 100:0, only Ara*f* is substituted.

4.4.3 Adsorption of GAX and HPTMA-GAX on bleached softwood kraft pulp fibres

A GAX reference and three different HPTMA-GAXs (possessing different degrees of cationization) were adsorbed on never-dried bleached softwood kraft pulp fibres. The amount of adsorbed xylan was measured according to three different subtractive methods: COD (Fig. 23a), carbohydrate analysis (Fig. 23b) and iodine complexation (Fig. 23c). The COD method gives slightly lower levels of adsorption than the carbohydrate analysis method, but the two methods generally correlate quite well. A small difference can however be expected, since impurities, i.e. non-xylan compounds, present in GAX/HPTMA-GAX fractions, will be detected by the COD method and consequently will affect the relative amount of adsorbed material. According to Fig. 23b, only about 20% of the reference xylan material was adsorbed after 180 minutes. Cationization of the xylan fractions increased the rate, as well as the magnitude, of adsorption. At the highest degree of modification, approximately 80% of the added xylan was adsorbed at apparent equilibrium, which was reached after less than 5 minutes.

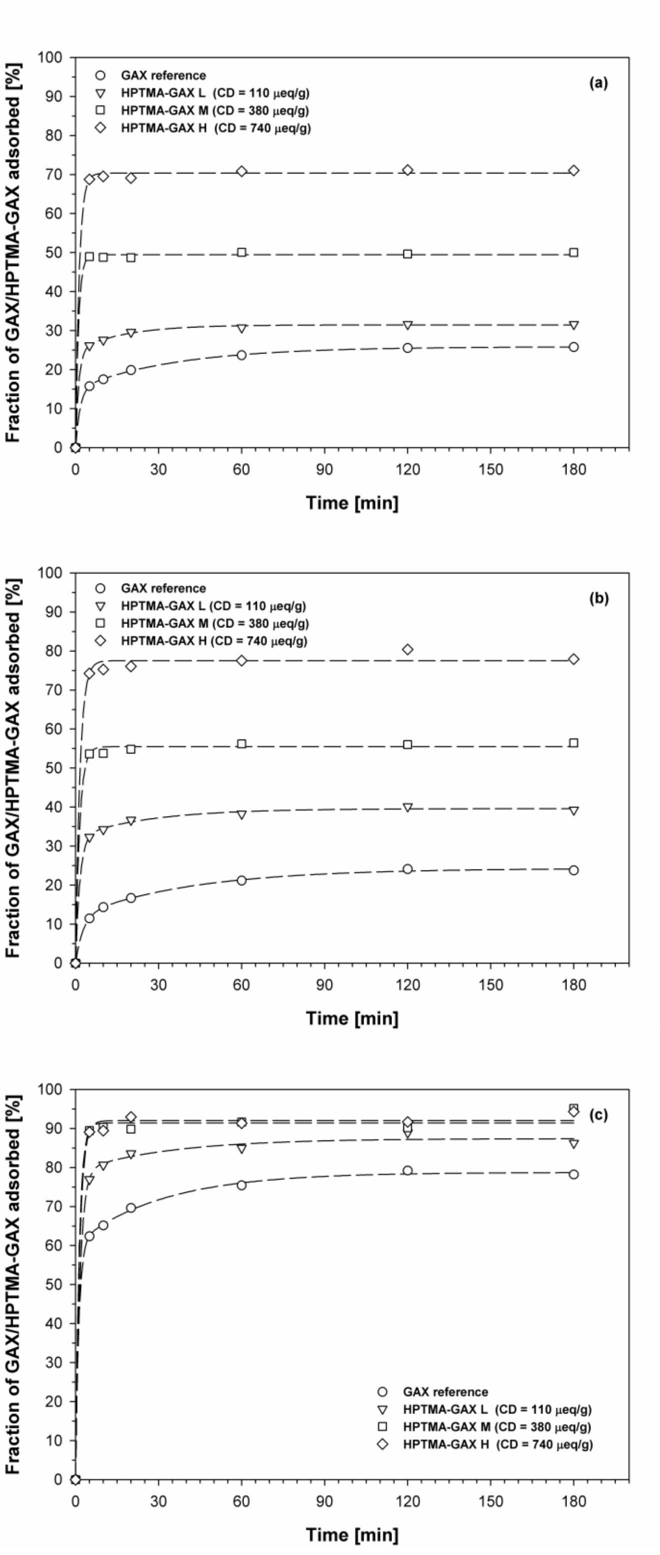

Fig. 23 Fraction of GAX/HPTMA-GAX adsorbed as a function of adsorption time, estimated by **(a)** chemical oxygen demand (COD) **(b)** neutral carbohydrate analysis **(c)** iodine-complexation of the separated liquid. Adsorption studies were performed at 80°C using an initial GAX/HPTMA-GAX concentration of 40 mg/g fibres, a pulp fibre concentration of 25 g/dm^3 and a NaCl concentration of 10 mM. Trend lines are used to guide the eye.

It is obvious that the iodine complexation method overestimates the adsorbed amount of xylan (Fig. 23c vs Figs. 23a, b). Consequently, the xylan fraction that primarily interacts with cellulose seems to be the same kind of xylan that forms iodine complexes. Since it has been reported that the tendency of xylan to react with iodine and give colouration decreases for highly branched xylan (Gaillard, Thompson 1971), the data imply that low Ara*f* substituted GAX, or xylan molecules with longer unsubstituted segments, are preferentially adsorbed on cellulose surfaces. This observation is consistent with results obtained when analysing the composition of adsorbed and non-adsorbed GAX (Fig. 16, *Paper VI* and *VII*).

4.4.4 Importance of electrostatic interaction for HPTMA-GAX adsorption

In order to obtain more information about the adsorption interactions of HPTMA-GAX, adsorption on kraft pulp fibres was studied as a function of NaCl concentration (Fig. 24).

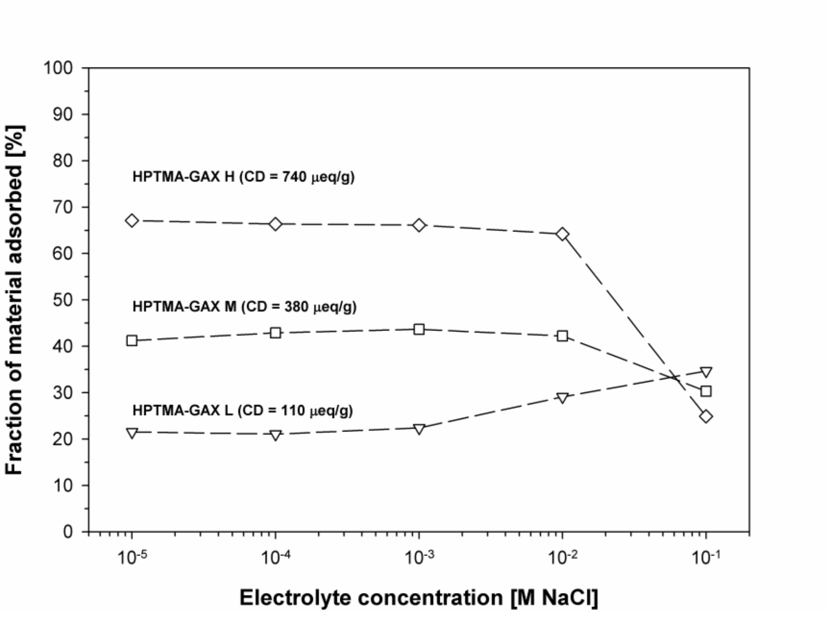

Fig. 24 Adsorption of HPTMA-GAX as a function of NaCl concentration. Adsorption studies were performed at 80°C using an initial HPTMA-GAX concentration of 40 mg/g fibres, a pulp fibre concentration of 25 g/dm^3 and an adsorption time of 60 min. Fraction of HPTMA-GAX adsorbed was estimated by chemical oxygen demand (COD) of the separated liquid. Trend lines are used to guide the eye.

It is evident that at low and moderate salt concentrations ($\leq 10^{-2}$ M), the adsorbed amount is promoted by an increase in the charge density of the HPTMA-GAX. As the system is far from the adsorption saturation point, and consequently total charge neutralisation is not reached (cf. *Paper VII*), the effects related to charge compensation (cf. van de Steeg et al. 1992), do not dominate. Under the applied conditions, highly charged HPTMA-GAX has a larger electrostatic contribution to the driving force for adsorption, and will consequently adsorb to a greater extent. At a higher salt concentration (>10^{-2} M), the adsorbed amount decreases for HPTMA-GAX H and HPTMA-GAX M, most probably due to electrostatic screening. In contrast, the adsorbed amount of HPTMA-GAX L increases at higher salt concentrations (>10^{-3} M), which could be an effect of a decrease in the solubility of the screened low charged HPTMA-GAX. If the solubility of a screened polyelectrolyte is poor, the polyelectrolyte might precipitate at high ionic strength. Before this precipitation occurs, the adsorption may increase, since the surface acts as a nucleus for phase separation (Fleer et al. 1993). The system also shows adsorption at high ionic strength, where most of the electrostatic contributions to the adsorption are screened. This indicates that the HPTMA-GAXs possess a non-electrostatic cellulose surface affinity, which is logical, since non-modified GAX adsorbs on cellulose fibres. Interestingly, the order in which the different HPTMA-GAXs adsorb at low ionic strength inverts at high salt concentration (~10^{-1} M). This could be an effect of variations in solubility of the screened HPTMA-GAXs, but sterical hindrance and/or conformational changes affecting the non-electrostatic interaction with cellulose, can also be anticipated. To confirm and verify the existence of non-electrostatical interaction and the inverted order of adsorption when the contribution of electrostatic interactions is suppressed, the adsorption experiments were repeated on neutralized fibres (cf. *Paper VII*). The essentially carboxyl-free fibres were from the same batch of pulp as used in the former experiments, but were esterified with propylene oxide in a neutral aqueous solution. The levels of adsorption decreased as the charge density of HPTMA-GAX increased, hence confirming the results obtained at high ionic strength (~10^{-1} M) in Fig. 24.

4.4.5 Effect of HPTMA-GAX adsorption on pulp properties

The adsorption potential of HPTMA-GAX (charge density of 1060 μeq/g) on never-dried bleached softwood kraft pulp, is illustrated in Fig 25. As shown in the figure, the degree of adsorption is quite high at lower amounts of added HPTMA-GAX, but levels out when approaching the charge neutralisation point.

In order to investigate the potential of using this HPTMA-GAX as a strength enhancing pulp additive, HPTMA-GAX was added to never-dried bleached softwood kraft pulp, which was tested for its pulp properties in the once-dried state. No major improvement (or impairment) in tensile strength was observed upon HPTMA-GAX adsorption (Fig. 26). This is in contrast to results obtained by adsorption of non-cationized GAX (Fig. 19, *Paper VI*) and anionic-xylan (Fig. 13, *Paper III*). Since no HPTMA-GAX was lost upon beating (as shown by COD measurements of the filtrate), it can tentatively be concluded that the introduced cationic charges counteract the positive effect of xylan adsorption. An explanation could be that the addition of HPTMA-GAX leads to an ion-exchange between the cationic xylan and the cationic counter-ions of the ionic groups of the fibre, which may result in a de-swelling of the fibre surfaces. Such fibre surface de-swelling has earlier been reported to negatively affect the formation of strong fibre/fibre joints (cf. Swerin et al. 1990; Torgnysdotter et al. 2007).

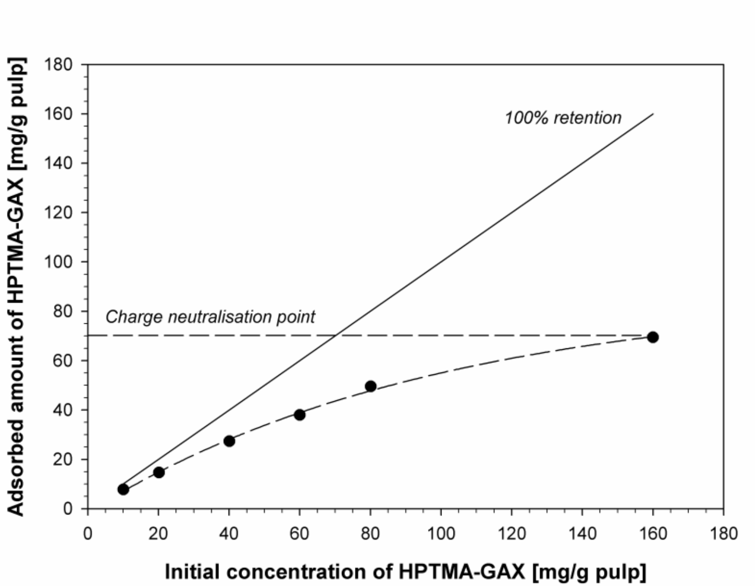

Fig. 25 Adsorption isotherm for HPTMA-GAX (CD = 1060 μeq/g) on never-dried bleached softwood kraft pulp fibres. Adsorption studies were performed at 60°C using a pulp fibre concentration of 30 g/dm^3, a NaHCO$_3$ concentration of 10 mM and an adsorption time of 60 min. The amount of adsorbed HPTMA-GAX was estimated by chemical oxygen demand (COD) of the separated liquid.

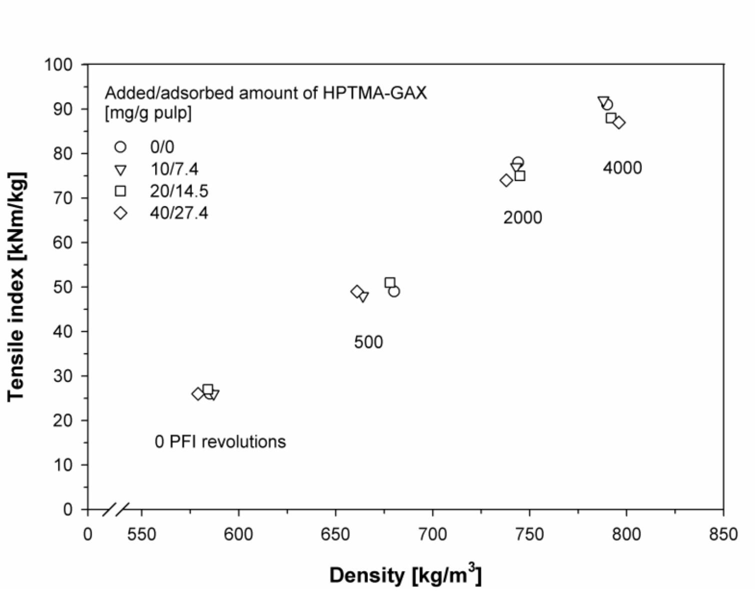

Fig. 26 Tensile strength as a function of sheet density, at different degrees of beating and added amounts of HPTMA-GAX (CD = 1060 μeq/g). Modifications were performed at 60°C using a pulp fibre concentration of 30 g/dm^3, a NaHCO$_3$ concentration of 10 mM and an adsorption time of 60 min. The amount of adsorbed HPTMA-GAX was estimated by chemical oxygen demand (COD) of the separated liquid.

4.4.6 Concluding remarks

Alkaline extracted barley husk xylan adsorbs on bleached softwood kraft pulp. However, the yield of adsorption is rather low. This is due to a low driving force of adsorption of GAX with a relatively high degree of Ara*f* substitution. Cationization of the isolated xylan increases the rate and the magnitude of adsorption extensively, as a result of the induced electrostatic interaction between the cationic xylan and the anionic fibres. Similar to non-modified xylan, cationic xylans possess a non-electrostatic cellulose surface affinity, as shown by adsorption at high ionic-strength and on esterified (carboxyl-free) pulp fibres. However, under these conditions, the driving force of adsorption decreased as the cationic charge density of xylan increased. Adsorption of cationized GAX with a charge density of 1060 μeq/g shows no or very small effect on the tensile strength of bleached softwood kraft pulp. The underlying cause of the small effect is not known, and has to be studied further.

All three methods used to quantify the adsorbed amount of GAX/HPTMA-GAX (COD, carbohydrate analysis and iodine complexation) give valuable information. The adsorption yield analysed by using the COD method and the carbohydrate analysis method correlates quite well. However, the carbohydrate analysis method has the advantage of providing information about the composition of non-adsorbing xylans. The iodine complexation method overestimates the adsorbed amount of xylan, due to differences in the formation of coloured complexes in unsubstituted and substituted xylan chain segments. Nevertheless, iodine complexation analyses in combination with results from carbohydrate analyses, can give valuable information about structural features of non-adsorbing xylan.

5 Conclusions

The research presented in this thesis provides further knowledge of how the composition of xylan fractions influences solution properties and characteristics of xylan adsorption on cellulosic fibres. The study also describes how xylan adsorption can be used to improve the strength properties of bleached softwood kraft pulp. Furthermore, the work investigates the potential of utilizing xylan isolated from agricultural waste materials in cellulose fibre modification.

The main findings of the presented investigations are:

- Lignin containing xylan fractions, dissolved in a pyridine/acetic acid/water mixture, can be purified from lignin not covalently attached to xylan by extraction with chloroform. While the removed lignin is not soluble in water in its isolated form, it is apparently water-soluble in the presence of xylan. This behaviour, along with results from experiments where lignin and xylan were mixed under controlled conditions, suggests that birch xylan is capable of forming inclusion complexes with lignin.

- Adsorption of birch glucuronoxylan (GX) on bleached softwood kraft pulp before drying preserves a considerable part of the fibre-swelling (water retention value and fibre saturation point), fibre wall porosity, 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 provides once-dried fibres with increased tensile strength and beatability.

- By fluorescent labelling of GX, followed by adsorption on never-dried bleached softwood kraft pulp fibres and subsequent imaging using confocal laser scanning microscopy, it is concluded that GX adsorbs on fibril surfaces throughout the fibre wall with enrichment on the outer fibre surface. The same conclusion can be drawn based on interpretations of total and surface charge measurements of fibres modified with GX.

- Water-soluble (glucurono)arabinoxylan (GAX) isolated from barley husks, a side-stream waste material from the manufacture of starch and ethanol, interacts with cellulose fibres. Adsorption is largely dependent on xylan molecular structure. GAX with a low degree of substitution has an enhanced propensity to form aggregates in aqueous solutions and adsorb on cellulose surfaces.

- An increase in the driving force for adsorption of more highly substituted GAX can be achieved by xylan cationization through a reaction in an aqueous alkaline medium with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC). Cationization increases the rate and magnitude of adsorption extensively, due to the induced electrostatic interaction between the anionic pulp fibres and the cationic xylan.

- Adsorption of GAX on never-dried fibres may be beneficial in the production of market pulps with increased tensile strength and beatability.

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