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# IMPROVING THE MATERIAL EFFICIENCY OF FURNISHES IN PAPERMAKING BY STRATIFICATION AND CHEMICAL MODIFICATIONS

by  
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## Preface

The studies presented in this doctoral thesis were carried out at VTT (Technical Research Centre of Finland) in Jyväskylä.

I would like to express my warmest thanks to Professor Jussi Timonen for his support and advice during this work. I would also like to thank Dr. Elias Retulainen for his encouragement, patience and extremely valuable advice during this thesis. I am also grateful to my pre-examiners Professor Emeritus Per Stenius and Dr. Markku Leskelä for their invaluable suggestions to enhance the content of this thesis. My sincerest thanks go to Dr. Anna Suurnäkki and Professor Harry Brumer for leading me into the depths of enzymes and polysaccharides.

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Jyväskylä, December 2012

Antti Oksanen

## Abstract

In this thesis the surface chemistry of fibres and z-directional paper structure were modified in order to improve the material efficiency of the fibres in the papermaking process. Material efficiency was estimated by measuring dewatering characteristics, wet web strength properties and end product quality from pulp and paper specimens. Chemical and mechanical pulps were modified by removing specific carbohydrates from the fibre and fines surface or alternatively polysaccharides were added to the fibre surface. Enzymes were utilised for the partial hydrolysis of cellulose and hemicelluloses from the fibre, whereas polysaccharides such as uncharged xyloglucan and cationic starch were added to pulp suspension or sprayed into wet paper sheets. The benefit of using uncharged chemicals is that they do not interfere with process waters like charged additives. Paper sheets of layered furnish structures were prepared with a multilayer sheet former. The effect of stratification of filler and chemical and mechanical pulps on papermaking and paper properties were evaluated. Additionally, two novel methods for analysis of z-directional furnish distribution in the paper were developed.

According to the results, dewatering characteristics of mechanical and chemical pulps in forming, wet pressing and drying sections can be enhanced by the use of hydrolytic enzymes. However, the role of different wood carbohydrates differs depending on the pulp type and structure of the dewatering section. Modification of merely the cellulose part of fibre seems to enhance dewatering in the forming section and in the drying section with both mechanical and chemical pulps. In general, nearly 1% hydrolysis of wood carbohydrates of TMP (thermomechanical pulp) was found to be necessary to enhance the dewatering in the forming section. In the case of TMP, it was also found that the combined partial hydrolysis/removal of cellulose and galactoglucomannan enables higher wet pressing pressure and thus dewatering without loss of bulk of the paper.

The introduction of xyloglucan-based chemicals and cationic starch into paper had positive influences on the dry strength properties of paper, as expected. Interestingly, xyloglucan-based treatments also increased the initial wet strength and drying forces of the paper samples, contrary to the effect of cationic starch. The cross-linking of xyloglucan with borate and the introduction of aldehyde groups to xyloglucan were found to further enhance both wet and dry paper strength properties. Aldehyde-xyloglucan was noted as being the most effective of the applied chemicals. The formation of covalent hemiacetal bonds due to aldehyde groups in the wet fibre network (before hydrogen bonds are created) was expected to have an important role in the strengthening of wet paper samples after wet pressing. Xyloglucan and xyloglucan-borate complex were also found to improve the bonding ability of the dried and re-pulped fibre. The xyloglucan-based treatment of the fibre surface could thus increase the strength of paper made of recovered fibres.

Contrary to cationic starch, xyloglucan was found to recover the strength properties decreased by treatments with hydrolytic enzymes. The uncharged nature, the high affinity to cellulose and the similarity of the XG backbone and cellulose chain may explain the results. Thus, the enzymatic treatment of pulp followed by xyloglucan modification of the fibre network offers an interesting possibility to enhance dewatering characteristics at the same time without any deterioration of dry strength properties. Water adsorbing polysaccharides forming a gel layer on the surface of the fibre were concluded to play an important role in the material efficiency of the fibre.

The reduction of softwood pulp content in fine paper combined with the stratification of TMP in the middle layer and hardwood pulp in the surface layer, enhanced wet web strength and dry sheet smoothness at the same time. The stratification of fillers into surface layers contributed to enhanced tensile strength compared to an even addition of filler to all layers. The result is probably due to the non-linear relationship between filler content and tensile strength. Additionally, it was noted that the utilisation of 10 to 20% of TMP enabled a 10% addition of filler without any deterioration in the wet web tension holding ability.

The results of this thesis demonstrate that the material efficiency of the fibre can be improved by utilising several unconventional methods. The modification of fibre surface chemistry and fibre network structure in the thickness direction of the paper can substantially improve production efficiency and improve end product quality. The results of this thesis can be utilised for example in enhancing the recyclability of pulp fibres, reducing the basis weight of paper and board or in utilising coarse (low energy) pulp in papermaking.

## List of Publications

- I. Oksanen, A., Edelmann, K., Kataja-aho, J., and Suurnäkki, A. (2011): Enhancing dewatering of thermomechanical pulp (TMP) based papermaking through enzymatic treatment. *Holzforschung*, 65, 787–795.
- II. Oksanen, A., Lehmonen J., and Pere, J. (2009): Improving paper making process by controlled modification of pulp carbohydrates. TAPPI Press - TAPPI Engineering, Pulping and Environmental Conference 2009 - Innovations in Energy, Fiber and Compliance. Memphis, USA, 2191 – 2216.
- III. Oksanen, A., Rantanen, T., Retulainen, E., Salminen, K., and Brumer, H. (2011): Improving Wet Web Runnability and Paper Quality by an Uncharged Polysaccharide. *J. Biobased Mater. Bioenergy*, 5, 1–5.
- IV. Oksanen, A., Retulainen, E., Rantanen, T., and Brumer, H. (2010): Improving recyclability of chemical pulp by introducing non-charged cross-linked polysaccharide on fiber surface. 2010 TAPPI PEERS Conference and 9th Research Forum on Recycling. Norfolk, USA, 1, 59-87.
- V. Oksanen, A., Retulainen, E., Kataja-aho, J., Somerkallio, M., Xu, C., and Brumer, H. (2012): Non-charge polysaccharides – Effects on runnability of wet web and efficiency of fibre material. *ipw*, (6), 51-55.
- VI. Oksanen, A., Salminen, K., and Kouko, J. (2007): Enhanced quality - strength and cost efficiency by means of layering. *Paperi ja Puu - Paper and Timber*. 89(4), 242–245.
- VII. Oksanen, A., Salminen, K., Kouko, K., and Retulainen, E. (2012): The effects of TMP and filler stratifying on wet web runnability and end product quality of fine paper. *NPPRJ*, 27(1), 130-136.

The author significantly contributed to creating the research ideas, planning the experiments and execution of all the research trials in these publications (Papers I-VII). Specifications for measurement of papermaking characteristics such as dewatering, wet and dry strength and other end quality measurements were mainly done by the author (Papers I-VII). Author had also a major role in selecting of the polysaccharide type, application methods and amounts used in trials (Papers III - V). Preparation of stratified paper samples and development of new analysis for layered paper structures were done by the author (Papers VI -VII). The author was responsible for analysing the experimental results of the trials. He had the main role in drawing the conclusions. He also wrote the first drafts of the articles.

However, the preparations of purified enzymes (Papers I-II) and modified xyloglucans (Paper V) were done by the co-authors in the publications. The conditions for the enzyme treatments were instructed by co-authors based on measurement of dissolved sugars in pre-trials (Papers I-II). Also, the planning and execution of the ESCA and HPLC analysis related to enzyme treatments were done by co-authors. Co-authors also significantly helped in the interpretation of ESCA and HPLC analysis results (Papers I-II).

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## List of abbreviations

BHW	Bleached hardwood pulp
ECF	Elemental chlorine free
EG	Endoglucanase
ESCA	Electron Spectroscopy for Chemical Analysis
G-PAM	Glyoxalated polyacrylamide
HPLC	High performance liquid chromatography
k	Light absorption
MAN	Mannanase
MeGlcA	Methyl glucuronic acid
PCC	Precipitated calcium carbonate
RH	Relative humidity
s	Light scattering
TKP	Tamarind kernel powder
TMP	Thermomechanical pulp
XG	Xyloglucan
XYL	Xylanase

# 1 Introduction

Papermakers are constantly seeking new means of improving the competitiveness of the current papermaking process. The production costs in the papermaking process are mainly formed of two factors: raw material costs and the energy costs. One approach to improve the competitiveness of the product is to increase its quality through the introduction of certain innovations in the process. However, one should remember that the investments in innovations should have a reasonable payback time.

Costs in paper production are typically estimated to divide into those caused by fibre 30%, energy 20%, fillers 10%, chemicals 10% and other costs (labour and environment) 30%. Basically, savings in raw material costs can be achieved by using less or cheaper raw materials in paper production. Reduction of raw material costs in papermaking is challenging due to boundary conditions defined by paper quality standards. Deteriorated quality may e.g. lead to poor printability, convertability or product quality.

The dewatering properties of the pulp greatly affect the energy efficiency of paper machines. Enhanced water removal in the forming and wet press section enables lower energy consumption in the dryer section or higher speed, or alternatively a shorter drying section, and thus decreased investment costs. It can be estimated that a 1% increase in the dry solids content of the web after wet press reduces drying costs by 4%.

The production profitability of a paper machine is strongly influenced by the frequency of web breaks i.e. runnability due to the low net profit of manufacturing. Therefore, innovations that can enhance the runnability of the paper machine directly improve the cost efficiency of papermaking. Due to the high-speed and width of modern paper machines, improving the runnability is challenging.

## 1.1 How to achieve material and energy savings

The adjustment of furnish properties and paper structure can have positive impacts on papermaking profitability and environmental issues. The principle ways of how the papermaking process can be enhanced towards better material efficiency are shown in *Fig. 1*.

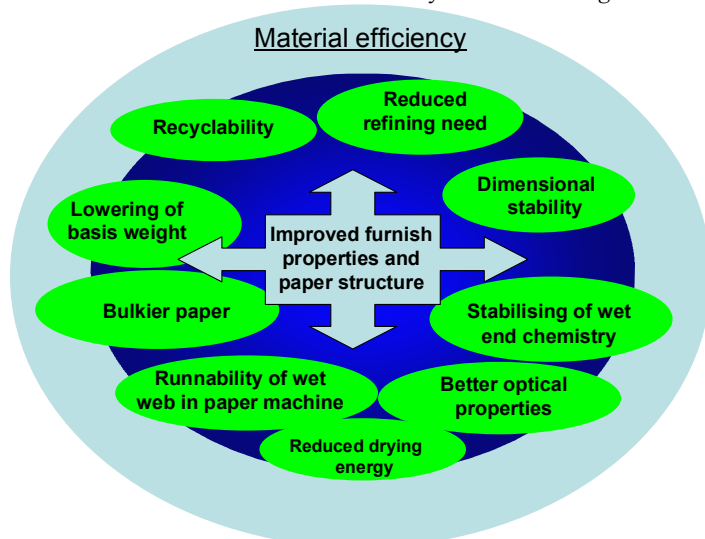


Fig 1. Positive effects on paper production due to adjustment of furnish and paper structure.

The reduction of grammage has positive effects on the fibre, energy, filler and chemicals consumption of papermaking. On the other hand, paper properties such as bending stiffness is strongly reduced and opacity substantially decreases when the grammage of paper is lowered. Bending stiffness and opacity influence the printability and the easiness of paper handling. The increase in the bulk of the sheet improves the posture of paper. The bulk of the paper made of chemical pulp can be increased by using stiff mechanical pulp fibres (Retulainen et al. 1993), long non-wood fibres like flax (Kärenlampi 1995), or hydrophobic synthetic fibres such as polyester (Soga et al. 2007). Compared to chemical pulp, mechanical pulp is also less expensive. The bonding strength of synthetic fibres or stiff

mechanical pulp fibres is typically relatively low compared to that of beaten chemical pulp fibres. TMP is not commonly used in fine paper grades because it does not meet the high brightness requirements and archiving standards of fine paper. An unconventional idea of making TMP from hardwood pulp provides higher brightness and light scattering coefficient compared to traditional TMP manufactured from softwood (Koran 1995). A decrease in grammage may, in addition to strength and runnability properties, deteriorate coating and printing quality of the product. Therefore, a decrease in paper grammage requires specific, tailored furnish composition and chemical treatments.

The replacement of fibres with inexpensive raw materials, fillers etc., can provide cost savings. The utilisation of fillers can also enhance the optical, structural and surface properties of paper. On the other hand, a high amount of filler in the paper will typically deteriorate the dry strength and posture of the paper. When reducing the grammage of printing paper grades, fillers are needed for enhancing the opacity and printability of the paper. Titanium oxide is known to have a high scattering coefficient and thus to effectively increase the opacity of the paper. The usage of titanium oxide is limited due to its high price (Soga et al. 2007). Specific filler types have been developed to increase the bulk of the sheet such as hollow and spherical filler particles made of calcium carbonate (Enomae and Tsujino 2002) or low density filler particles made of silicon dioxide or nanostructured fillers made of calcium silicate (Johnston et al. 2002). The utilisation of specific particle sizes of precipitated calcium carbonate (PCC) has been reported to increase bulk and enable a decreased grammage of wood-free book-printing paper by Ochi (2006). According to the literature, end product quality, e.g. the posture of paper, can be further enhanced by silica treatment of PCC (Soga et al. 2007). The effects of filler on the properties of fibre network and retention also depend on pulp type. In the case of mechanical pulp containing paper grades, positive effects have been observed of specific urea formaldehyde filler on printability and optical properties, without losing the strength of the paper (Kramer 1993). In general, non-conventional fillers are very limited in conventional paper grades due to the restricted availability and high price of these products. Therefore, controlled exploitation of common low-cost fillers in paper mills is still of great interest. According to the literature, the mixing of low-cost filler grades can lead to substantially enhanced opacity, for example in low grammage paper grades (Rae 2002).

An unconventional addition procedure of fibres, filler and chemicals to furnish can have a positive influence on paper machine runnability and end product quality, and further to the cost efficiency of paper production. The application of filler and starch to the surface of fibres has been reported to enhance the dewatering of furnish, the bulk and strength of the sheet and to reduce chemical consumption and drying costs (Ozersky 2008). The stratification of furnishes may enable the use of less or cheaper raw material. For example, layering may enable the utilisation of mechanical pulp in fine paper grades (Häggbloom-Ahnger 1998) or increase of the filler content in the paper.

As the tensile strength of the paper is reduced due to decreased grammage, increased bulk or by replacing fibres with filler, the strength of the fibre bonds is essential. The topochemistry of the fibre has crucial role in creation of strong fibre bonds. The lignin content of the fibre surface has been reported to increase the paper bulk and thus to decrease the relative bonded area of the fibre network (Yang 2003). Fibre stiffness is major contributor to the paper bulk. Thus, a decrease in bulk due to a reduced lignin content is related to increased fibre flexibility. Also, lignin on the fibre surface is not beneficial for fibre bonding. It has been reported that the addition or removal of hemicelluloses in chemical pulp furnish has no influence on the bulk of the paper (Pekkala 2006). However, hemicelluloses are assumed to contribute positively to the bonding strength of fibres.

The bonding strength between different types of fibres and fillers, and the porosity and smoothness of the paper, can be enhanced with additives, such as starch. The strength and other critical converting properties of the paper are conventionally improved in sizing (Nada et al. 2001). The utilisation of uncommon sizing techniques, such as spraying of chemicals, could retain the bulk of the sheet more effectively. In addition, the spraying of chemicals at the end of the former section does not influence the white water system as much as the addition of charged chemicals to furnish before the headbox. Spraying may also enable the utilisation of cheaper uncharged chemicals such as native starch in papermaking. Spraying has not yet become common due to some practical restrictions inherent in the spraying technology. However, innovations in the filtration systems for homogenous and low viscosity spray chemicals can increase the applications of spray technology. At the moment, spray technology is typically used in paperboard production.

The dewatering properties of the furnish and further the runnability of the paper machine, greatly affect the cost efficiency of papermaking. In mechanical pulping, refiners are used to separate and further fibrillate fibres. The share of short fibre fractions and fibrils is increased during refining. An



increase in small particles decreases the drainage rate of the wet web in the paper machine. Conventionally, dewatering is improved in the paper machine by means of drainage aids in the former section or more intense wet pressing in the press section. Drainage aids can, however, worsen the formation (Caram et al. 1996), and high wet press load levels reduce the bulk of the end product. For these reasons, new methods of pulp modification and dewatering innovations are required with new high-speed paper machines (King et al. 1998). The amount of residual water after the former and wet press sections is related to the structural and chemical composition of pulp. Fines with a high surface area retain more water than coarse fibres. Also, hemicelluloses are capable of retaining more water than the lignin or cellulose part of the fibre. An increase in the dry solids content of the web after wet pressing reduces the drying energy demand in the drier section of the paper machine. Therefore, modification of surface chemistry of fibres with conventional pulping chemicals or unconventionally with enzymes is interesting. Besides, the chemical composition of furnish as well as the fibre network characteristics can influence the drying efficiency. The density and porosity of the fibre network have a significant role in the heat transfer in wet web and on the release of water vapour from the fibre network.

In addition to the drying energy demand, the dry solids content after wet pressing also has a significant influence on the wet web strength and the runnability of the web (Kurki et al. 2004). There are many known additives for improving the dry strength of the end product, such as starch. In contrast, however, the existing range of chemicals for enhancing the initial wet web strength in paper production is limited. Utilisation of runnability chemical can have significant influence on the profitability of the paper mill. G-PAM, used for a number of paper grades, is one of the few known paper machine runnability additives (Lindström et al. 2005; Xu et al. 2002).

The material efficiency becomes more and more critical in papermaking as the end product prices go down and the use of lower quality raw materials, such as recycled fibre increases. The influence of fibre topochemistry on specific paper properties has been studied in several earlier publications. However, there are not many studies available where the effects are estimated through all paper machine sections. Also the potential of furnish stratification in improving both wet and dry web properties and end product quality is little studied. The objective was to modify the surface chemistry of the fibres and the z-directional paper structure in order to find tools to improve the material efficiency of the furnish. Material efficiency aspects were evaluated in several critical papermaking sections and in end product. The surface chemistry of fibres was altered by specific enzymatic actions and by the spray application of chemicals on the fibre network. Especially, spraying of non-charged strength additive xyloglucan into wet web was on focus. The z-directional paper structure was tailored by furnish stratification and by controlling the location of different furnish components.

## 2 Materials and methods

In this section we present the standard and unconventional methods applied in the studies of this thesis. Standard methods are listed and specified in *Table 1*, whereas unconventional analyses are described in more detail in the sub-sections. A summary of enzyme treatment procedures, measurement of wet web strength and drying characteristics, application of chemicals by spraying and preparation of multilayer handsheets, based on publications I – VII, is also presented. Besides utilising established methods, new analyses were developed in order to confirm the success of furnish stratification. Two novel methods of analysis are described, which reliably expose the distribution of fibre and filler material in the thickness direction of paper. The measured fibre and filler distributions in the z-direction of paper have supported the interpretation of results.

### 2.1 Standards of pulp and sheet analyses

Standard laboratory procedures were utilised in the studies of pulp and sheet samples. Conventional once-dried market chemical pulp and commercial never-dried chemical and thermomechanical pulp samples were delivered by Finnish pulp and paper mills. ECF (Elemental Chlorine Free) never-dried birch kraft pulp was delivered at a 15% consistency. Pulp samples were kept in a cold-storage room (5 °C) before pulp modification and sheet preparation. Some of the thermomechanical pulp was stored in the freezer for later use. Disintegration procedures (*Table 1*) depended on the pulp type and dry solids content of the sample. Sheet samples were dried and stored in an air-conditioned laboratory environment (RH 50, 23 °C) before technical paper analysis.

Table 1. Standards of pulp and sheet analysis.

Procedure	Standard
Bendtsen air permeability	SCAN-P 26:78
Bendtsen roughness	SCAN-P 84:01
Disintegration (cold and hot)	SCAN-C 18:65
Fibre length (L&W FiberMaster STF1)	ISO/DIS 16065-2
Freeness	SCAN-C 21:65
Grammage	SCAN-P 6:75
Preparation of hand sheets	SCAN-C 26:76
Scott Bond	TAPPI T 403
Tensile strength	SCAN-P 38:30
Thickness	SCAN-P 7:75

## 2.2 Enzymatic treatments of pulps and related analysis

Enzymatic treatments of TMP and ECF (elemental chlorine free) chemical birch pulp have been described in publications I and II. TMP (in 5% consistency) and never-dried chemical pulp (in 11% consistency) were obtained from Finnish pulp mills. The freeness value of the TMP was 60 ml and the length-weighted average fibre length was 1.4 mm, with 40% fines content. The TMP pulp was stored in a freezer and melted and disintegrated by SCAN-C 18:65 prior to the experiments. The freeness of chemical pulp was 580 ml and the mean fibre length was 0.92 mm with 6% fines content. Chemical pulp was further refined with an LR40 laboratory refiner at a low intensity of 0.3 J/m to 80 kWh/t energy level (370 ml).

Xylanase, mannanase, endoglucanase I (EG I) and endoglucanase II (EG II) originating from the fungus *Trichoderma reesei* were produced and purified at VTT as previously described (Tenkanen et al. 1992; Ståhlbrand et al. 1993; Suurnäkki et al. 2000). Commercial cellulase preparations Ecostone L900 (courtesy of AB Enzymes, Finland) and Novozym 476 (courtesy of Novozymes, Denmark) were also used in the pulp treatments. The enzyme types and protein content or activity of the enzyme preparations are presented in Table 2. Enzyme dosages used in the pulp treatments were: 0.01, 0.05, 0.1, 0.2, 0.25, 0.5 and 1.0 mg protein/g of the dry pulp. In addition, a dosage of 0.1 + 0.1 mg protein/g of the dry pulp was applied in a combined xylanase + mannanase treatment. The standard conditions of enzyme treatments were as follows: 5% pulp consistency, pH 5 adjusted by 0.1 M sulphuric acid at 50°C and for 2, 5 or 24 hours. Replicates were done for each enzymatic treatment. After the enzymatic treatment, the pulp was filtered twice, then a filtrate sample was taken, and finally the pulp was washed with distilled water prior to testing for papermaking properties. The reference treatments were performed as described above, but without the addition of enzymes.

Table 2. Enzyme preparations and their characteristics.

Abbreviation of enzyme	Description	Protein cont. (mg ml <sup>-1</sup> )	Reference in text
EG I	<i>T. reesei</i> endoglucanase I, purified	5.1	EG I
EG II	<i>T. reesei</i> endoglucanase II, purified	10.0	EG II
MAN	<i>T. reesei</i> mannanase, purified	4.4	mannanase
XYL	<i>T. reesei</i> xylanase, purified	3.2	xylanase
Ecostone L900	Commercial EG-rich cellulase and hemicellulase preparation	162	Commercial enzyme 1
Novozym 476	Commercial monocomponent cellulase preparation	14.8	Commercial enzyme 2

Carbohydrates solubilised in the enzymatic treatments were analysed as monomers after secondary enzymatic hydrolysis by HPLC, as previously described (Buchert et al. 1993). The coefficient of variation in the HPLC analysis was under 5%. The surface composition of the pulps was measured with electron spectroscopy for chemical analysis (ESCA) (Koljonen et al. 2003).

Fines particles of the TMP sample were classified into fibrillar and non-fibrillar material by image analysis (Luukko, 1999) and the results were expressed as apparent mass shares including the ray cell proportion of the fibrillar material.

Capillary viscosity (Standard T 230 om-99) of the enzyme-treated pulp samples was measured in the Department of Chemistry at the University of Jyväskylä.

### 2.3 Measurement of runnability potential and drying characteristics

In all publications from I to VII, the dynamic tensile strength and relaxation properties of wet web samples were measured with a fast tensile strength testing rig called Impact (Kurki et al. 2004). A special feature of Impact is the high average straining velocity, 1 m/s, when the test velocity in a standard tensile tester is 0.00037 m/s. The relaxation properties of wet samples after 0.475 s relaxation time are measured at a strain of 1% or 2%. The selected straining velocity, amount of strain and relaxation time in the Impact test, simulate the forces directed at the wet web in the paper machine when the wet web is transferred from the press section to the drier section. A web break is likely to occur in the early part of the drying section if the tension of the wet web is low. High tension of the wet web in the relaxation test indicates its good runnability in the paper machine. The principle of the relaxation test is shown in Fig. 2.

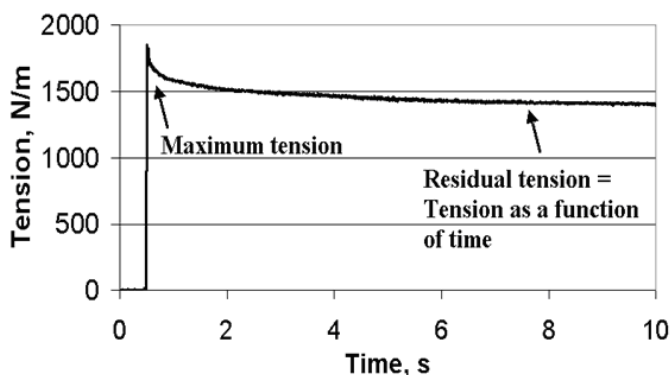


Fig 2. A dry paper relaxation curve at 1% straining by the Impact test rig.

In publications I, II and III the drying characteristics of the wet sheet samples were measured. In order to measure the drying time and forces, an impingement drying (Hartnett, Irvine 1977) unit (Fig 3) was applied to a standard tensile tester with an infrared online dry content measurement. Testing parameters were as follows: temperature of the drying air 110°C, distance between the sample holding clamps, 100 mm, width of the sample 70 mm, pre-load of the sample 1 N. Dry content and shrinkage force data as a function of time were recorded on a hard disk during the measurement, where they could be refined and visualised as required.

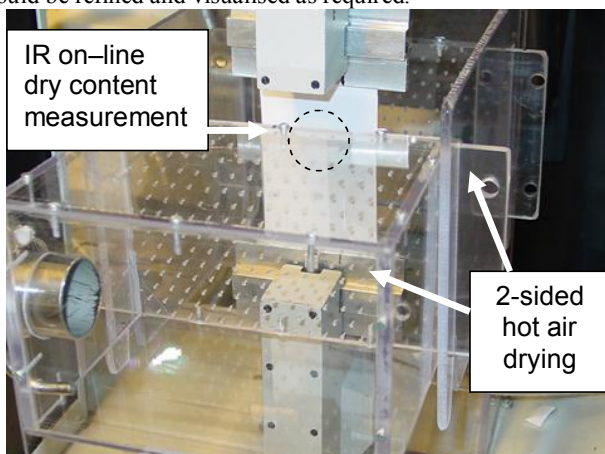


Fig 3. Measurement of the drying time and forces as a function of dry solids content of a paper sample.

## 2.4 Chemicals applied in spraying studies and operation of the spraying unit

In publications III, IV and V, xyloglucan-based chemicals and cationic starch (Raisamyl 135, degree of substitution 0.035) were introduced onto wet sheets by spraying. Xyloglucan and cellulose are built up by the same  $\beta$ -1,4-D-glucose backbone structure (Fig. 4), additionally XG is extensively branched (Ahrenstedt 2007). Native xyloglucan ( $M_w \sim 1000$  kDa, Fig. 4) was obtained originally from Innovasyth Technologies Ltd., India. For the work in this thesis, XG purified from deoiled tamarind (*Tamarindus indica*) kernel powder was utilised. Tamarind kernel powder contains  $\sim 60\%$  XG by weight.

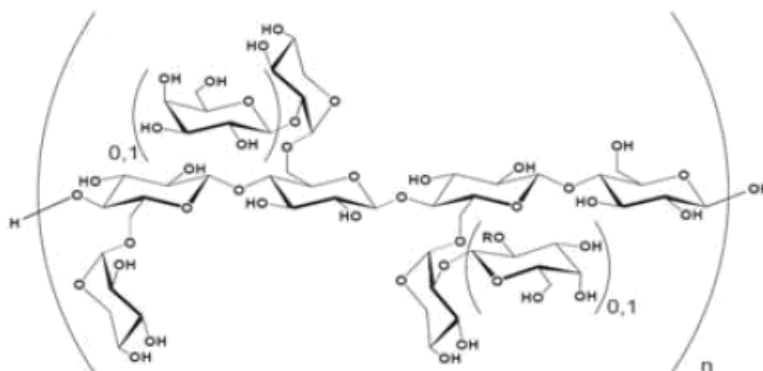


Fig 4. The structure of tamarind XG, with a possible galactose substitution indicated:  $n \approx 700$  (Fry et al. 1993; Ahrenstedt 2007).

Additionally, XG was mixed with borax because borates are known to form complexes with polysaccharides. The application of borax with XG was expected to introduce covalent bonds between XG and cellulose or between two adsorbed XG molecules (Pezron et al. 1988; O'Neill et al. 1996; Martin et al. 2003; Bishop et al. 2004; Ahrenstedt 2007). Covalent bonds were further expected to strengthen the initial wet web strength and dry paper strength. The borax (di-natriumtetraborate decahydrate) sample was supplied by Merck KGaA, 64271 Darmstadt, Germany.

The effect of molecular weight and oxidation of XG on initial wet web strength and dry paper properties were examined. Enzymatic modifications of XG (lowered molar mass xyloglucan and oxidised xyloglucan) were done by Dr. Chunlin Xu at KTH Royal Institute of Technology.

Xyloglucan with lowered  $M_w$  was prepared from purified xyloglucan via partial digestion with endo-xyloglucanase from *Chrysosporium lucknowense* (Grishutin et al. 2004), obtained from Dyadic NL, The Netherlands. The  $M_w$  of different XG fractions was determined by gel permeation chromatography (GPC) measurements on a Waters 616 HPLC system equipped with two Tosoh gel columns, G5000HHR and G3000HHR (both  $7.8 \times 300$  mm), connected in series. HPLC-grade dimethyl sulfoxide (DMSO) was used as the eluent at a flow rate of 1 mL/min, and the column temperature was maintained at  $60^\circ\text{C}$ . Analyte detection was performed by evaporative light scattering detection (Polymer Laboratories PLELS 1000). Pullulan polysaccharide standards were used to calibrate the system over the molecular weight range 180-788 000.

Galactose oxidase from *Fusarium graminearum* was produced recombinantly in *Pichia pastoris* according to the protocol described by Spadiut et al. (2010) and Whittaker (2003). Optimised xyloglucan oxidation conditions were as follows (Xu et al. 2012): to a 10 ml XG aqueous solution, catalase (Cat., 1100-110 000 units, Sigma-Aldrich, Cat. no. P8250), horseradish peroxidase (H.R.P., 1.7-170 units, Sigma-Aldrich, Cat. no. C1345), and GalOx (0.75 or 1.5 units) were added. GalOx activity was measured with the standard chromogenic ABTS [2,2'-azinobis(3-ethylbenzthiazolinesulfonic acid)] assay (Baron et al. 1994). The solution was kept at room temperature with air bubbled-in at various time intervals. The enzyme was denatured by incubation in a  $95^\circ\text{C}$  water bath for five minutes, and removed by centrifugation. As a result of the modification of XG, full conversion of primary alcohols on galactose C-6 to aldehyde was achieved (Fig. 5).

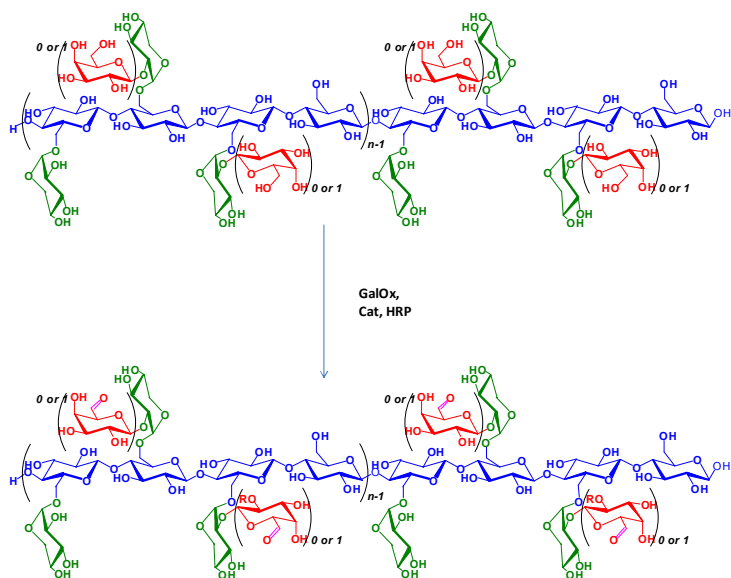


Fig 5. Modification XG with galactose oxidase (*Fusarium graminearum*); Full conversion of primary alcohols on galactose C-6 to aldehyde (Xu et al. 2012).

A spraying rig developed by VTT in Jyväskylä was used for the spray application of the chemicals in publications III, IV and V. The principal scheme of the device is presented in Fig. 6.

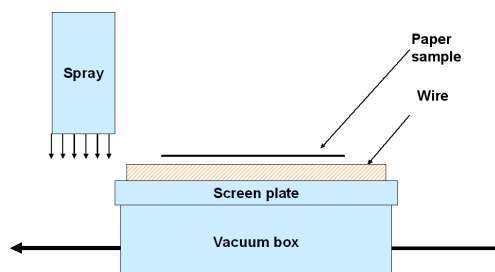


Fig 6. Operation principle of the spraying unit.

In the spray application of chemicals, wet or dry sheet samples are placed on a sledge, which passes below the spraying unit (Ahrenstedt et al. 2008). The amount of sprayed chemical can be varied by the velocity of the sledge and the consistency of the chemical. In this work, the consistency of sprayed chemicals was 1.0% of the dry weight in all trials, thus the amount of chemical was altered by the velocity of the sledge. The vacuum below the samples holds the sample in place during spraying and helps the chemical to penetrate through the paper sample. After spraying, laboratory sheets were wet pressed in the laboratory (laboratory wet presser by Lorentzen & Wettre) and dried with their shrinkage restrained in an air-conditioned laboratory environment (23 °C, RH 50%). Wet samples after wet pressing were used in the measurement of runnability potential and drying characteristics described in the previous sub-section.

## 2.5 Preparation of enzymatic and xyloglucan-treated handsheet samples

In this case study, xyloglucan and starch were applied by spraying on wet handsheets made of TMP pulp treated with purified *Trichoderma reesei* cellulases and hemicellulases (EG II = endoglucanase II, MAN=mannanase, XYL=xylanase) and with a Commercial enzyme 2 for 24 h. Handsheets of enzyme-treated TMP were prepared with a laboratory sheet mould to 60 g/m<sup>2</sup> basis weight according to SCAN-C 26:76. After sheet forming, sheets were wet pressed at a light 0.5 bar load for 5 min (wet presser by Lorentzen & Wettre). After the spraying of additives, samples were wet pressed again (0.5 bar for 2 min) and dried in an air-conditioned laboratory (23°C, RH50) with their strain retained. The procedure applied simulated the spray bar technology utilised in the press section of a paper machine.

The average xyloglucan and starch (Raisamyl 135) dosage was ~2% of the dry weight of the sheet. The consistency of sprayed XG and starch solution was 1%.

## 2.6 Preparation of multilayer paper sheets

In publications VI and VII, handsheets with layered furnish structures were considered. Sheets of 60 g/m<sup>2</sup> were manufactured with a multilayer sheet former (Puurtinen et al. 2003). A special feature of this multilayer sheet former is two-sided water removal. The principle of multilayer sheet forming is presented in Fig. 7.

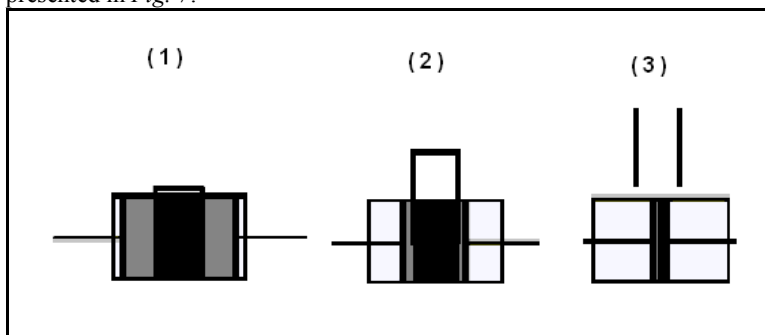


Fig 7. Principle of multilayer sheet forming: (1) pulps and chemicals are placed in three chambers, (2) fabrics are pushed towards the centre of the sheet mould and surface layers of the sheet are formed, (3) dividing plates are removed and finally the centre layer of the sheet is formed, completing the multilayer structure.

In the first phase of the forming of multilayer handsheets, the pulp and chemicals are added into separated chambers (Fig. 7, part 1). Next, the furnishes are mixed by introducing pressure air in to chambers before the actual sheet forming, where the fabrics are pushed towards each other (Fig. 7, part 2). When the fabrics are moved close to the dividing plates between chambers, the plates are removed in a vertical direction (Fig. 7, part 3). After the multilayer handsheet is formed, it is wet pressed and dried according to the standards of laboratory sheet preparation (SCAN-C 26:76). The furnish used in the stratification trials consisted of bleached softwood pulp, bleached hardwood pulp and TMP delivered by Finnish pulp and paper mills. In publication VII, variation of the filler (PCC) content in the thickness direction of the paper was also considered.

In publication VI, the pulps used in forming were bleached softwood pulp (CSF 620 ml, fibre length 2.20 mm), bleached hardwood pulp (CSF 450 ml, fibre length 0.88 mm) and bleached TMP (CSF 60 ml, average fibre length 1.86 mm). Trial points are presented in Table 3.

Table 3. Percentages of pulp components and pulp types in the layers of stratified samples.

Trial point	Top layer, %	Middle layer, %	Bottom layer, %
1	45% [HW]	10% [TMP]	45% [HW]
2	37.5% [HW]	25% [TMP]	37.5% [HW]
3	30% [HW]	40% [TMP]	30% [HW]
4	90% [HW] + 10% [TMP] evenly in all layers		
5	75% [HW] + 25% [TMP] evenly in all layers		
6	60% [HW] + 40% [TMP] evenly in all layers		
7	60% [HW] + 40% [SW] evenly in all layers		
8	30% [HW]	40% [SW]	30% [HW]

In publication VII, the chemical pulp mix consisted of 60% bleached birch kraft pulp and 40% bleached pine kraft pulp (Table 4). Once-dried chemical pulp sheets were beaten with a ProLab refiner (at 4% consistency) to the same dry tensile index level (48 Nm/g, birch CSF 350 ml, pine CSF 610 ml) as TMP (CSF 60 ml). The cationic retention aid (cationic polyacrylamide) by Ciba (Percol 47) was used at all the trial points. The filler used was precipitated calcium carbonate (PCC) provided by Specialty Minerals Inc. (Albacar LO).

Table 4. The relative amounts of filler and pulp in the three layers of stratified samples. HW = hardwood, SW = softwood.

Trial point	Filler content			bottom [%]	Fibre share		
	bottom [%]	middle [%]	top [%]		middle [%]	top [%]	
1	0	0	0	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW	
2	5	0	5	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW	
3	10	0	10	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW	
4	tot. 20% evenly to all layers			mix 60 HW/40SW	mix 60HW/40SW	mix 60HW/40SW	
5	5	0	5	45(60HW/40SW)	10TMP	45(60HW/40SW)	
6	10	0	10	45(60HW/40SW)	10TMP	45(60HW/40SW)	
7	5	0	5	40(60HW/40SW)	20TMP	40(60HW/40SW)	
8	10	0	10	40(60HW/40SW)	20TMP	40(60HW/40SW)	
9	tot. 20% evenly to all layers			40(60HW/40SW)	20TMP	40(60HW/40SW)	
10	tot. 20% evenly to all layers			mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	
11	10	0	10	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	
12	tot. 20% evenly to all layers			TMP	TMP	TMP	
13	0	0	0	TMP	TMP	TMP	

## 2.7 Characterisation of furnish distribution in the thickness direction of paper

Fibre length and filler distributions in the thickness direction of paper are known to correlate with the technical properties of paper such as smoothness (Häggbloom-Ahnger 1998). For coating and printing quality, particle distribution is essential in the z-direction of the paper. For example, uneven fines distribution may induce paper curl and reduce the internal strength of the paper. There are only a few methods to determine the particle size distribution in the thickness direction of paper. These methods are typically quite inaccurate, time-consuming and require expensive equipment. Two novel methods to characterise the success of furnish stratification are presented in this *section*. One way to split the paper sample into layers is to use the tape stripping method (Erkkilä 1995). The tape stripping technique is generally used to determine the filler distribution and fibre orientation in the thickness direction of paper. With tape splitting, a large number of layers can be produced. The size of the sample can even be A3, as the splitting of the paper with this method is very uniform. The two new z-directional methods are based on the tape stripping technique. In publication VI, optical differences of the pulp in different tape strips were used to determine distributions of furnishes in the thickness direction of the paper samples. In publication VII, characterisation was done of furnish samples released from the tape strips.

In publication VI, the analysis of paper structure in the thickness direction is based on differences in the light scattering and absorption properties of pulp. Scattering and absorption coefficients ( $s$  and  $k$ ) were determined with spectrophotometry for the tape stripped layers of the samples using black and white backgrounds (Pauler 1998, eq. 1 - 4).

$$a = \frac{1}{2} \cdot \frac{(R_{gv} - R_{gs})(1 + R_v R_s) - (R_v - R_s)(1 + R_{gv} R_{gs})}{R_s R_{gv} - R_v R_{gs}} \quad (1)$$

$$R_\infty = a - \sqrt{a^2 - 1} \quad (2)$$

$$s = \frac{1}{w \left( \frac{1}{R_\infty} - R_\infty \right)} \cdot \ln \frac{(1 - R_s R_\infty)(R_\infty - R_{gs})}{(1 - R_\infty R_{gs})(R_\infty - R_s)} \quad (3)$$

$$k = \frac{s \cdot (1 - R_\infty)^2}{2 \cdot R_\infty} \quad (4)$$

where

- $R_v$  = reflectance factor of the sample measured on a white background
- $R_s$  = reflectance factor of the sample measured on a black background
- $R_{gv}$  = reflectance factor of the white background
- $R_{gs}$  = reflectance factor of the black background
- $s$  = light scattering
- $k$  = light absorption

The stripped layer should be even and contain enough fibres for a reliable optical measurement. Other sources of error were the effect of tape and the limitations of Kubelka & Munk theories for paper of low grammage (Bristow, Kolseth 1986; Rundlöf, Bristow 1997). Weaknesses in Kubelka & Munk's theories for very low grammages were found to be nondominant if there was a significant difference ( $>0.2 \text{ m}^2/\text{kg}$ ) in the absorption coefficients of the layers. A tape of high transparency was selected to minimise the effect of tape on the analysis. Hence, the layered structure of tape and sample was not considered in the analysis. The additive rule utilised in the determination of the absorption coefficient of paper (eq. 5) with a homogenous structure was used to compensate for the effect of tape on the absorption coefficient (Pauler 1998):

$$k_{\text{paper}} = \frac{k_{\text{paper+tape}} - k_{\text{tape}}(1 - X_{\text{paper}})}{X_{\text{paper}}} \quad (5)$$

where

- $k_{\text{paper}}$  = absorption coefficient of paper,
- $k_{\text{paper+tape}}$  = absorption coefficient of paper and tape,
- $k_{\text{tape}}$  = absorption coefficient of tape,
- $X_{\text{paper}}$  = mass share of paper in the tape stripped layer.

At the trial points where TMP was rationed to the middle layer, TMP was spread only a little towards the surfaces. This can be seen in Fig. 8 where the optically measured TMP distribution (solid line) and theoretical TMP distribution (dashed line) are shown in the sample's thickness direction. The theoretical TMP distribution curves are based on pulp dosages in different layers and the  $k$  values of pure hardwood and TMP samples. The trial point of 10% TMP in the middle layer gave lower values for the absorption coefficient. This was due to mixing of the boundary layers. Minor mixing of boundary layers is desired to achieve a proper internal strength with a three-layer structure. Based on the results from tape strips, stratifying of the TMP and chemical pulps succeeded excellently.

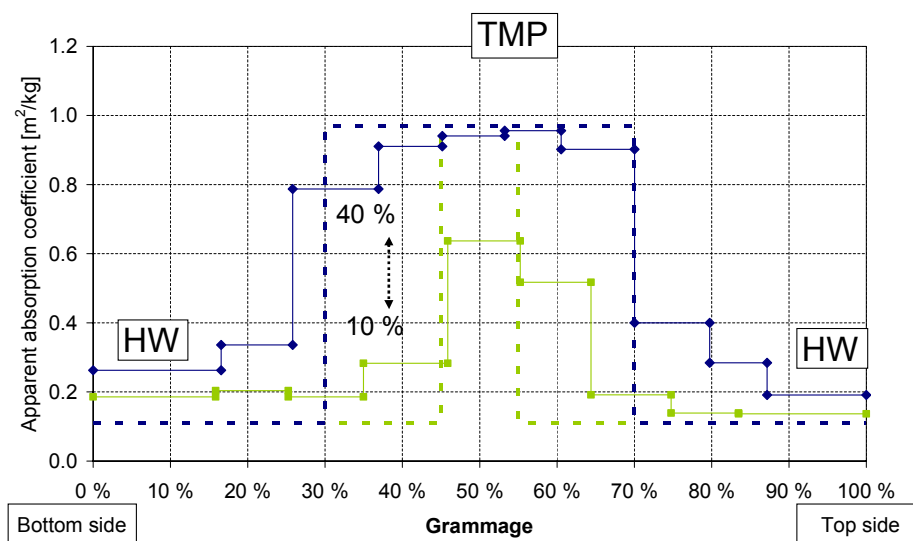


Fig 8. Determination of layer purity of the stratified samples by measuring the absorption coefficients of the tape stripped layers. Solid lines represent measured data while dashed lines are theoretical curves for 10% and 40% TMP content in the middle layer. Abbreviations: HW = hardwood, TMP = Thermomechanical pulp.

In publication VII, the furnish samples of layered paper structures were obtained from tape strips. The main aim of this method was to release fibres from the glue of the tape without causing any significant change in the amount of fines or defects in the fibres. The optimised method parameters



were the tape and solvent type and dissolution conditions. The following procedure was developed in this work in order to release fibres from the tape: tape strips were first sprayed twice with solvent (Label off 50, CRC industries Europe). Second treatment with the solvent was done 2 min after the first spraying. 5 min after the first spraying, the fibres and glue were scraped off from the tape and blended with 80 ml of water. At this point, the suspension still contained glue, which has to be removed. Because glue floats in water, the suspension was mixed for more than 30 s with a blender bar until most of the glue separated on the surface of the suspension, from where it could be removed with a spatula and pipette. Finally, any residual glue was separated on to the surface of the suspension by centrifugation for 10 min at 4100 rpm. Some glue was likely to remain in the suspension after these treatments, but this residual glue was not noticed to influence the results of fibre dimension analysis. After releasing fibres from the tape, the fibre dimensions could be measured further with a conventional fibre dimension analyser. However, the influence of residual glue in the suspension on an fibre dimension analyser with narrow flow capillaries is not known. In this study, the fibre dimension analyser used – the L&W FiberMaster STFI – has large flow channels compared to many other analysers. It was observed that fines were also quite effectively released from the glue of the tape because the total amount of fines decreased only slightly compared to the fines content of the initial reference pulp.

The fibre fraction distributions in the thickness direction of the layered structures are shown in Fig. 9A and Fig. 9B.

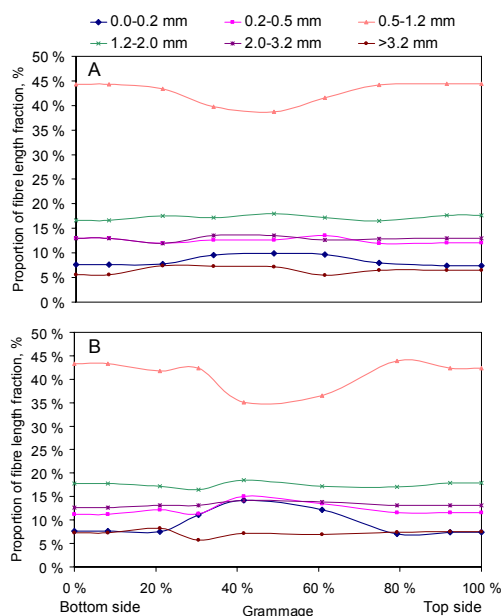


Fig 9. Fibre fraction distributions in the thickness direction of fine paper samples when stratified by (A) 10% TMP (trial point 5) and (B) 20% TMP (trial point 7) in the middle layer of fine paper. The preparation of samples in the thickness direction of the paper was based on the tape stripping technique. The fibre fraction distributions were determined with the L&W FiberMaster STFI fibre quality analyser from the fibre samples released from tape strips.

The addition of TMP into the middle layer by 10 or 20% can be seen as a bend in the curves in the middle layers of the distributions. The increase in the TMP content from 10 to 20% of the total dry weight can be observed as a higher fines content (0.0-0.2 mm) and a decrease in the proportion of fibre 0.5-1.2 mm fraction in the middle layer. The fibre length fraction of 0.0-0.2 mm is considered to be the fines fraction. According to the fines distributions in the thickness direction of the sample, the intermixed layers made up ~10% of the total grammage. In order to prevent delamination of the multilayer sheet structure (e.g. in printing), a certain degree of intermixing between the layers is desirable. These methods can be useful in the adjustment of process parameters of paper and board machines. For example, vacuum levels in the former section can greatly influence the fines and filler distribution and further the end product quality.

New methods were introduced to characterise the distribution of furnishes in the thickness direction of the paper sample. Based on the optical measurements and fibre fraction results for tape strips of layered structures, the development of these methods was found to be relevant and their results repeatable.

### 3 Modification of cellulose and hemicelluloses by enzymatic treatments

The results of the effect of enzymatic treatments on the topochemistry of TMP and bleached hardwood (HW) kraft pulp, and the influence of these changes on the papermaking properties of the fibres, are presented in this section. In addition, the influence of surface chemistry modification on papermaking characteristics is presented here. A detailed description of the methods and results of these treatments can be found in publications I and II.

Enzymes are excellent tools in the pulp and paper research and processes due to their high specificity towards the wood components. The application of enzymes in the pulp and paper industry has been reviewed by Viikari et al. (2009). Among the many potential spheres of utilisation, hydrolytic enzymes have been shown to be very effective in the improvement of the drainage of papermaking furnishes. The positive effect of enzymatic treatments on drainage properties of chemical pulps and thus also the papermaking process and paper quality has been reported by several authors (Mansfield et al. 1996; Moran et al. 1996; Kantelinen et al. 1997; Mooney et al. 1999; Suchy et al. 2009). Only a few studies on the effect of enzymatic treatments on the drainage improvement of mechanical pulps has, however, been reported (Mansfield et al. 1996; Wong et al. 2000). Furthermore, the influence of specific wood carbohydrates, cellulose and hemicelluloses, on the dewatering characteristics of pulp through a whole paper machine is not entirely understood. The influence of surface chemical properties of fibre on water removal in the wet pressing or drying section has received only little research. An interesting hypothesis is that the modification of hemicelluloses between cellulose fibrils and mainly amorphous cellulose of fibrils may open the fibre structure such a way that water removal would be enhanced. Galactoglucomannan (GGM) and especially its galactose side units attached to mannose has been reported to influence the partial water solubility of galactoglucomannan and thus the formation of a gel layer on the surface of the fibre (Thornton et al. 1994; Pere et al. 2000). Modification of this colloidal polysaccharide layer on the surfaces of fibres could also affect the initial wet web strength, shrinkage and end product quality (Myllytie 2009). The number of publications related to the role of surface carbohydrates of the fibre in the initial wet web strength, and runnability of the paper machine is limited (Pommier et al. 1990; Caram et al. 1996). In general, a deeper understanding of the role of specific carbohydrates in paper production can be utilised in pulp and paper mills in order to enhance the cost efficiency of paper production.

In this thesis, the effect of a partial enzymatic removal of cellulose and hemicelluloses (GGM and xylan) from TMP and bleached birch chemical pulp was elucidated in terms of dewatering and other papermaking properties. Purified cellulases (endoglucanases, EGs) and hemicellulases (xylanase and mannanase) originating from fungus *Trichoderma reesei* and their mixtures, as well as two commercial cellulase preparations (specified in section 2.2) were applied. The effects of purified *Trichoderma reesei* cellulases on the fibre strength properties of chemical and mechanical pulps has previously been reported in several papers (Pere et al. 1995; Pere et al. 2000; Suurnäkki et al. 2000). The commercial enzyme 1 consisted of both cellulase (EG) and hemicellulase activities. The commercial enzyme 2 was a monocomponent cellulase, classified as endoglucanase type V (Liu et al. 2009). All used enzymes besides the purified xylanase had a cellulose binding domain (CBD). According to the literature, the presence of CBD in *T. reesei* endoglucanases influence the cellulose hydrolysis level but not the mode or site of action and technical effects of the enzymes on the bleached kraft pulp (Suurnäkki et al. 2000). However, the influence of CBD in the endoglucanases on the enzymatic hydrolysis in the case of mechanical pulps has not been widely explored.

The mechanism of enzyme-aided dewatering of mechanical pulp and chemical pulp was clarified by studying the correlation between the amount, type and location of carbohydrates modified by the hydrolytic enzymes and the dewatering properties of enzymatically modified TMP and bleached chemical/kraft birch pulp.

### 3.1 Influence of enzyme treatment on the chemical composition of fibre

The influence of enzymatic modification on the chemical composition of the TMP and bleached kraft pulp fibres was evaluated based on the analysis of carbohydrates solubilized from the pulps by HPLC and handsheet surface chemistry analysis by ESCA analysis (see section 2.2). The extent of enzymatic modification of pulps was varied by the enzyme dosage and treatment time.

In publication I, the chemical composition of TMP was varied by purified enzymes and commercial enzyme preparations. *Table 5* presents the composition of solubilised carbohydrates. According to the results of solubilised carbohydrates, EG I and EG II attacked both cellulose and galactoglucomannan, GGM, of the pulp. Interestingly, GGM was the most readily hydrolysed component in the pulp in the beginning of the *T. reesei* EG treatments. Mannanase degraded most of the mannan but only a little glucose, whereas xylanase was found to specifically hydrolyse xylan (arabinoglucuronoxylan) in the fibre. The mixture containing mannanase and xylanase solubilised mainly the mannan and xylan parts of the fibre as expected. Besides glucose commercial endoglucanase, enzyme 1 was found to also degrade hemicellulose parts (mannan and xylan) of the fibre. On the contrary, commercial enzyme 2 had high specificity for glucose according to *Table 5*.

Table 5. Carbohydrates solubilised as determined by HPLC analysis from TMP in treatments with purified *T. reesei* cellulases and hemicellulases and with commercial enzyme preparations 1 and 2 (see section 2.2). Standard treatment conditions were (50°C, 2 h, 5 h\* or 24 h\*\*). EG I = endoglucanase I, EG II = endoglucanase II, MAN=mannanase, XYL=xylanase. Percentages are based on own dry weight.

Enzyme	Dosage (mg g <sup>-1</sup> )	Σ of solubil. CH (%)	Composition of solubilised carbohydrates (CH)					
			Glc (%)	Man (%)	Gal (%)	Xyl (%)	Ara (%)	MeGlcA (%)
EGI	0.01	0.23	0.07	0.12	0.01	0.02	0.01	0
	0.05	0.44	0.16	0.20	0.01	0.04	0.02	0.01
	0.1	0.56	0.23	0.23	0.01	0.06	0.02	0.01
	0.5*	1.39	0.67	0.47	0.03	0.17	0.02	0.03
EGII	0.01	0.07	0.01	0.04	0	0.01	0.01	0
	0.05	0.17	0.06	0.10	0	0.01	0	0
	0.1	0.33	0.11	0.19	0.01	0.01	0.01	0
	0.5*	1.27	0.72	0.52	0.03	0	0	0
	0.5**	1.31	0.73	0.52	0.03	0.03	0.01	0
MAN	0.01	0.25	0.05	0.19	0.01	0	0	0
	0.05	0.64	0.13	0.48	0.03	0	0	0
	0.1	0.74	0.15	0.55	0.03	0	0.01	0
	0.5*	1.04	0.23	0.76	0.05	0	0	0
XYL	0.01	0.34	0	0	0	0.27	0.03	0.04
	0.05	0.57	0	0	0	0.45	0.05	0.07
	0.1	0.62	0	0	0	0.50	0.06	0.08
	0.5*	1.02	0	0.02	0	0.80	0.08	0.12
XYL+MAN	0.1+0.1	1.28	0.15	0.56	0.03	0.43	0.05	0.06
	0.1+0.1**	1.50	0.15	0.50	0.04	0.64	0.06	0.11
Commercial enzyme 1	0.5	1.01	0.52	0.30	0.01	0.14	0.03	0
	0.5**	1.88	0.94	0.43	0.03	0.37	0.05	0.06
Commercial enzyme 2	0.5	0.43	0.38	0.05	0	0	0	0
	0.5**	0.81	0.67	0.11	0.01	0.02	0	0

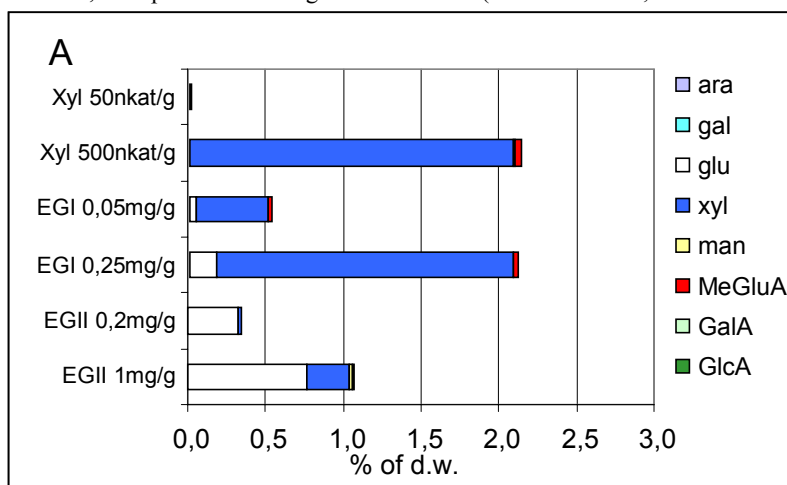
An increase in aliphatic carbon bonds (C-C), indicating an exposure of lignin and/or extractives on the pulp surfaces, was observed in EG II and commercial enzyme 1 treated TMP handsheet samples by ESCA (*Table 6*). A decrease in the content of carbon-oxygen (C-O) bonds, indicating the reduction of carbohydrates on the pulp surfaces, was clearly observed only in a commercial enzyme 1 treated sample having also the highest level of hydrolysis, 1.9% on the d.w. of pulp (*Table 5*). Treatment of TMP with commercial enzyme 2 as such or together with mannanase resulted in a reduction in aliphatic carbon-containing structures and an increase in C-O bond related to carbohydrates analysed from the handsheet outermost surface (*Table 6*). The limited hydrolysis of cellulose and GGM from TMP with commercial enzyme 2 (*Table 5*) seems therefore to expose fibre surfaces with a higher carbohydrate content probably by removal of lignin and/or extractives from the fibre surface. The

combined xylanase-mannanase treatment had minor effect on the carbohydrate or aromatic group or aliphatic carbon coverage of the pulp surfaces (*Table 6*). Both commercial enzyme 1 and combined xylanase-mannanase treatments, removing uronic acid containing xylan from the pulp, clearly reduced, however, the carboxylic acid content of the fibre surface.

Table 6. ESCA analysis of the handsheets prepared from TMP samples treated with various purified and commercial enzyme preparations 1 and 2 (std. treatment conditions). The units in ESCA analysis indicate the relative amount of carbons in different oxidation levels (rel. % of C).

Enzyme treatment of TMP		Data of ESCA analysis			
Enzyme	Dosage, time	C-C	C-O	C=O	O-C=O
-	24 h	44.0±0.1	44.4±0.4	8.6±0.4	3.1±0.1
EG II	0.5 mg g <sup>-1</sup> , 24 h	45.4±0.7	44.0±0.6	8.1±0.3	2.5±0.3
Enzyme 1	0.5 mg g <sup>-1</sup> , 24 h	47.2±0.5	43.1±0.3	7.8±0.2	2.0±0
Enzyme 2	0.5 mg g <sup>-1</sup> , 2 h	40.4±0.5	48.0±0.3	9.0±0.1	2.7±0.2
Enzyme 2	0.5 mg g <sup>-1</sup> , 24 h	38.0±0.5	50.5±0.4	8.9±0.2	2.5±0.2
Enzyme 2 + MAN	0.5 + 0.01 mg g <sup>-1</sup> 2 h	40.7±0.5	47.9±0.2	8.9±0.2	2.5±0
MAN	0.01 mg g <sup>-1</sup> , 2h	43.1±0.2	45.6±0.4	8.9±0.3	2.5±0.3
XYL+MAN	0.1+0.1 mg g <sup>-1</sup> , 24h	45.0±0.9	45.2±0.5	7.8±0.2	2.0±0.2

Publication II explored the effects of enzymatic modification of bleached chemical birch kraft pulp. The carbohydrates dissolved in the laboratory pulp treatments are shown in *Fig. 10A* and *10b*. In the pulp treatments, purified *T. reesei* endoglucanases and xylanase were utilised for the partial hydrolysis of the pulp. According to the analysis of solubilized carbohydrates, xylanase treatment was found to be very specific for pulp glucuronoxylan whereas EG I and EG II hydrolysed both xylan and cellulose of the fibre. Treatment of hardwood pulp with EGII was found to be much more specific for glucose than EGI, as expected according to the literature (Pere et al. 1995; Suurnäkki et al. 2000).



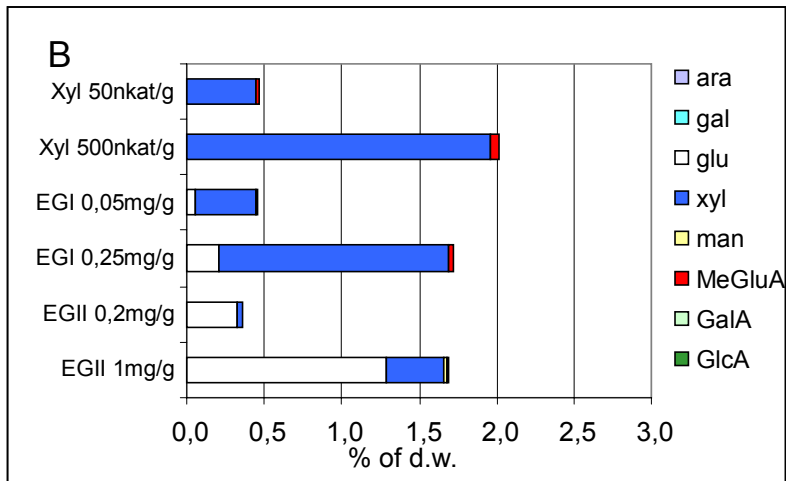


Fig 10. Composition and amount of dissolved sugars released in the enzymatic treatment with purified *T. reesei* cellulases and hemicellulases of (A) unrefined and (B) refined bleached kraft birch pulp, as analysed by HPLC. Pulp refined with an LR40 laboratory refiner with a low intensity of 0.3 J/m to 80 kWh/t energy level. Explanation for enzyme abbreviations: EG I = endoglucanase I, EG II = endoglucanase II, MAN=mannanase, XYL=xylanase. Explanation for dissolved substances: Ara = arabinose, Gal = galactose, Glu = glucose, Xyl = xylose, man = mannose, MeGluA = methyl glucuronic acid, GalA = galacturonic acid, GlcA = glucuronic acid. Percentages are based on the o.d. weight.

The influence of enzyme treatment on the degree of polymerisation of the unrefined and refined bleached chemical birch pulp was estimated by measuring the capillary viscosity (Capillary viscosity method T 230 om-99) of the pulp samples (Fig. 11). According to these results, xylanase treatment did not influence the capillary viscosity of the unrefined or refined fibres. The modification of pulp with EG I affected the capillary viscosity only for higher enzyme dosages. Logically, EG II hydrolysing mostly the glucose backbone, radically decreased the capillary viscosity of the pulp. A decrease in the capillary viscosity due to EG I and EG II treatments of chemical pulp has also been reported by Pere et al. (1995).

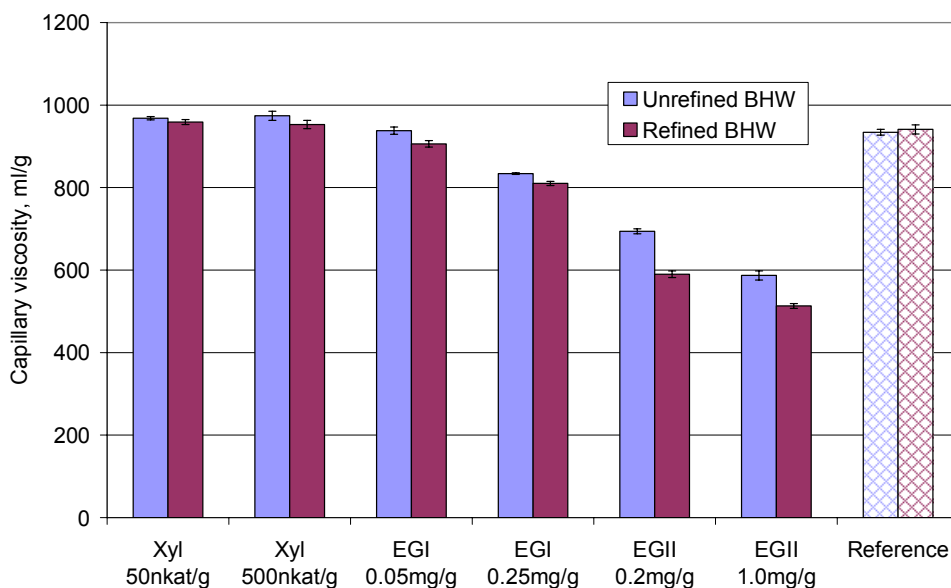


Fig 11. Capillary viscosity of bleached chemical birch pulp samples treated with purified *T. reesei* cellulases and hemicellulase. EG I = endoglucanase I, EG II = endoglucanase II, XYL=xylanase. Capillary viscosity method T 230 om-99. Error bars show a 95% confidence interval of the mean of the measurement.

According to the fibre dimension analysis (FiberMaster), the applied enzymatic treatments did not significantly influence the fibre length, width or fines content of chemical birch pulp. However, a slight increase in fibre bendability was observed due to extensive enzymatic modification of unrefined bleached birch kraft pulp (Fig. 12).

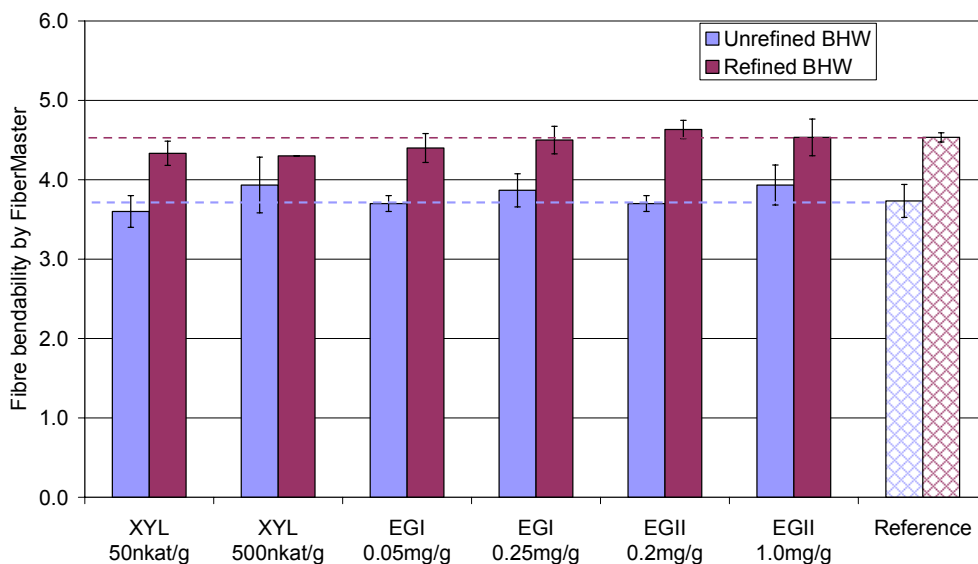


Fig 12. Fibre bendability as determined by FiberMaster of bleached kraft birch pulp samples treated with purified *T. reesei* cellulases and hemicellulase. EG I = endoglucanase I, EG II = endoglucanase II, XYL=xylanase. Error bars show the 95% confidence interval of the mean of the measurement.

### 3.2 Drainage properties

In publication I, the effects of the specific and partial enzymatic removal of carbohydrates from TMP on the water removal properties were evaluated by plotting the freeness values of enzymatically modified TMP against the amount of carbohydrates solubilised (Fig. 13).

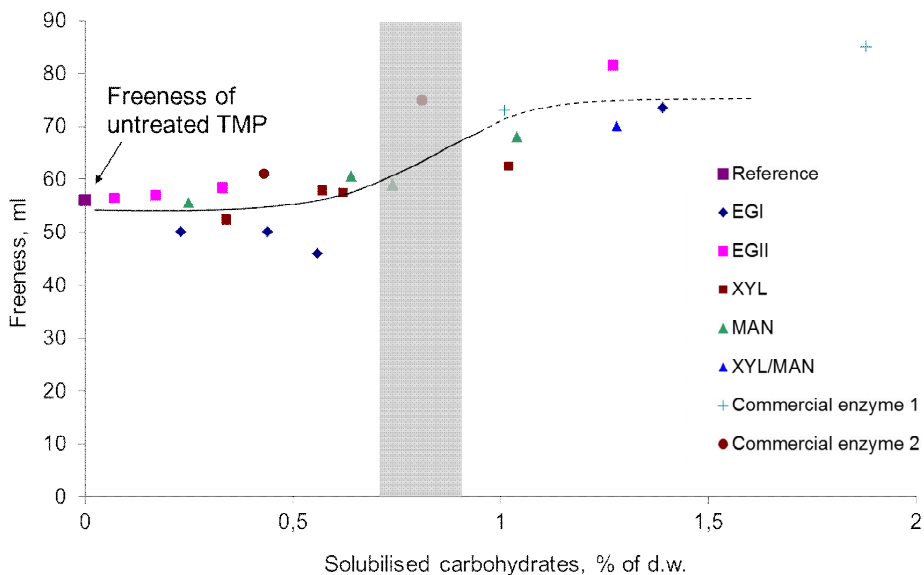


Fig 13. Freeness vs. the amount of carbohydrates solubilised in the enzyme-treated TMP. Enzymatic treatments are explained in section 2.2. Reference = treatment without enzyme, EG I = endoglucanase I, EG II = endoglucanase II, MAN=mannanase, XYL=xylanase, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476.

As can be seen from *Fig. 13*, to elevate the freeness value of the pulp significantly, i.e. by 10 units or more, carbohydrate solubilisation of 1% or more of the pulp dry weight was needed. EG II treatment resulted in a greater improvement of freeness than EG I treatment did. This result indicates that modification of mainly cellulose and GGM of the pulp by EGII increases the drainage rate of TMP more than the combined modification of cellulose, GGM and xylan of the fibre with EGI. The freeness value of TMP was also higher after treatment with mannanase than with xylanase or after a combined xylanase-mannanase treatment. Obviously, partial removal of xylan from TMP was not beneficial to the freeness improvement. TMP treated extensively with either of the commercial enzyme preparations had more than 15% higher freeness values than the reference TMP. The commercial monocomponent cellulase of EGV type, named here as commercial enzyme 2, was found to effectively increase the freeness value of TMP in particular. Drainage results are supported by the results of other authors: for mechanical pulps (Mansfield et al. 1996; Wong et al. 2000) and recycled pulps (Pommier et al. 1989; Stork et al. 1996; Nagarajan, Sarkar 1996; Caram et al. 1996). Also, better drainage has been observed in the paper machine after enzymatic treatments.

In publication II, the effect of carbohydrate modification on the laboratory-measured dewatering characteristics of bleached chemical birch pulps was measured (*Table 7*).

Table 7. Canadian Standard Freeness (CSF) values of refined and unrefined bleached kraft birch pulp after enzymatic treatments. Explanation for abbreviations: Reference = treatment without enzyme, Xyl = xylanase, EGI = endoglucanase I, EGII = endoglucanase II. The enzyme dosage unit is nkat/g (activity)/g (pulp) or mg (protein)/g (pulp).

Pulp treatment	CSF	
	Unrefined	Refined
Reference	580	370
Xyl, 50 nkat/g	590	365
Xyl, 500 nkat/g	595	380
EGI, 0.05 mg/g	560	390
EGI, 0.25 mg/g	615	470
EGII, 0.2 mg/g	535	435
EGII, 1 mg/g	565	455

Hydrolysis of cellulose by EG II had a different effect on the unrefined than on the refined chemical pulps: dewatering of the unrefined pulp was deteriorated whereas dewatering of the fibrillated (refined) pulp was improved (*Table 7*). Results indicate that refining improves the accessibility of carbohydrates to the enzymes. When xylan together with cellulose was hydrolysed extensively by EG I, the highest increase of CSF was detected. Under the conditions used, EG I acted more as a xylanase than a cellulase, as described earlier (Surnäkki 2000). Modifying only the surface xylan of the fibre cell wall with xylanase had only minor effects on CSF, for both the unrefined and refined pulps. This result is also supported by other authors (Blomstedt et al. 2010). A drainage improvement of up to 26% measured as an SR value with highly refined chemical pulps modified by various enzymatic treatments has also been reported by other authors (Kantelinen 1997; Mooney et al. 1999; Mansfield et al. 1996; Moran 1996).

Enzyme mixtures containing cellulases and hemicellulases have been reported to affect dewatering of different types of pulp by the hydrolysis of fines, resulting in a reduced surface area of the pulp (Richardson et al. 1998) and by modification of the colloidal polysaccharide layer on the fibre surface (Kantelinen et al. 1997; Stork et al. 1995). It has also been suggested that shorter fibres are more susceptible to enzymatic attack than longer ones, as their larger specific surface areas are exposed to the enzymes (Pala et al. 2001). Other effects of enzymatic treatments related to improved drainage are the reduction of fibre fibrillation (Stork et al. 1995), the shortening of damaged fibres, and the swelling of the cell wall of broken fibres (Gruber, Gelbrich 1997).

According to the fibre quality analyser (FiberMaster), no significant changes in the fibre fraction composition of TMP and birch pulp or in the amount of fibrillated fines material of TMP were noticed due to enzymatic treatments. Although small-scale changes may have occurred, they cannot be seen

with the utilised measurement devices. The bendability of the bleached chemical pulp fibre was noted to increase and fibre width to slightly decrease due to enzymatic actions. These results support the findings of other authors (Kantelinen et al. 1997; Stork et al. 1995) who suggested that modification of the colloidal polysaccharide layer can be important for the sake of drainage of the furnish. Galactoglucomannan in TMP was found to be effectively hydrolysed by purified cellulases and mannanase as well as commercial enzymes used (Table 5). Galactose units attached to the main chain in the chemical structure are known to cause partial solubility in water and thus the formation of a gel layer on the fibre surface (Thornton et al. 1994; Pere et al. 2000). The drainage increase was, however, observed only in the samples treated with EG II and commercial enzyme 2 throughout the whole hydrolysis level area tested (Fig. 13). Furthermore, as the inspection of the chemical composition of TMP fibre and fines surface by ESCA (Table 6) indicated that EGII and commercial enzyme 2 modified the accessible pulp surfaces very differently it is suggested that a reduction of the GGM gel layer together with the limited hydrolysis of surface cellulose in the TMP can be beneficial for water removal. In case of bleached chemical birch pulp increase of freeness value was more clearly connected to hydrolysis of cellulose than hemicellulose (xylan) part of the fibre. The result that xylanase treatment of chemical birch pulp has small effect to dewatering (freeness) is also supported by Blomstedt et al. 2010.

It has also been suggested (Myllytie 2009) that this gel layer on the surface of fibre fibrils can influence the strength properties of the wet web and dry paper. However, the importance of specific carbohydrates in this gel layer for interactions between fibres is still not fully understood, particularly in the wet fibre network. In this thesis, the surface gel layer is also assumed to have an important role throughout the entire papermaking process.

### 3.3 Water removal in wet pressing

In publication I, the effect of enzymatic treatment on water removal in wet pressing (laboratory handsheet press by Lorentzen & Wettre) was measured by analysing the dry solids content of TMP handsheets after wet pressing.

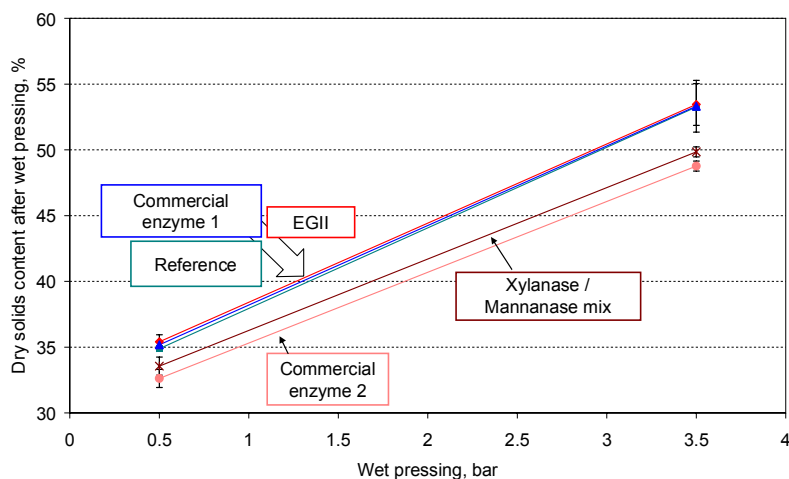


Fig 14. Dry content of enzyme-treated and reference TMP after wet pressing with changing pressure. Treatment dosage and time: 0.5 mg protein/g dry pulp, 24 hrs. Reference = treatment without enzyme, EG II = endoglucanase II. Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476. Error bars show the 95% confidence interval of the mean of the measurement.

TMP treated with commercial enzyme 1 or with EG II gave the same dry solids content after wet pressing as the untreated reference (Fig. 14). The results indicate that combined modification of the cellulose and glucomannan (Table 5) part of the TMP fibre does not significantly influence the dewatering in wet pressing. Degradation of only hemicellulose or cellulose of TMP by a combined xylanase-mannanase treatment or by commercial enzyme 2 treatment, respectively, had a negative effect on dry solids content of the wet pressed handsheets (Fig. 14). This conclusion was supported by the water retention value (WRV) results of enzymatic treated TMP (Fig. 15), where no clear correlation was observed between specific solubilised carbohydrates and WRV. Low WRV of the pulp



is known to improve the dewatering in wet pressing. However, according to literature (Laine, Stenius 1997; Dang 2007) the decrease in acidic groups (carboxylic groups) due to enzyme treatments could have reduced the fibre swelling and further decreased the WRV.

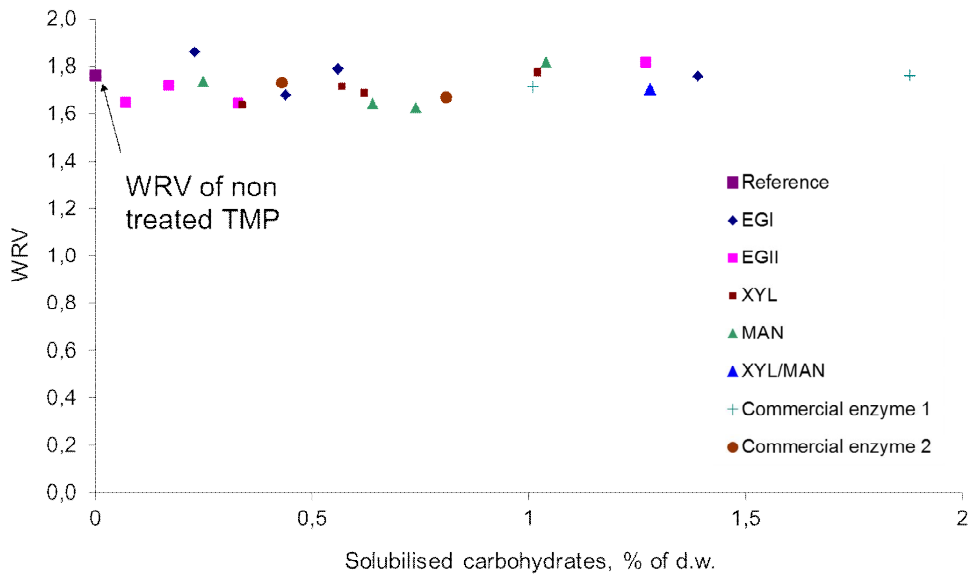


Fig 15. Water Retention Value (WRV) of TMP vs. the amount of carbohydrates solubilised in the enzyme-treated TMP. Enzymatic treatments are explained in section 2.2. Reference = treatment without enzyme, EG I = endoglucanase I, EG II = endoglucanase II, MAN=mannanase, XYL=xylanase, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476.

Solubilisation of cellulose and GGM from the TMP pulp with EG II or commercial enzyme 1 increased, however, the bulk of dry sheets (*Fig. 16*). An increase of dry sheet bulk enables a higher wet pressing load and thus water removal without loss of bulk compared to an untreated reference sample. The bulk of the sheet further affects the opacity and bending stiffness of the paper. At a constant dry sheet bulk treatment with commercial enzyme 1 raised the dry solids content of TMP by 5% after wet pressing compared to an untreated reference. After the wet press section, a 5% higher dry solids content signifies substantial energy savings in the dryer section, as the drying energy can be reduced or alternatively the production capacity increased (Moran 1996). Xylanase-mannanase and commercial enzyme 2 treatments did not increase the dry sheet bulk, thus an increase in the wet pressing loads cannot be realised without loss of dry sheet bulk. Based on these results, it seems that both cellulose and glucomannan need to be partially removed from TMP in order to achieve increase in the dry sheet bulk and improvement of dewatering in the press section.

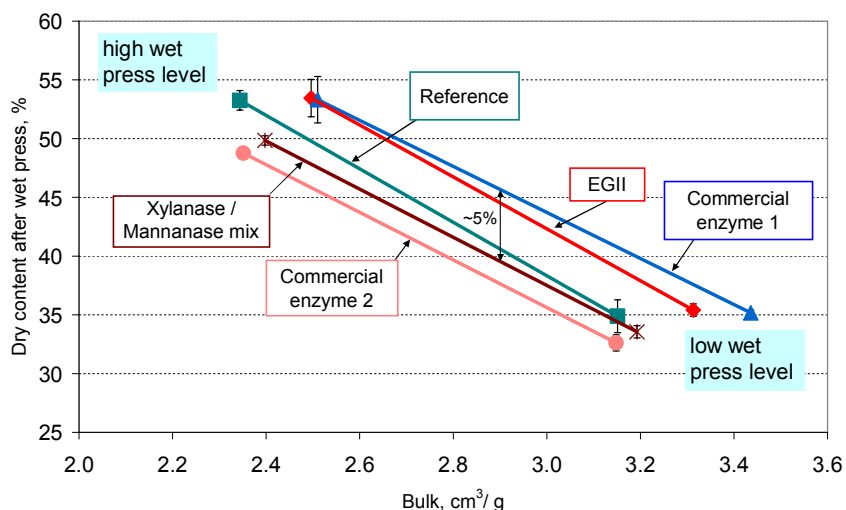


Fig 16. Dry content of enzyme-treated TMP after wet pressing as a function of dry sheet bulk. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 hrs. Reference = treatment without enzyme, EG II = endoglucanase II, Commercial enzyme 1 = Ecoston L900, Commercial enzyme 2 = Novozym 476. Error bars show the 95% confidence interval of the mean of the measurement.

Publication II studied the effect of enzymatic treatment of bleached kraft birch pulp on WRV. The refining of pulp increased WRV from 1.7 to 2.0 g/g. According to the results (Table 8), enzymatic treatment with xylanase or endoglucanases did not affect the WRV of refined chemical birch pulp. On the contrary, modification of unrefined bleached chemical birch pulp with EG I and especially with EG II increased WRV. An explanation for the results can be that enzymatic treatment opens the fibre surface of unrefined pulp, and thus increases the amount of hydroxyl groups that can bind to water. In other words, enzymatic treatment may affect the amount of bonded water in the fibre cell wall. The amount of bonded water in the pulp is further known to be connected to the rate and extent of water removal in wet pressing. In refined pulp, the fibre surface is already open and fibrillated. Therefore, the enzymatic treatment may not significantly influence the amount of hydroxyl groups on the fibre surface.

Table 8. Water Retention Value (WRV) of refined and unrefined bleached chemical birch pulp after enzymatic treatments. Explanation for abbreviations: Reference = treatment without enzyme, Xyl = xylanase, EGI = endoglucanase I, EGII = endoglucanase II. Enzyme dosage unit is nkat/g (activity)/g (pulp) or mg (protein)/g (pulp).

Pulp treatment	WRV	
	Unrefined	Refined
Reference	1,68	1,98
Xyl, 50 nkat/g	1,65	1,96
Xyl, 500 nkat/g	1,68	1,99
EGI, 0.05 mg/g	1,72	1,98
EGI, 0.25 mg/g	1,73	1,95
EGII, 0.2 mg/g	1,76	1,96
EGII, 1 mg/g	1,82	1,95

### 3.4 Initial wet strength properties

Publication I showed that the tension holding ability of the wet TMP sheet was decreased as a result of all the enzyme treatments with a given dry solids content (Fig. 17A). On the other hand, the increased dry solids content after wet pressing with a given dry sheet bulk for EG II and commercial enzyme 1 treated TMP observed (Fig. 16) is expected to enhance the wet paper tension and thus the paper machine runnability. In the case of TMP treated with a mixture of xylanase and mannanase or

commercial enzyme 2, the reduced tension holding ability cannot be compensated by an increased dry content after the wet press without loss of bulk (Fig. 16).

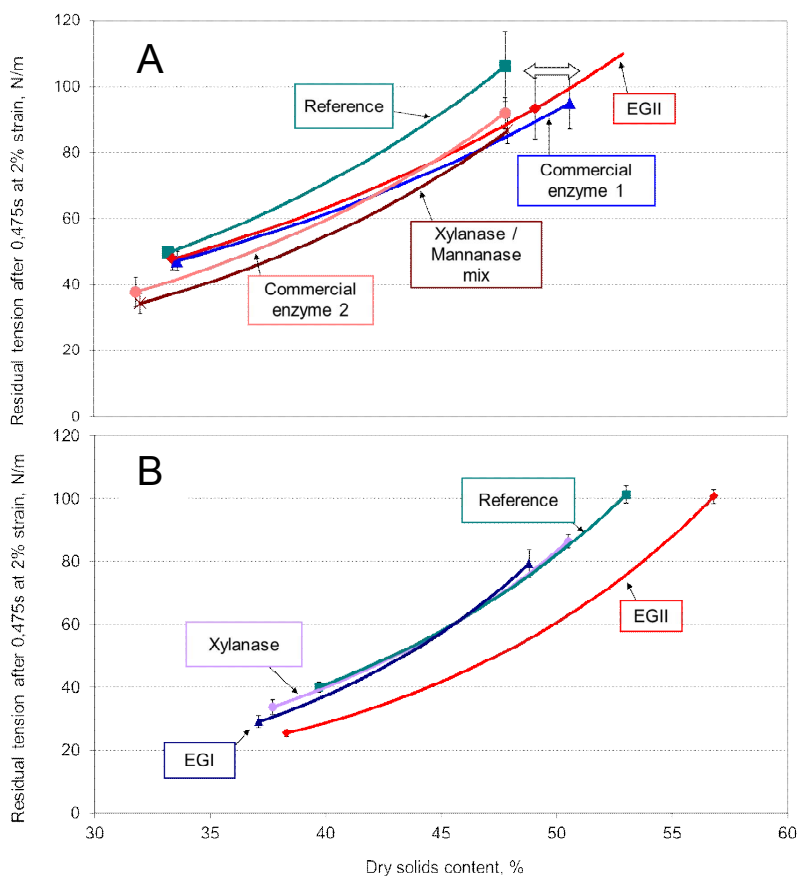


Fig 17. Residual tension of wet web (A) TMP and (B) bleached birch kraft pulp for a given strain as a function of dry solids content. Treatment dosage and time with (A): 0.5 mg protein g<sup>-1</sup> dry pulp, 24 hrs, treatment dosage with (B): EGI 0.25 mg/g pulp, EG II 1.0 mg/g pulp and xylanase 500 nkat/g pulp. Reference = treatment without enzyme, EGI = endoglucanase I, EGII = endoglucanase II, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476. Error bars show the 95% confidence interval of the mean of the measurement.

In publication II, the effects of enzymatic modification of carbohydrates on the tension holding ability of wet handsheets made of bleached kraft birch pulp were explored (Fig. 17B). The composition and amount of dissolved sugars of each enzymatic treatment were revealed by an HPLC analysis (Fig. 10). Substantial hydrolysis of cellulose together with xylan by EG II reduced the tensile strength of wet sheets by 20% for chemical birch pulp. On the contrary, modification of mainly xylan with xylanase or EG I did not significantly affect the residual tension for a fixed dry solids content level.

At a mill scale, the influence of enzymatic treatment on the wet strength of the web has also been observed by Rutledge-Cropsey et al. (1998). It has been reported that an increase of wet web strength in the press section is due to cellulase treatment of recycled paper in a paper mill. This increase of wet web strength may be related to increased solids content of the web. In addition, with dewatering-limited paper machines, up to a 15% increase in the machine speed has been reported due to enzymatic treatments (Caram et al. 1996; Pommier et al. 1990). The results indicate that hydrolysis and thus the diminished adhesive colloidal polysaccharide layer is beneficial to the runnability of the paper machine. Besides hemicellulose (Alinec et al. 2006), amorphous parts of cellulose can also bind to water molecules better than crystalline structures, and thus form a gel layer which can influence the initial wet web strength. It has been reported that amorphous cellulose films can be degraded quite extensively by enzymatic actions (Suchy 2011). It is also possible that enzymes attack defects of TMP

and chemical pulp fibre. Defective areas are likely to be attractive to enzymes due to exposed cellulose and hemicellulose material below the surface lignin. Enzymatic actions are expected to further weaken the defected area of the fibres and increase the amount of kinks in the furnish. A negative effect of fibre deformations on wet web strength has been reported by Kunnari et al. (2007).

In general, a negative influence on the wet strength properties was noticed with both TMP and hardwood pulps when the carbohydrates of the fibres were hydrolysed with enzymes.

### 3.5 Drying characteristics

The influence of enzyme treatment of TMP on the drying time of a paper sheet was studied in Publication I. According to the results, the drying time of wet samples was decreased by approximately 8% due to treatment with the commercial enzyme 1 (Fig. 18A). Combined xylanase and mannanase treatment was found to slightly enhance the drying of TMP sheets.

The effects of modification of carbohydrates on the drying time of laboratory sheets made of chemical hardwood pulp as reported in publication II are shown in Fig. 18B. A decrease in the drying time of a laboratory sheets was observed for EGI and EGII modifications. Drying time decreased 8 to 15% depending on the enzyme type. In the case of chemical pulp, results indicated that modification of the cellulose part of the fibre is a more efficient way of decreasing the drying time than the hydrolysing of xylan. As in the case of TMP, the partial hydrolysis of only xylan in bleached chemical birch pulp did not decrease the drying time of the samples.

On the other hand, the measured drying time depends strongly on the initial dry solids content and drying characteristics such as air temperature and air flow. Therefore, one should consider these results as only preliminary.

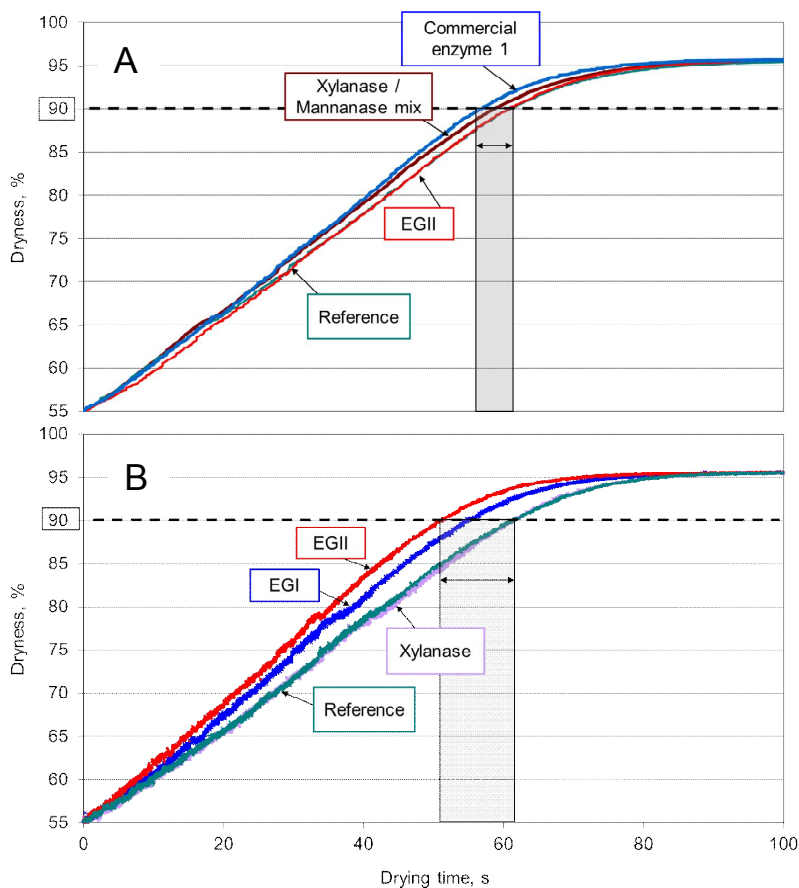


Fig 18. Dryness as a function of drying time of wet sheets made of enzyme-treated (A) TMP and (B) bleached birch kraft pulp. Treatment dosage and time with (A): 0.5 mg protein g<sup>-1</sup> dry pulp, 24 hrs and with (B): EGI 0.25 mg/g pulp, EG II 1.0 mg/g pulp and xylanase 500 nkat/g pulp.. Online IR -measurement of dry content during hot-air drying of wet pressed sheets. Plots are the average results of 8 parallel measurements. Reference = treatment without enzyme, EG I = endoglucanase I, EG II = endoglucanase II, Commercial enzyme 1 = Ecostone L900.

Combination of increased bulk and air permeability of TMP handsheets (*Table 9*) due to commercial enzyme 1 treatment seems to correlate with the improved drying efficiency of the sample. An increase in air permeability can be due to increased porosity and loosening of the cell wall structure as a result of enzymatic treatment.

Table 9. Bulk and air permeability at 0.5 and 3.5 bar wet press levels of paper samples made of enzyme-treated TMP. Samples for shrinkage measurement were wet pressed at a load of 3.5 bar. Treatment dosage and time: 0.5 mg protein/g dry pulp, except with XYL+MAN 0.1 + 0.1 mg protein/g dry pulp, 24 hrs.

TMP treatment	Bulk (m <sup>3</sup> 10 <sup>-3</sup> kg) at		Air permeability (ml min <sup>-1</sup> ) at		Shrinkage, (%)
	0.5 bar	3.5 bar	0.5 bar	3.5 bar	
Reference	3.15	2.34	241 ± 3	77 ± 5	2.3 ± 0.14
EG II	3.31	2.50	433 ± 24	154 ± 9	2.0 ± 0.08
Commercial enzyme 1	3.44	2.51	542 ± 39	190 ± 20	1.8 ± 0.07
Commercial enzyme 2	3.15	2.35	425 ± 26	139 ± 12	2.1 ± 0.04
XYL+MAN	3.19	2.40	267 ± 4	88 ± 3	1.9 ± 0.02

All enzyme treatments of TMP reduced the drying shrinkage of the sheet (*Table 9*). The most pronounced reduction was observed in the handsheets with reduced surface xylan content (commercial enzyme 1 and XYL+MAN, *Table 9*). According to HPLC analysis of dissolved sugars and image analysis based measurement of sheet shrinkage characteristics, reduction of especially surface xylan by a combined xylanase-mannanase mix and by commercial enzyme 1 treatment significantly reduced the shrinkage of laboratory sheets (by 20%). It is known that fibre swelling has an influence on the shrinkage of the fibre network. Fibre charge influences fibre swelling (WRV) (Schönberg et al. 2001) and thus sheet shrinkage; furthermore, the hemicellulose content correlates with the anionicity of the fibre (Stenius et al. 2000; Schönberg et al. 2001). On the other hand, softening of moist hemicelluloses and lignin due to heating in the drier section also changes the fibre morphology and possibly also influences the shrinkage of the fibre network. Softened fibre surfaces may decrease friction between fibres and thus enable fibres to slide in the fibre network, and further influence the dimensional stability (shrinkage) of the paper. Both of these phenomena are supported by the results of ESCA analysis of the handsheets (*Table 6*). The decrease of the COOH groups by removal of anionic surface xylan leading to reduced swelling/shrinkage was observed. Note! In commercial enzyme 1 and XYL-MAN samples aliphatic structures = lignin/extractives exposed AND acidic groups reduced!

### 3.6 Dry sheet properties

The effect of enzymatic treatment of TMP on dry sheet properties was evaluated in Publication I. The combined modification of cellulose and glucomannan in the pulp was found to increase the bulk of handsheets (*Fig. 19*). The partial removal of xylan in addition increased this effect. In the wood fibre cell wall structure, glucomannan is tightly connected to cellulose fibrils while xylan and lignin form the matrix between the fibrils. Therefore, combined partial enzymatic hydrolysis of the cellulose and glucomannan in accessible pulp surfaces may induce an opening of the fibre cell wall (Suurnäkki et al. 1996), which would affect the consolidation of the fibre network during drying. In addition, the hemicelluloses are known to influence the bond strength of fibres in the dry paper (Schönberg et al. 2001). Removal of carboxylic groups from hemicelluloses, due to enzyme treatments, decreases fibre swelling (Laine, Stenius 1997; Deng 2007) and thus reduces the shrinkage of the fibre and finally increases the bulk of the sheet. Typically, high shrinkage forces during drying in the in-plane and out of plane direction of paper are related to high dry strength of the paper. Shrinkage in planar directions can be mainly prevented in the paper machine. However, shrinkage in the thickness direction cannot be controlled without losses in dewatering rate in wet pressing and in strength properties of paper. Modification of merely hemicelluloses or cellulose did not affect to bulk of the sheet (*Fig. 19*).

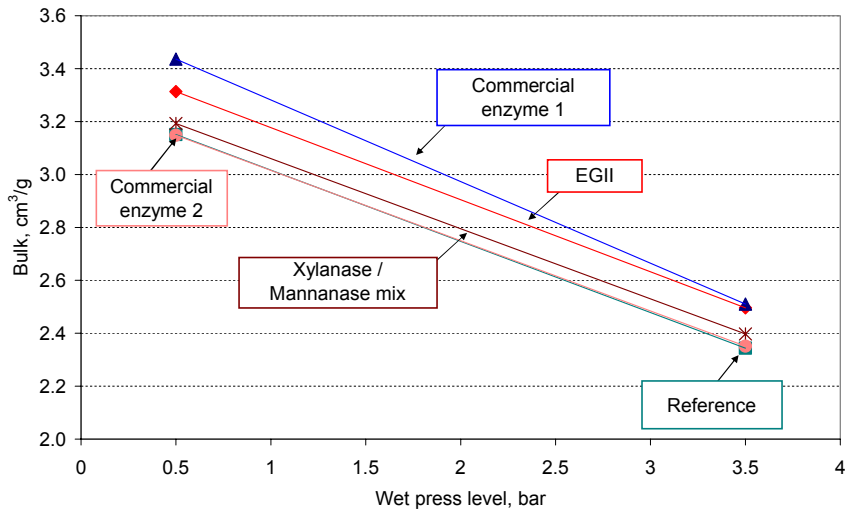


Fig 19. Bulk of sheets made of enzyme-treated TMP as a function of the wet pressing load (Wet press loads, 0.5 bar and 3.5 bar). Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h. Reference = treatment without enzyme, EGII = endoglucanase II, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476.

Figure 20 shows dry sheet bulk values for enzyme-treated unrefined and refined bleached chemical pulp (Publication II). Contrary to TMP (Fig. 19), endoglucanase treatment (EG I and EG II) of unrefined bleached chemical birch pulp decreased the bulk of the sheet. A slight increase in the bulk of the sheet was observed when unrefined BHW was modified with xylanase. The effects of all enzyme treatments on handsheets made of refined BHW were modest. The increase in sheet density due to endoglucanase I or II treatment of chemical pulp has been reported by Pere et al. (1995). As an explanation, it has been suggested that enzymatic treatment weakens the fibre cell wall so that it collapses more easily during drying than an untreated fibre cell wall (Pere et al. 1995). The huge drop in the capillary viscosity (Fig. 11) with EG I and especially with EG II treated pulp samples supports the theory. Capillary viscosity is related to the degree of polymerisation of glucose chains, which further correlates with the strength of the fibre.

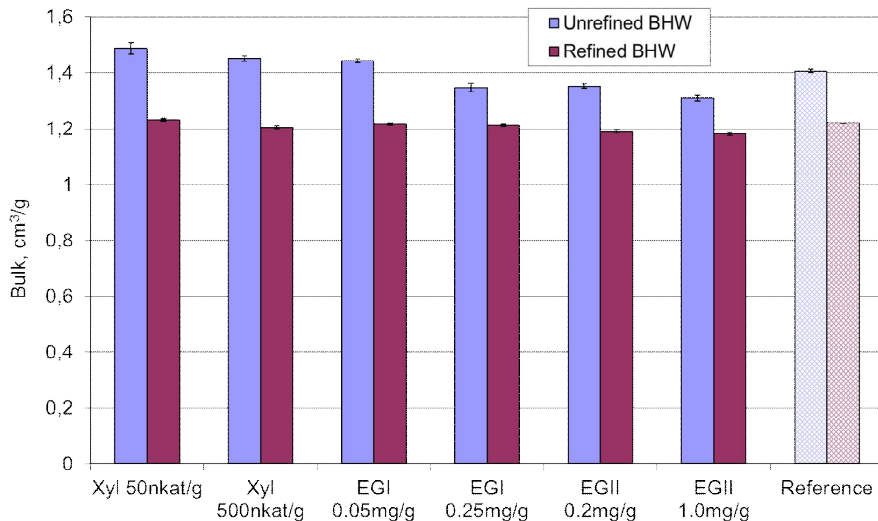


Fig 20. Bulk of sheets made of enzyme-treated bleached chemical birch pulp (wet press load 3.5 bar). Reference = treatment without enzyme, Xyl = xylanase, EGI = endoglucanase I, EGII = endoglucanase II, BHW = bleached hardwood pulp. Error bars show the 95% confidence interval of the mean of the measurement.

According to air permeability measurements of TMP sheets, modification of the cellulose parts alone or combined with hemicellulose degradation, increased the air permeability (Fig. 21). XYL+MAN treatment of TMP gave same air permeability as reference.

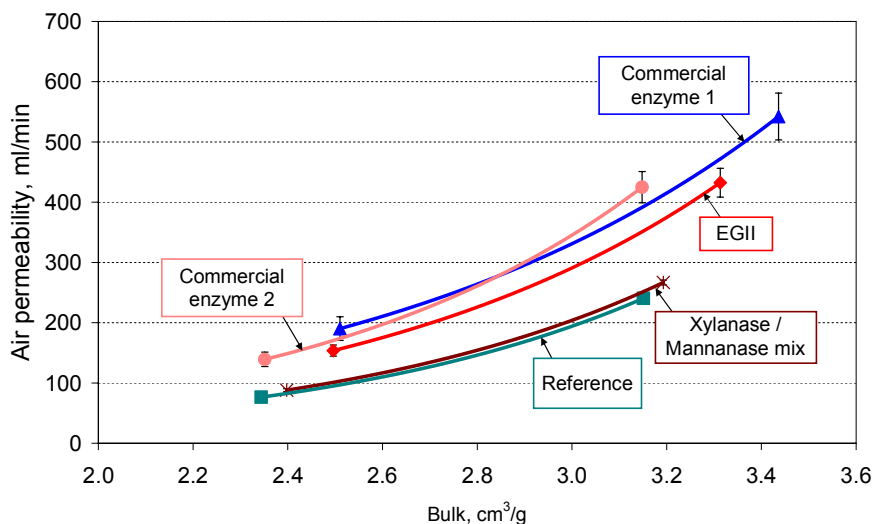


Fig 21. Air permeability (by Lorentzen & Wettre) of sheets made of enzyme-treated TMP as a function of dry sheet bulk. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h. Reference = treatment without enzyme, EGII = endoglucanase II, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476. Error bars show the 95% confidence interval of the mean of the measured values.

The results of air penetration resistance for handsheets made of enzyme-treated unrefined bleached chemical birch pulp (publication II) are shown in Fig. 22. Endoglucanase treatment reduced the resistance whereas xylanase treatment had no effect on it or even increased it. This result is supported by the results of Pere et al. (1995), where endoglucanase treatments (EG I and EG II) was observed to increase the sheet density and to increase the resistance. As in the case of increased sheet density, an explanation for this result has been suggested to be that endoglucanase treatment hydrolyses the cell wall and induce a denser structure, which further influences the air penetration resistance of the paper (Pere et al. 1995).

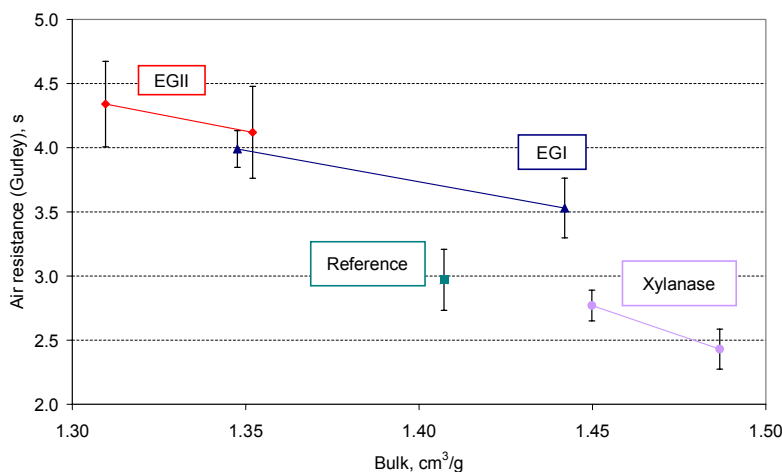


Fig 22. Air resistance (Gurley) of sheets made of enzyme-treated unrefined bleached chemical birch pulp as a function of dry sheet bulk. Reference = treatment without enzyme, EGI = endoglucanase I, EGII = endoglucanase II, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476 (linear fit is used to describe the effect of bulk). Error bars show the 95% confidence interval of the mean of the measurement.

In Publication I hydrolysis of the cellulose or hemicellulose part of TMP fibre reduced the tensile index by 10 - 20% or 20 - 30%, respectively (Fig. 23A). However, the influence of hydrolysis of the cellulose part of the fibre on Scott Bond (Fig. 23C) was limited (- 10%), while the modification of hemicelluloses induced a substantial decrease in Scott Bond. The z-directional strength measurement is known to correlate strongly with bond strengths of fibre-fibre contacts, whereas the in-plane strength properties are also influenced by many other fibre characteristics such as fibre strength, length and shape.

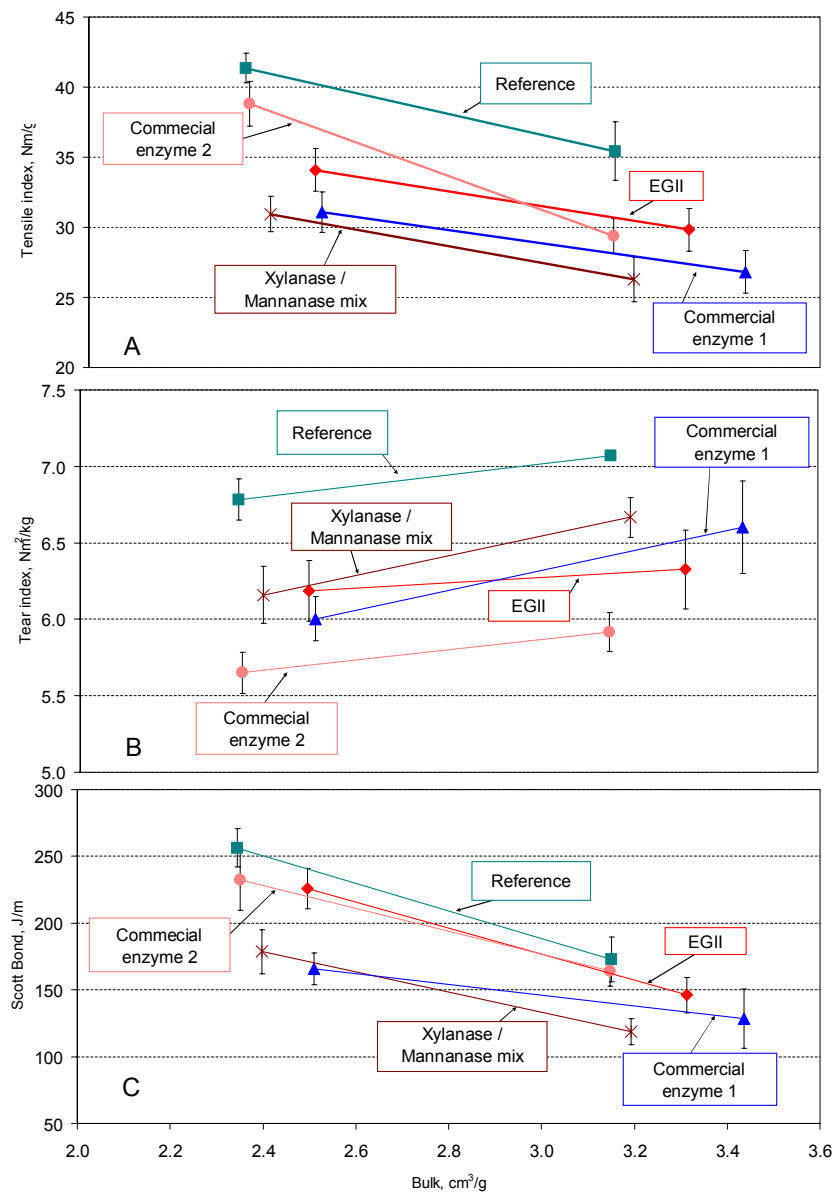


Fig 23. (A) Tensile index, (B) tear index and (C) Scott Bond of sheets made of enzyme-treated TMP as a function of dry sheet bulk. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 hrs, Reference = treatment without enzyme, EGII = endoglucanase II, Commercial enzyme 1 = Ecostone L900, Commercial enzyme 2 = Novozym 476, (linear fit is used to describe the effect of bulk). Error bars show the 95% confidence interval of the mean of the measurement.



Of the hemicellulose structure in wood, GGM when having high enough side group substitution is prone for solubilisation in water (Thornton et al. 1995; Pere et al. 2000). Thus, a colloidal polysaccharide layer that acts like glue between fibres can be formed on the surface of GGM containing fibres. The importance of the colloidal polysaccharide layer for dry strength properties has been emphasised by Myllytie (2009). The fact that the commercial enzyme 2 treatment was found to remove lignin and/or extractives from the TMP fibre surface without removing acidic xylan (ESCA analysis, Table 6), could be the reason for the highest tensile index in this case of the samples. Partial removal of lignin exposes carbohydrates with hydroxyl groups, thus improving the bonding ability of the fibre and ultimately the tensile strength of the paper. Interestingly, the commercial enzyme 2 treatment resulted in the lowest tear index (Fig. 23B) of the samples. These results indicate that by partial hydrolysis of cellulose resulting in lower surface coverage of lignin and/or extractives, fibre strength is also substantially decreased. Modification of TMP hemicelluloses did not influence the tear strength as much as degradation of the cellulose, which supports the hypothesis that hemicelluloses mainly affect the bond strength of fibre-fibre contacts and less the fibre strength.

In the case of bleached chemical birch pulp (publication II), endoglucanase treatments (EGI and EGII) increased the sheet smoothness at a fixed freeness level (24A). This result may be connected to increased fibre flexibility due to enzymatic treatment. Further, it indicates that by enzymatic treatments also refining of the hardwood pulp could be decreased, resulting in savings in the energy consumption. Also, treatments could alternatively be utilised to improve the drainage of highly refined birch pulp by cellulase without significant loss in the tensile index (Fig. 24B) and roughness.

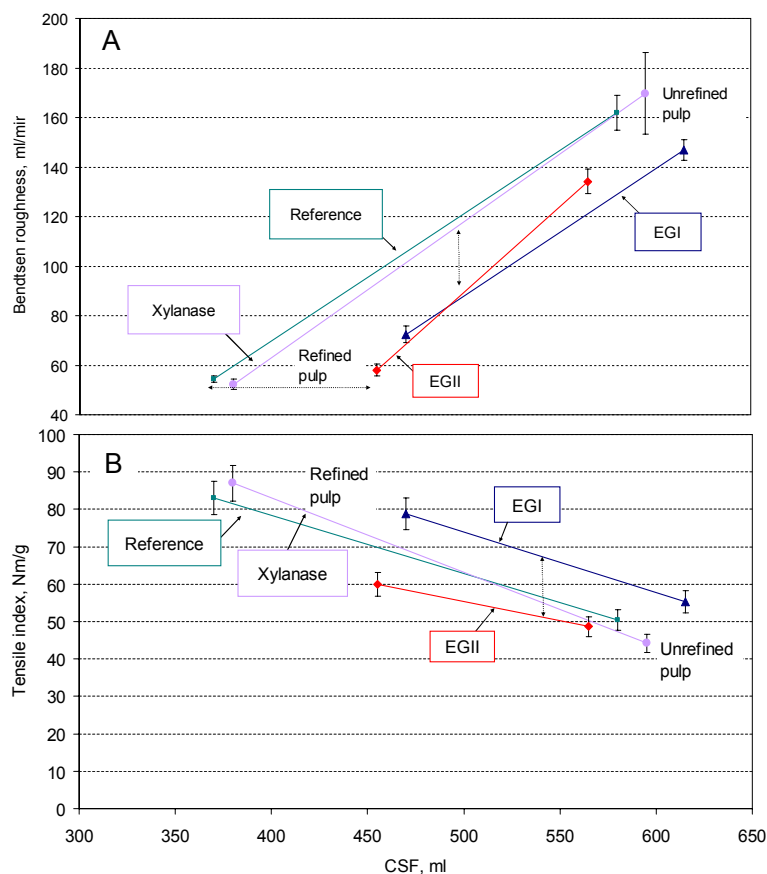


Fig 24. (A) Bendtsen roughness and (B) tensile index of sheets made of enzyme-treated bleached chemical birch pulp as a function of Canadian Standard Freeness (CSF). Reference = treatment without enzyme, EGI = endoglucanase I (dosage 0.25 mg protein/g pulp), EGII = endoglucanase II (dosage 1.0 mg protein/g pulp), xylanase dosage 500 nkat/g (linear fit is used to describe the effect of bulk). Error bars show the 95% confidence interval of the mean of the measurement.

Enzymes are also expected to attack surface areas where cellulose and hemicellulose are exposed, and defect areas, kinks and dislocations in TMP fibres are therefore attractive to enzymes. Fibre deformations are reported to decrease the dry strength properties of the sheet (Kunnari et al. 2007). Enzymatic modification of these weak areas further decreases the fibre and finally the sheet strength properties.

### 3.7 Summary

In the tables we show the effect of various enzymatic treatments with purified enzymes and two commercial enzyme preparations on papermaking characteristics and properties of sheets made of TMP and BHW kraft pulp.

In order to increase the freeness value of TMP, the solubilisation of approximately 1% of carbohydrates was needed. Partial hydrolysis of the cellulose of the pulp was found to increase the initial dewatering of TMP more than modification of the hemicelluloses. The most beneficial for dewatering was the combined partial hydrolysis of cellulose and GGM in TMP. In the case of bleached hardwood kraft pulp, freeness was increased substantially by modification of cellulose or additionally by combined modification of cellulose and xylan of the fibre. Results indicate that energy savings could be achieved in the forming section of the paper machine by the introduction of enzymatic treatments of TMP and chemical hardwood pulp.

Clear evidence of improved dewatering in wet pressing due to enzymatic treatments was not observed. However, dry sheet bulk was increased due to specific enzyme treatments of TMP. The increase of bulk enables higher wet pressing loads and thus increased dry solids content of the web after wet pressing in the paper machine without deterioration of paper properties (bending stiffness and opacity). The dry solids content of TMP sheets increased by 5% after wet pressing for a given dry sheet bulk as a result of commercial enzyme I and EGII treatments. It was concluded that both the cellulose and glucomannan of the fibre had to be modified in order to increase the dry solids content after wet pressing of sheets made of TMP based furnish. Also, removal of the carboxylic groups was found to be related to the increase of the bulk of the TMP sheet. Contrary to the TMP results, enzymatic treatment of unrefined chemical hardwood pulp with endoglucanases decreased the bulk of the sheets. The increase in sheet density due to enzymatic treatments was observed to contribute to improved smoothness of sheets made of unrefined chemical pulp. The more pronounced cell wall collapse in chemical pulp due to cellulase treatment may explain the decrease in the sheet bulk. Mechanical pulp fibres are covered with lignin, which makes the fibre cell wall stiffer than in the chemical pulp fibre, thus in TMP the fibre cell wall is not easily collapsed due to enzymatic actions. The increase in the bulk of the sheets made of TMP can be related to their decreased shrinkage during drying as the colloidal polysaccharide layer on the fibre surface is modified by enzymes. ESCA analysis of the samples supports this hypothesis as the commercial enzyme I treatment was found to increase the surface coverage of the TMP fibres with lignin and/or extractives, which further reduces the shrinkage tendency of the wet sample during drying. In addition, the increased initial dewatering due to endoglucanase treatment of TMP can affect the consolidation of the fibre network and further the bulk of the sheet.

The tension holding ability of the wet web was reduced as a result of a both cellulase and hemicellulase treatment of TMP and chemical birch pulp. An explanation for the decreased wet strength properties can be a reduced colloidal polysaccharide layer on the fibre surface due to enzymatic actions. This gel layer influences the adhesive forces between fibres and further the wet strength properties of the web. But then, enzymatic treatment of TMP (but not of chemical pulp) with commercial enzyme I and EGII increased the dry solids content after wet pressing of the sheet for a fixed dry sheet bulk. Increased dry solids content enhanced the wet web strength due to an increase in the friction between fibres as (fibres were closer to each other). Increased dry solids content also induces an increase in the surface tension of water, keeping fibres together under the mechanical stress of the wet web. Indications of an increased drying rate were observed in sheets made of both TMP and chemical birch pulp which had been treated with enzymes. Modification of the cellulose part of the fibre in particular can be important for the increase in the drying rate. Increased air permeability of the sheets due to enzymatic treatments may be related to enhanced drying rate with impingement drying. The effect of enzymatic treatments on the drying rate can be different in conventional cylinder drying of the paper than in impingement drying.

Dry sheet strength properties were decreased due to hydrolysis of all carbohydrates in sheets made of TMP and BHW. Degradation of the colloidal polysaccharide layer on the fibre surface is assumed

to not be beneficial for the dry strength properties of the paper. This gel layer consists of amorphous cellulose and hemicelluloses that are able to bind water molecules. Removal of anionic water binding groups from hemicellulose due enzyme treatments, especially carboxylic groups, probably decreases the thickness of this gel layer thickness on the surface of the fibre. Based on the strength results for the TMP sheets, it was concluded that degradation of the hemicelluloses influences mostly on the bond strength of inter-fibre contacts, but not so much the fibre strength. On the contrary, dissolving the cellulosic part of the fibre cell wall will contribute to the deteriorated fibre strength properties of TMP. However, hydrolysis of cellulose part of unrefined BHW with enzymes could provide interesting possibility to remove or decrease refining process in order to achieve adequate surface and strength criteria without deterioration in the drainage of the furnish. A graphical representation of the findings can be found in *Table 10*.

Table 10. Effects of various enzymatic treatments on some papermaking characteristics and paper properties for bleached birch kraft pulp and TMP pulp. Treatment dosage for TMP: 0.5 mg protein/g of dry pulp, Treatment time: 24 hrs. Xyl/Man = xylanase and mannanase mixture. EGII = endoglucanase II. Explanation of signs: ↑ increase, ↓ decrease and — no change in the measured value. The nature of changes is colour coded such that green is positive, red is negative and gray is positive or negative change.

		Unrefined bleached chemical birch pulp					
		Xyl 50nkat/g	Xyl 500nkat/g	EGII 0.05mg/g	EGII 0.25mg/g	EGII 0.2 mg/g	EGII 1.0mg/g
Pulp	CSF	↑	↑	↓↓	↑↑	↓↓↓	↑↓
	WRV	—	—	↑	↑↑	↑↑	—
	Capillary viscosity	—	—	↓	↓↓	↓↓↓	↓↓↓
	Fibre bendability	—	↑	—	↑	—	↑↑
Dry sheet	Density	↓↓	↓	↓	↑↑	↑↑	↑↑↑
	Air permeability	↑↑	↑	↓	↑↓	↑↑	↑↓
	Roughness	↑↑	↑↓	↓	↑	↑	↑↓
	Tensile strength	↓↓↓	—	↓	↑↑	↑	↑↓
	Tear strength	↓↓↓	—	↓↓	↓↓↓	↓↓↓	↓↓↓
	Scott Bond	↓↓↓	↓↓	↓↓	↑↑↑	↑↑↑	↑↑↑
	Brightness	↑	↑↑	—	—	↓	↓

		Refined bleached chemical birch pulp					
		Xyl 50nkat/g	Xyl 500nkat/g	EGII 0.05mg/g	EGII 0.25mg/g	EGII 0.2 mg/g	EGII 1.0mg/g
Pulp	CSF	—	↑	↑	↑↑↑	↑↑	↑↑↑
	WRV	—	—	—	↓↓	↓↓↓	↓↓↓
	Capillary viscosity	—	—	↓	—	—	—
	Fibre bendability	—	—	—	—	—	—
Dry sheet	Density	—	↑	—	—	↑	↑↑
	Air permeability	—	↓↓	↓↓↓	↑↑↑	↑↑	—
	Roughness	↑	—	—	↓	↑↑	↑↓
	Tensile strength	—	—	—	↑↓	↓	↓↓
	Tear strength	—	—	—	↓↓↓	↓↓↓	↓↓↓
	Scott Bond	↑	↓	↑↑	↓↓↓	↑↑↑	↑↑↑
	Brightness	↑↑	↑↑	—	—	↓	↓
Wet sh.	Res. Tension	↓	—	↑↑	↓	↓	↓↓
	Wet strength	↓	↑	↑↑	↓	↓	↓↓
	Wet pressing potential	—	—	↓	↓↓	↓↓	↓↓
	Drying rate	↑	—	↑	↑↑	↑↑	↑↑↑

		TMP			
		Xyl/Man	EGII	Com. enzyme 1	Com. enzyme 2
Pulp	CSF	↑↓	↑↑↑	↑↑↑	↑↑↑
	WRV	↓	↓↓↓	↓	↓
Dry sheet	Bulk	—	↑↑↑	↑↑↑	—
	Air permeability	—	↑↑↑	↑↑↑	↑↑↑
	Tensile index	↓↓↓	↓↓	↓↓↓	↓↓
	Tear strength	↓↓↓	↓↓↓	↓↓↓	↓↓↓
	Scott Bond	↓↓↓	↓	↓↓	↓
Wet sh.	Res. Tension	↓	—	—	—
	Wet strength	↓	↑↑	↑↑	↑
	Wet pressing potential	—	↑↑↑	↑↑↑	↑
	Shrinkage	↓↓↓	↓↓	↓↓↓	↓
Drying rate	↑	↑↑↑	↑↑	↑↑	

Overall, it can be concluded that through controlled carbohydrate modifications of TMP or chemical hardwood pulp it is possible to enhance the dewatering characteristics in a paper machine without dramatically deteriorating its runnability. Also, the critical end product qualities such as strength

properties and sheet smoothness can be maintained at an acceptable level when specific enzymatic treatments are used.

#### 4 Introduction of plant hemicellulose xyloglucan to fibre network by spraying

The effects of xyloglucan-based modification of fibre surface on papermaking characteristics are described in this section. The results of publications III, IV and V are summarised.

In contrast with degradation of the cell wall polysaccharides by enzymatic actions, the bonding ability of the fibre can be enhanced by the introduction of chemicals onto the fibre surface. Utilisation of non-charged low-cost additives, such as plant hemicellulose xyloglucan (XG), offers interesting potential for influencing the bonding properties of fibres without disturbing the white water system. XG consists of (1→6)-linked  $\alpha$ -xylosyl residues along a  $\beta$ (1→4)-D-Glucopyranosyl backbone. It has been reported that XG has a strong natural adsorption onto cellulose (Vincken et al. 1995; Christiernin et al. 2003; Zhou et al. 2007; Eronen 2011). The structure of XG is shown in Fig. 25.

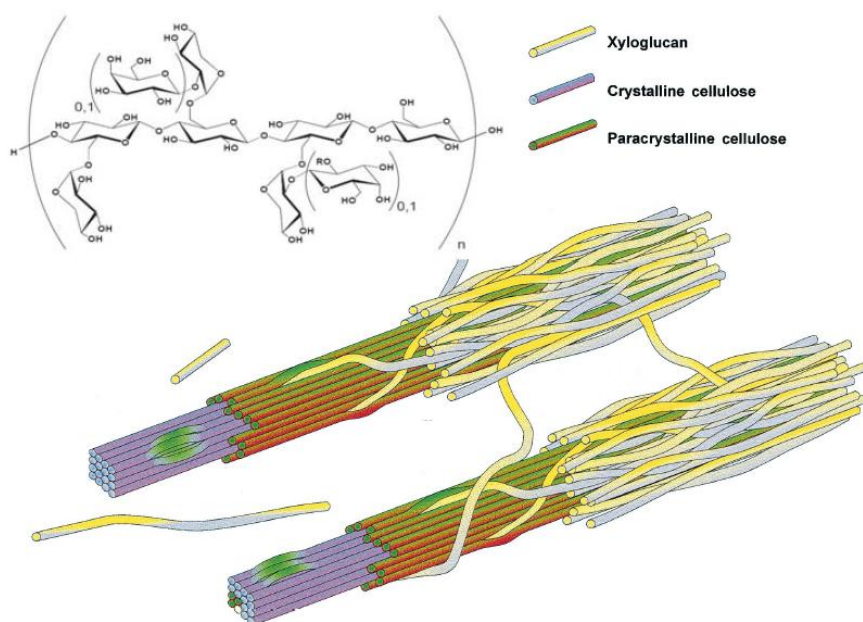


Fig 25. The structure of tamarind XG, with possible galactose substitution indicated,  $n \approx 700$  (Fry et al. 1993; Ahrenstedt 2008), and schematic representation of the cellulose-xyloglucan network in the plant primary cell wall (Rose et al. 1999).

Contrary to many other chemical strength additives, XG can readily adsorb irreversibly to cellulose surfaces at low temperatures. Interestingly, XG has also been observed at the same time to reduce friction and to increase adhesive forces between wet cellulose surfaces (Stiernstedt et al. 2006a; Stiernstedt et al. 2006b). As a consequence of decreased friction between fibres, XG has been reported to improve sheet formation (Christiernin et al. 2003). Improved formation is explained as an increase in the repulsive steric forces between XG covered surfaces in pulp suspension. It has also been mentioned that xyloglucan molecules have a more viscoelastic (time dependent), flexible structure compared to the rigid galactoglucomannan structure (Eronen 2011). A viscoelastic structure influences the adsorption characteristics of the chemical on surfaces (Eronen 2011). Time dependent settling of xyloglucan molecules on the surface of cellulose can further influence the friction and adhesive properties and finally the wet web strength properties. An explanation for the increase of adhesive forces between XG covered wet cellulosic surfaces is the bridging (cross-linking) ability of XG (Hanus and Mazeau 2006).

Additionally, the dry bonding strength of XG can be further strengthened by elemental cross-linking using borate (Ahrenstedt et al. 2008). Borates readily form complexes with galactose units (Pezron 1998). The fact that the XG borate complex does not form gel is essential for the application of this

complex in the papermaking environment (Martin 2003). The effect of XG borate complex on wet web strength and drying characteristics of the paper machine has not been widely studied. It is also known that chemicals consisting of aldehyde groups can enhance the wet web strength of tissue products (Thornton 2001). Respectively, the effect of aldehyde groups in XG on the initial wet web strength and thus on the runnability of the paper machine is not known. A special feature of the applied oxidation method is that the molecular weight of XG is not decreased when the primary alcohols on galactose are converted to aldehydes (Parikka et al. 2010; Xu et al. 2012). The expected result was here that the preservation of molecular weight in oxidation has positive influences on both wet and dry strength properties.

The special characteristic offered by xyloglucan is its strong irreversible adsorption onto cellulose fibre (Vincken et al. 1995; Zhou et al. 2007; Christiernin et al. 2003), making it highly attractive as an additive to improve the recyclability of the fibre. It has been shown that xyloglucan endures in the fibre surface in the refining process, and improves the strength of refined pulp (Lima et al. 2003; Christiernin et al. 2003). Refining is generally used in paper mills to recover the bonding ability of recycled fibres. According to the literature, the hemicelluloses content (xylan and glucomannan) of fibre plays a significant role in preventing hornification by decreasing the aggregation of fibrils (Oksanen et al. 1997; Duchesne et al. 2001; Cao et al. 1998), whereas lignin has a smaller effect on fibre hornification (Cao et al. 1998). Decreased aggregation of fibrils is further expected to preserve the gel layer on the surface of the recycled fibre. Properties of the gel layer on the fibre surface influences the wet and dry web strength properties (Myllytie 2009). Respectively, xyloglucan as a plant hemicellulose is expected to contribute to enhanced papermaking properties and the end product quality of recovered pulp. The hydrodynamic thickness of xyloglucan mono-layer (11.5 nm) and other polysaccharide layers has been reported (Eronen 2011). The molecular weight has been found to be important for the hydrodynamic thickness influencing the packing and bonding of the molecules. Cross-linkage of xyloglucan is assumed to further increase the hydrodynamic thickness of the gel layer.

In order to overcome the low wet-end retention of non-charged chemicals, xyloglucan can be sprayed onto the fibre network. Additives applied by spraying are more likely to reach the fibre surface, whereas additives introduced to the pulp suspension may adsorb preferably to fines due to the their high surface area. Compared to the addition of XG to pulp suspension, spray application has been reported to be a more efficient way of increasing the dry strength properties (Ahrenstedt et al. 2008). However, the influence on the initial wet strength of spraying of XG on to the wet fibre network has not been explored. The hypothesis of this research was that introduction of strength chemicals at the end of the former section could improve the wet web strength properties, without deterioration in the dewatering characteristics of the web.

At the start of the research, the hypothesis that the utilisation of several conventional paper chemicals could be replaced with just one xyloglucan-based additive was seen as attractive. Simplified additive chemistry enables savings in chemicals and logistics, and gives a more stabile wet-end chemistry. In the following sections, the influences of xyloglucan-based chemicals on the wet web strength, residual tension of the web, drying forces, end product quality and recyclability of the paper were explored. The effects of the molecular size of xyloglucan, elemental cross-linking with borate and introduction of aldehyde groups on xyloglucan, were particularly tested.

#### 4.1 Initial wet strength properties

In this study, additives were applied by spraying on the wet fibre network or alternatively mixed with the furnish before sheet forming. Never-dried and once-dried bleached chemical hardwood pulps were used in the experiments.

The spraying of XG onto wet sheets of unrefined never-dried (*Fig. 26A*) and once-dried (*Fig. 26B*) pulp increased the initial wet web strength of the samples. In these trials, XG was found to be a more effective wet strength additive than cationic starch (Raisamyl 135, D.S. 0.035). A dosage of approx. 0.8% of XG was as effective as a dosage of 1.4–2.0% of starch. Compared to the untreated sample, the introduction of XG to a fibre network increased the initial wet web strength by 20–50% depending on the dosage level. The increase of initial wet strength due to XG addition was the same in never-dried and once-dried sheets. The molecular weight and viscosity of the applied XG and cationic starch solutions were rather similar, thus differences in the adhesive characteristics of the sprayed gel-like layer may better explain the wet web strengthening effect of XG. The adhesive characteristics of XG

can be influenced by its ability to bridge cellulosic surfaces (Rose et al. 1999, Hanus and Mazeau 2006). In addition, the cationic charge of starch may influence the adsorption rate, and therefore the gel layer characteristics. Furthermore, the water soluble galactose side groups of XG may play an important role in the formation of the gel layer on the fibre surface.

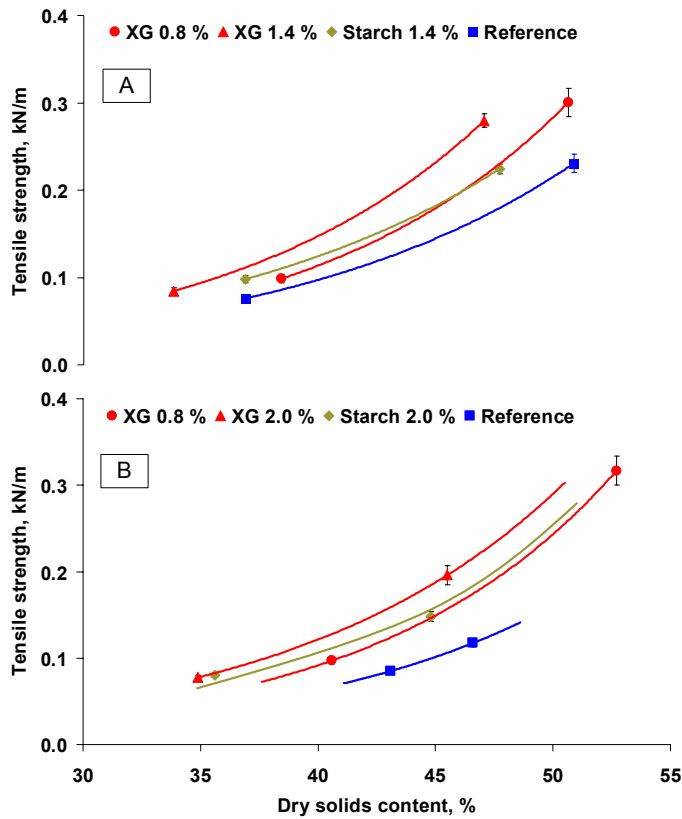


Fig 26. (A) Wet web strength of never-dried and (B) once-dried pulp samples (spray application). Reference sample was sprayed with plain water. An exponential fit was used to describe the effect of dry solids content (Kurki et al. 2004; Retulainen and Salminen 2009). Error bars show the 95% confidence interval of the mean of the measured values.

The effect of XG molecular weight and cross-linking of XG by borax on the initial wet tensile strength and residual tension are shown in Fig. 27.

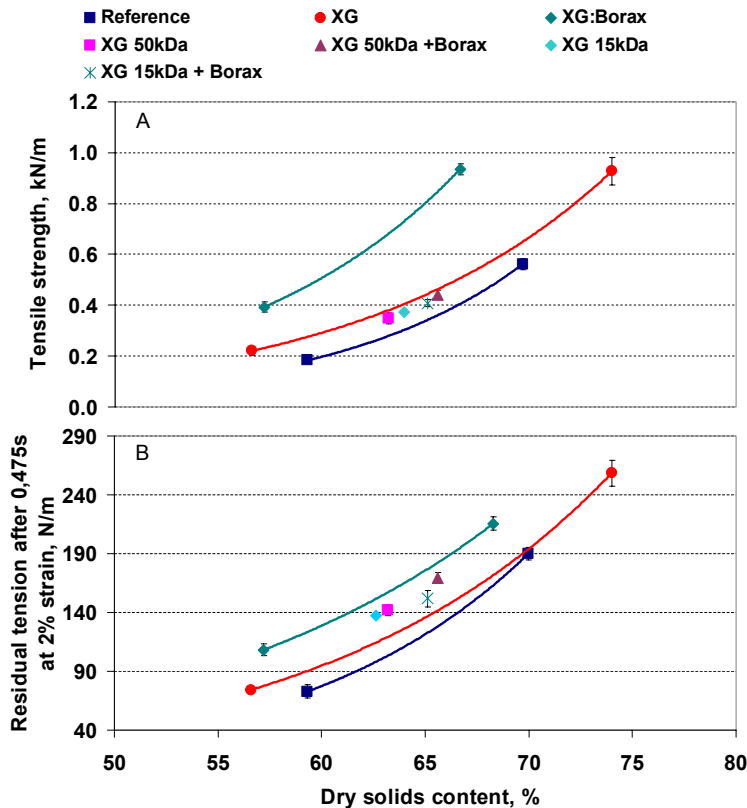


Fig 27. Influence of the cross-linking of xyloglucan with borax and the reduction of molecular weight (original xyloglucan ~1000kDa, 50kDa and 15kDa Mw) on the initial wet tensile strength (A) and residual tension (B) of laboratory sheets made of bleached unrefined birch pulp as a function of sheet dry solids content. The dry solids content was varied using two different wet press levels (0.5 bar, 3.5 bar) on a laboratory sheet presser. Chemicals were introduced by spraying onto wet sheets. The xyloglucan dosage was 0.5% of dry weight in all XG trial points. XG and borax were mixed in ratios of 0.5% and 2.5% of the dry weight. The reference sample was sprayed with plain water. An exponential fit is used to describe the effect of dry solids content on wet strength characteristics (Kurki et al. 2004; Retulainen and Salminen 2009). Error bars show the 95% confidence interval of the mean of the measured values.

Spraying of unhydrolysed xyloglucan or xyloglucan of reduced molecular weight (50 kDa and 15 kDa) alone brought about a slight increase in the initial wet tensile strength and residual tension of the wet web. However, the initial tensile strength and residual tension of wet samples were increased much more by cross-linkage of unmodified xyloglucan with borax. The positive effect was higher for wet tensile strength than residual tension. Conversely, this synergy benefit of xyloglucan with borax was not seen to the same extent with xyloglucan samples of decreased molecular weight. According to the literature, the decreased molecular weight of XG induces a fairly flat settling of XG molecules on the cellulose surface (Lima et al. 2004), whereas loops of the high molecular weight XG directed away from the cellulose surface may be essential for the cross-linkage of XG with borate. In particular, the availability of galactose side groups is important for the cross-linking to appear (Pezron et al. 1998). Further, the degree of cross-linkage influences the gel layer thickness and thus wet strength characteristics.

The effects of native, oxidised and borax-based cross-linked xyloglucan on the wet tensile strength and residual tension are shown in Fig. 28. Spraying of native xyloglucan at dosages of 0.5 and 1.0% of the dry weight produced a slight increase in the wet tensile strength and residual tension. As with the previous results, xyloglucan synergism with borax significantly increased the tensile strength and residual tension of wet sheets. However, the highest wet strength was found for oxidised xyloglucan. An increase in tensile strength and residual tension by more than 100% was measured when dosages of 0.5 – 1.0% of oxidised xyloglucan were used. Addition of oxidised xyloglucan at a dosage of 0.5% of the dry weight enhanced the wet tensile strength and residual tension by approximately the same

amount as addition of xyloglucan (0.5% of d.w.) and borax at a mixing ratio of 1:5. Utilisation of oxidised XG may be more convenient in a paper mill environment than of the XG – borax mixture. As the XG – borax complex, the oxidised XG is expected to increase the thickness of gel layer on the fibre surface. Wet strength improvement of a re-wetted paper due to the introduction of aldehyde groups on cellulose fibres, starch and guar has also been reported (Saito, Isogai 2005; Saito, Isogai 2006; Hofreiter et al. 1974; Thornton et al. 2005; Opie et al. 1965). These publications tested the wet strength properties of re-wetted paper, whilst the capability of the aldehyde groups to enhance the initial wet web strength in the paper machine has not been explored. Increase of the initial wet web strength means improved paper machine runnability. Based on the wet strength results in *Fig. 28*, aldehyde groups in XG enhance the strength of the fibre network at 50% dry solids content. This result indicates that aldehyde groups can form covalent hemiacetal linkages (Saito, Isogai 2005; Saito, Isogai 2006; Hofreiter et al. 1974) between fibres and enhance the runnability of the wet web at the beginning of the drying section, where web breaks are most likely to happen.

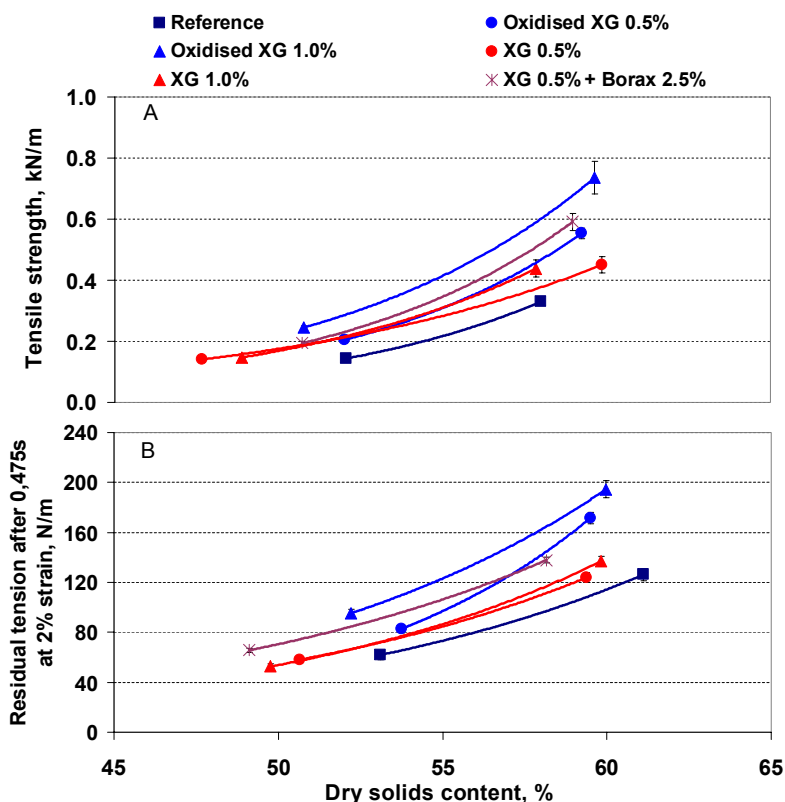


Fig 28. Influence of oxidation and borax-based cross-linking of xyloglucan on the initial wet strength (A) and residual tension (B) of laboratory sheets made of bleached unrefined birch pulp as a function of sheet dry solids content. The dry solids content was varied using two different wet press levels (0.5 bar, 3.5 bar). Chemicals were introduced by spraying onto wet sheets. The xyloglucan dosage was 0.5% or 1.0% and that of borax 2.5% of the dry weight. An exponential fit was used to describe the effect of dry solids content (Kurki et al. 2004; Retulainen and Salminen 2009). Error bars show the 95% confidence interval of the mean of the measured values.

#### 4.2 Drying characteristics

Drying tension was found to increase earlier after XG was sprayed onto wet sheets made of never-dried (*Fig. 29A*) or once-dried (*Fig. 29B*) pulp. Xyloglucan dosages of 0.8 to 2.0% lead to almost identical drying tension developments as a function of dry solids content. In other words, Increase of the XG dosage from 0.8% did not further advance the development of drying tension. Therefore, a xyloglucan dosage of less than 1% seems to be enough from the runnability perspective of the dryer section in the paper machine. Increase of adhesive forces between xyloglucan-treated wet cellulose surfaces has been reported by Stiernstedt et al. (2006a). According to the literature, the time



dependence of the separation work of xyloglucan-treated surfaces suggests that adhesive forces are controlled by a diffusion process (Stiernstedt et al. 2006a; Rutland et al. 1992; Plunkett et al. 2002). In contrast, addition of starch delayed in both pulps the creation of drying tension and has thus a negative effect on wet web tension. A delayed strength formation during drying in the case of starch addition has also been reported by Myllytie (2009). These results indicate that starch probably makes the fibre surface more slippery, whereas XG increases the adhesiveness of the surfaces.

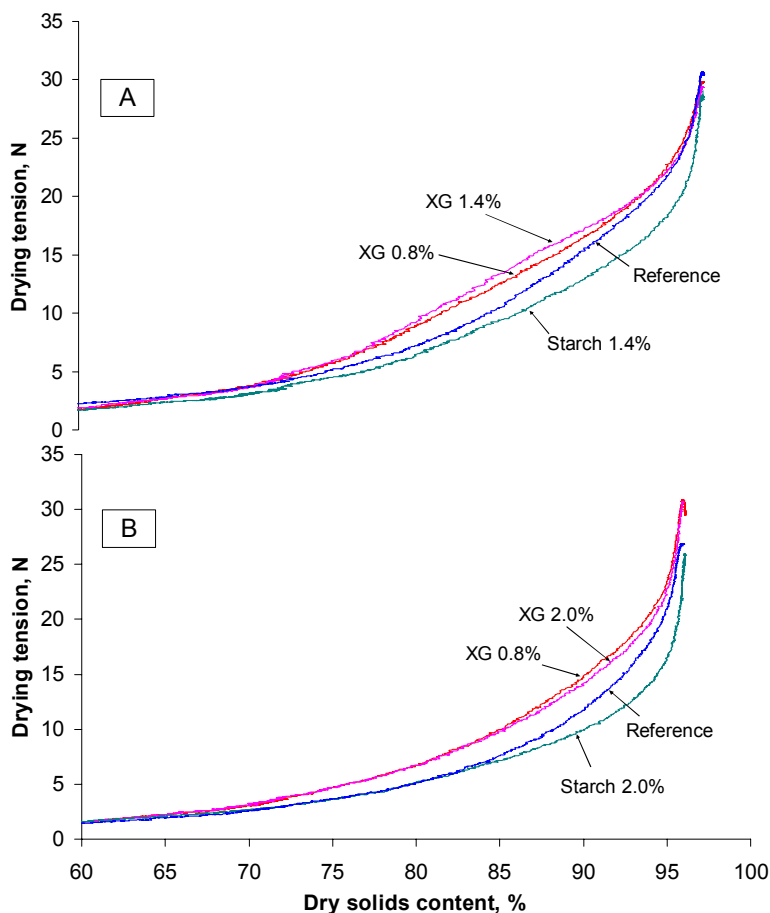


Fig 29. (A) Formation of drying tension in never-dried and (B) once-dried samples as a function of dry solids content. XG and starch were applied by spraying. Xyloglucan dosage was 0.8% or 2.0% and that of starch was 2.0% of the dry weight. Reference samples were sprayed with plain water. Plots are the average results of 8 parallel measurements.

### 4.3 Dry sheet properties

Application of xyloglucan onto sheets by spraying, enhanced the dry strength of samples made of never-dried (Fig. 30A) and once-dried (Fig. 30B) pulp. The dry strength improvement due to xyloglucan treatment was similar to that found by other authors (Christiernin et al. 2003; Lima et al. 2003, Ahrenstedt 2007). However, the relative tensile strength improvement was higher for the sample made of once-dried pulp than for those of never-dried pulp. Starch was found to effectively increase the dry tensile strength as much as xyloglucan at the same sheet density level. Tensile stiffness of dry sheets was found to be higher and breaking strain lower in the xyloglucan sample than in the starch sample. Differences in the stiffness and breaking strain results between starch and xyloglucan can be linked to differences in the tension profile development during drying. Increased adhesive forces during drying between wet fibres due to xyloglucan treatment (Stiernstedt 2006a) increases the load bearing activity of the fibre and fibre network (shrinkage restrained), which increases the tensile stiffness and decreases the strain at break of dry paper. Contrary to XG, starch treatment of fibre

surfaces was found to induce sliding of the fibres in the fibre network during drying and further decreases tensile stiffness and increases strain at break of the dry paper.

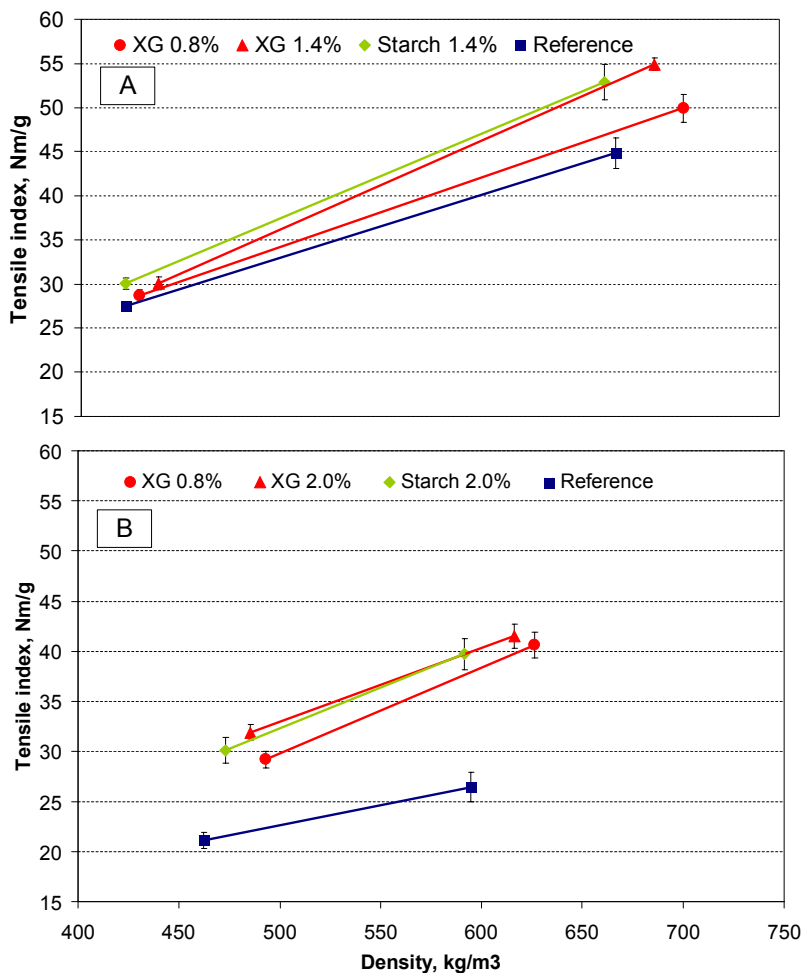


Fig 30. Dry strength of (A) never-dried and (B) once-dried samples as a function of dry sheet density. XG and starch were applied by spraying. Reference samples sprayed with plain water. Xyloglucan dosage was 0.8%, 1.4% or 2.0% and starch dosage 1.4% or 2.0% of the dry weight. Linear fits were made to data points of given dosage values of both XG and starch. Error bars show the 95% confidence interval of the mean of the measured values.

Addition of unmodified (1000 kDa) or decreased molecular weight (15 kDa or 50 kDa) XG improved the tensile strength of the samples at a constant sheet density (Fig. 31). The highest increase in the tensile index, 10 units, was observed for the xyloglucan - borax complex. As in the case of wet strength properties, the synergism between xyloglucan and borax, which lead to improved dry strength, was decreased when the molecular weight of xyloglucan was reduced. On the molecular level, long xyloglucan loops consisting of galactose side groups, which stick out of cellulose surfaces, may be important for the cross-linking of cellulose surfaces with xyloglucan-borax complexes (Lima et al. 2004). Therefore, the reduction in the molecular weight of XG may decrease its ability to bind cellulose surfaces together.

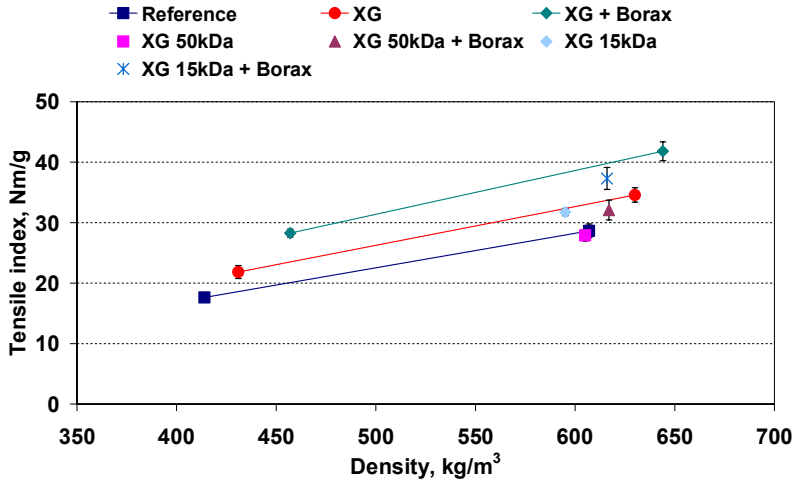


Fig 31. Influence of borax-based cross-linking and molecular weight of xyloglucan (unmodified xyloglucan 1000kDa, 50kDa and 15kDa Mw) on the dry tensile index of laboratory sheets made of bleached unrefined birch pulp as a function of dry sheet density. The latter was varied by using two different wet press levels (0.5 bar, 3.5 bar) on a laboratory sheet presser. Chemicals were introduced by spraying onto wet sheets. The reference samples were sprayed with plain water. The xyloglucan (1000kDa, 50 kDa and 15 kDa) dosage was 0.5% and borax dosage was 2.5% of the dry weight. Linear fit to data points were used to display the dependence on dry sheet density. Error bars show the 95% confidence interval of the mean of the measured values.

The effects of native xyloglucan, oxidised xyloglucan and xyloglucan cross-linked with borax on the tensile index are shown in *Fig. 32*. Addition of unmodified xyloglucan at a dosage of 0.5 or 1.0% of the dry weight produced a slight increase in the tensile index, and it was improved by 25% when 0.5% xyloglucan was mixed with 2.5% borax of the dry weight. Oxidation of xyloglucan enhanced the dry strength of the samples considerably. Spraying of oxidised xyloglucan at a dosage of 0.5% and 1.0% of the dry weight increased the tensile index by 30% and ~60%, respectively. Indications of a slight increase in the tensile index due to the introduction of aldehyde groups onto cellulose fibre surface has also been reported by Saito and Isogai (2005). However, the effects of aldehyde-xyloglucan on the dry sheet strength properties has not been explored. A 30% increase in the tensile strength with 2% (of the dry weight) addition of dialdehyde starch, has been reported (Hofreiter et al. 1974). As in the case of wet strength of the cellulose fibre network, the formation of inter-fibre covalent hemiacetal bonds may explain the increase of dry tensile strength by addition of aldehyde-xyloglucan or aldehyde-starch (Saito and Isogai 2005; Saito and Isogai 2006). Spraying of 2.5% borax with 0.5% oxidised XG of the dry weight did not further increase the tensile index observed after the addition of merely oxidised XG by 0.5% of the dry weight. An explanation for this result is that full conversion of primary alcohols on galactose C-6 to aldehyde probably hinders the complex formation between borax and xyloglucan.

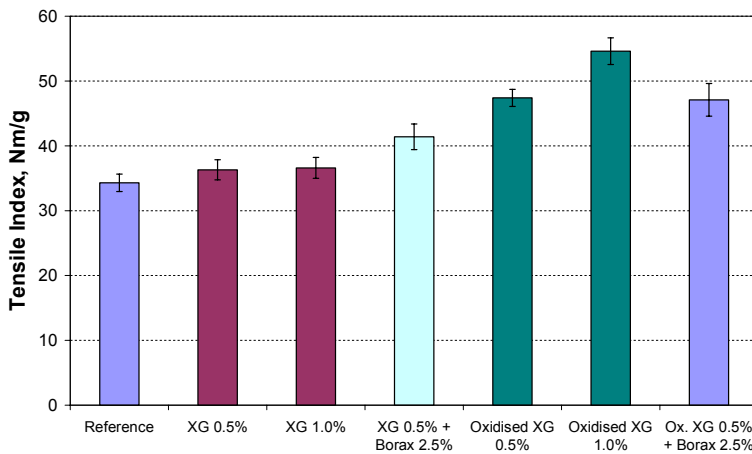


Fig 32. Influence of oxidation and borax-based cross-linking of xyloglucan on the dry tensile index of laboratory sheets made of unrefined bleached birch pulp. Chemicals were introduced by spraying onto wet sheets. The reference samples were sprayed with plain water. The xyloglucan (native and oxidised) dosage was 0.5% or 1.0% and borax dosage was 2.5% of the dry weight. The bars show the 95% confidence interval of the mean of the measured values.

The spray addition of xyloglucan decreased the air permeability (*Fig. 33A*) and sheet roughness (*Fig. 33B*) of the fibre network compared to reference samples made of once-dried chemical pulp. Substantial effects due xyloglucan treatments were only observed in sheets made of once-dried pulp (stiff fibres) but not in dense sheets made of never-dried pulp (flexible fibres). The reduction of air permeability was slightly higher for xyloglucan than for starch treatments. This result may also be explained by different film forming and cross-linking characteristics of these polysaccharides (Freitas et al. 2005). In the case of wet-end application of xyloglucan, a reduction in the sheet porosity has been observed (Lima et al. 2003). The effects of treatments were bigger for a 0.8% dosage than for a 2.0% dosage on both the air permeability and roughness. Spraying of a high amount of low concentration additive may reduce fibre contacts and thus increase roughness and air permeability. Application of a 2.0% starch dosage by spraying increased the roughness of the sheet.

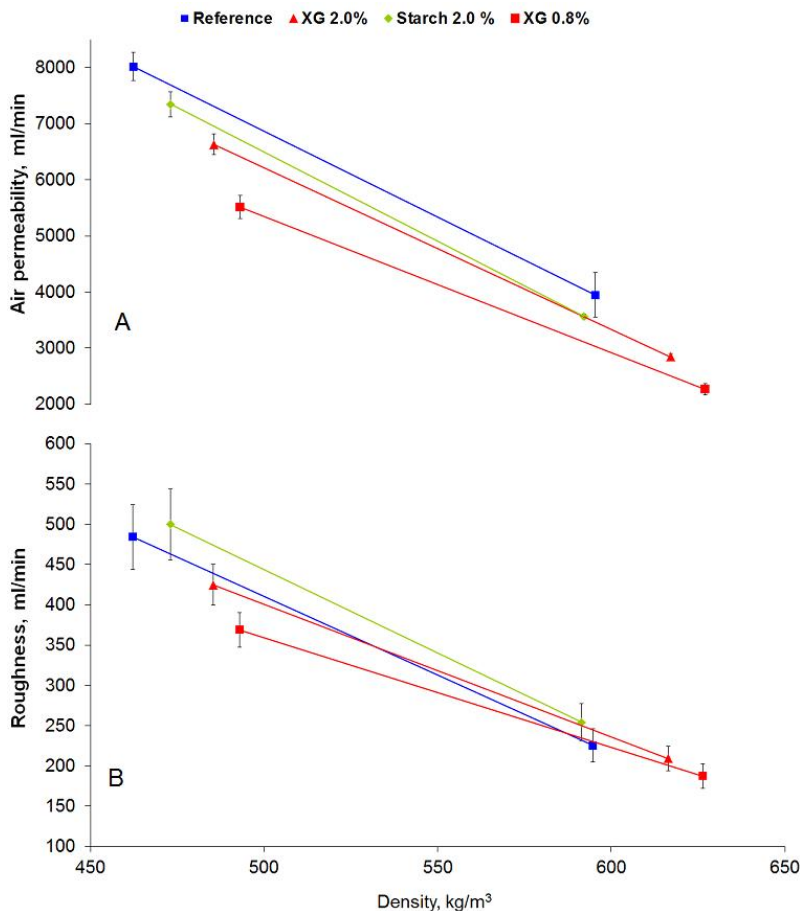


Fig 33. (A) Air permeability and (B) roughness of once-dried samples as a function of dry sheet density. XG and starch were applied by spraying. The reference samples were sprayed with plain water. Xyloglucan dosage was 0.8% or 2.0% and starch dosage was 2.0% of the dry weight. Linear fits were used to display the dependence on dry sheet density. Error bars show the 95% confidence interval of the mean of the measured values.

#### 4.4 Recyclability

The effect of XG and the XG-borax complex treatment of the fibre network on the strength reduction in recycling of paper is shown in *Fig. 34*. Chemicals were applied by spraying wet sheets made of unrefined never-dried bleached chemical birch pulp. The cell wall of never-dried hardwood pulp is not stiffened in drying as in the case of once-dried pulp. Cell wall stiffening during drying is related to loss of swelling ability (Weise 1997) of the fibre, which was expected to influence the adsorption and absorption of chemical additives into the fibre. The amount of retained polysaccharide on the fibre surface affects the gel layer properties and further the wet and dry paper characteristics.

An increase of dry tensile strength due to addition of xyloglucan (Christiernin et al. 2003) or the xyloglucan-borate complex (Ahrenstedt 2007) to the fibre network has been demonstrated by several authors. In addition, xyloglucan has been found to remain firmly on the surface of cellulose (Lima et al. 2003; Myllytie 2009) even in the refining process of the pulp (Christiernin et al. 2003). However, the effects of drying and rewetting cycles (recycling) on the bonding ability of xyloglucan and xyloglucan-borate complex has not been explored. As expected, recycling (re-pulping and re-drying) of paper samples decreased the dry strength of paper (*Fig. 34*). Fibre hornification in the recycling process typically refers to loss of the swelling ability, fibre stiffness, conformability and bonding ability of fibres due to drying and rewetting cycles (Jayme 1944; Weise 1997; Somwang 2002). Before and after recycling the highest tensile strength was observed in a mixture of 1% xyloglucan and 2.5% borax of the dry weight. Based on the tensile index results, the activity and further bonding ability of xyloglucan and the xyloglucan-borate complex in the fibre surface endures the re-pulping process.

According to the literature, dry strength additives do not typically affect the strength loss caused by drying and rewetting cycles. However, the treatment of fibres with chemicals such as xyloglucan has been suggested to mainly improve the hydrogen bonding ability of recycled cellulose material (Hubbe 2005). Hemicelluloses content (xylan and glucomannan) of the fibre has been reported to play a significant role in hornification by decreasing the aggregation of fibrils (Oksanen et al. 1997; Duchesne et al. 2001; Rebutzi and Evtuguin 2006), whereas lignin has a smaller effect on fibre hornification (Cao et al. 1998). Therefore, xyloglucan as a plant hemicellulose is also an interesting chemical for improving the dry strength of recycled paper. Because the molecular size of unmodified xyloglucan is relatively big, it only interacts with the surface of the fibre. The re-swelling (softening) capability of xyloglucan and the xyloglucan-borax gel layer in the surface of recycled fibres enhances the bonding ability of recovered fibres.

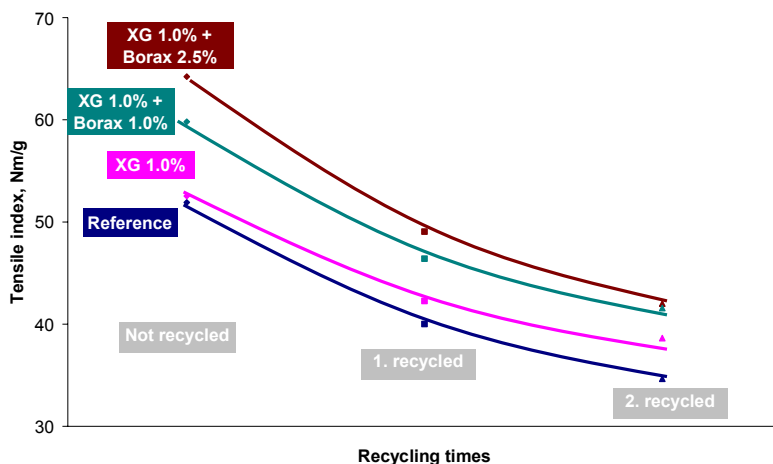


Fig 34. Influence of recycling on the dry tensile index of sheets made of originally never-dried pulps. Wet sheets made of virgin pulp were sprayed before recycling with xyloglucan (1% of the dry weight) or with xyloglucan with borax (1% xyloglucan + 1% or 2.5% borax of the dry weight). The reference samples were sprayed with plain water.

#### 4.5 Summary

The probability of web breaks is known to be closely related to the wet web strength and web tension profiles (Kurki et al. 2004). Due to the low solids content (40–55%) after wet pressing, minimal hydrogen bonding occurs in the web at this stage, and therefore the formation of covalent bonds, e.g. by a xyloglucan-borax complex or by introducing aldehyde groups to xyloglucan, have an important role in strengthening the wet fibre network.

Xyloglucan-borax complex and aldehyde-xyloglucan (by XG oxidation) treatments of the wet fibre network strongly enhanced the wet and dry strength properties of the web. These XG-based chemical treatments can result in formation of a thick gel-like polysaccharide layer on the surface of the fibres. According to the results, long bridging xyloglucan molecules were required in cross-linking with borax for improving fibre bonds in the wet and dry web. The adhesive characteristics of an XG-based gel layer can influence the wet web and dry paper strength properties (Kantelinen et al. 2007; Myllytie 2009). Web strength improvements were higher when chemicals were added by spraying on the wet web than when added to the pulp suspension. The dry sheet strength benefit due to spraying compared to pulp addition has also been reported by other authors (Ahrenstedt 2008).

The increased adhesion between wet xyloglucan covered fibre surfaces (Stiernstedt 2006a) may explain the observed advanced creation of drying tension compared to the untreated reference. Cationic starch was even found to delay the formation of shrinkage forces in drying, probably due to sliding of fibres in the fibre network during drying. Advanced drying tension may improve the runnability of the wet web in the dryer section by decreasing the fluttering and bagging of the web, for example.

Additionally, the fact that xyloglucan has strong natural affinity (Christiernin et al. 2003; Myllytie 2009) to cellulose and it forms complexes with borate, which further strengthens the fibre network, was found to enhance the recyclability of the chemical pulp.

In general, xyloglucan-based treatments of the fibre network were found to have a positive impact on the runnability potential of the paper machine, combined with the enhanced strength and structural properties of dry paper. A graphical representation of the findings can be found in *Table 11*.

Table 11. Effects of various xyloglucan-based treatments on some papermaking characteristics and paper properties for unrefined bleached chemical birch pulp. Explanation for signs: ↑ increase, ↓ decrease and — no change in the measured value. X means that measurement was not carried out. The nature of changes is colour coded such that green is positive, red is negative and grey is positive or negative change.

		Native XG	XG + Borax	Decreased Mw of XG	Decr. Mw of XG + Borax	Oxidised XG	Starch
Dry sheet	Density	↑↑	↑↑↑	—	↑	↑↑↑	↑↑↑
	Roughness	↓↓	X	X	X	X	↓↓
	Air permeability	↓↓	X	X	X	X	↓↓
	Tensile index	↑↑	↑↑↑	↑	↑↑	↑↑↑	↑↑
Wet sh.	Wet strength	↑↑	↑↑↑	↑	↑↑	↑↑↑	↑↑
	Res. Tension	↑	↑↑	↑	↑↑	↑↑↑	↑↓
	Advanced drying tension	↑↑↑	X	X	X	X	↓↓

## 5 Synergism of enzymatic modification and xyloglucan treatment

In this thesis, positive influences on the dewatering properties of pulp due to enzymatic treatments were reported. On the other hand, a partial hydrolysis of fibre was observed to reduce the strength properties of paper. However, this thesis also demonstrated that addition of uncharged polysaccharide, XG, or cationic starch improves the dry strength properties of paper. Thus, the research hypothesis was to demonstrate that the drainage of TMP can be enhanced without deterioration of wet and dry web strength properties by combined sequential enzymatic and xyloglucan treatments of fibres.

### 5.1 Drainage and strength properties

*Figure 35* shows the effect of enzyme and strength additive treatments on drainage (freeness) of TMP and the dry sheet tensile index. With endoglucanase rich enzymes EGII and enzyme 1, a substantial 20 to 30 units increase in the freeness value of TMP was observed.

It is known that xyloglucan (Ahrenstedt 2007) or starch is not a very effective strength aid for mechanical pulp fibres covered with lignin. Moreover, in our trials xyloglucan and starch did not significantly influence the tensile index of the samples (see ‘no enzyme’ spots in *Fig. 35*). Interestingly, xyloglucan was found to affect the sheet strength properties of TMP. The dry tensile strength of the sheet was decreased for all the endoglucanase and hemicellulase treatments of TMP. The introduction of XG (2% of the dry weight) by spraying recovered the tensile strength properties of the sheet to almost the same level as before the enzymatic treatments (*Fig. 35*). On the other hand, the addition of starch did not have much influence on the strength properties of paper. An explanation to this can be that enzymes reveal hemicellulose and cellulose surfaces in the fibre to which XG can attach. Unlike in the case of starch, conformation of the XG backbone and cellulose chains are effectively similar in most of the xyloglucan types, which could partly explain the good results for XG compared to starch. The uncharged nature of xyloglucan can also be beneficial, so that XG will adsorb merely to the cellulose or hemicellulose part of the fibre while charged areas of fibres, such as extractives, attract cationic starch. Variations in the surface charge density of TMP due to extractives, carboxylic and hydroxyl groups affecting the adsorption of cationic starch have been reported (Tammelin et al. 2007; Kontturi et al. 2008). It has been suggested that interaction between XG and cellulose results from a complex contribution of van der Waals, dispersion, and electrostatic forces, and that hydrogen bonds are not the only factor influencing and determining the geometry of adsorption (Hanus et al. 2006). Bearing in mind that enzymatic modification can be in ultra-scale, the molecular weight and conformation of strength additives also has a significant influence on where the strength additives can find their way. The molecular size of cationic starch has been reported to influence its penetration into the cellulose matrix (Kontturi et al. 2008). As enzymes prefer open dislocation areas of the fibre (Suchy et al. 2009), then xyloglucan could be considered to be a repair additive for the weak areas of the fibre.

Overall, the sequential treatment of TMP with an endoglucanase rich enzyme and xyloglucan enables enhanced dewatering of the pulp in the paper machine without significant strength loss of

paper. The paper strengthening effect of xyloglucan could be further enhanced by cross-linking with borax or oxidation.

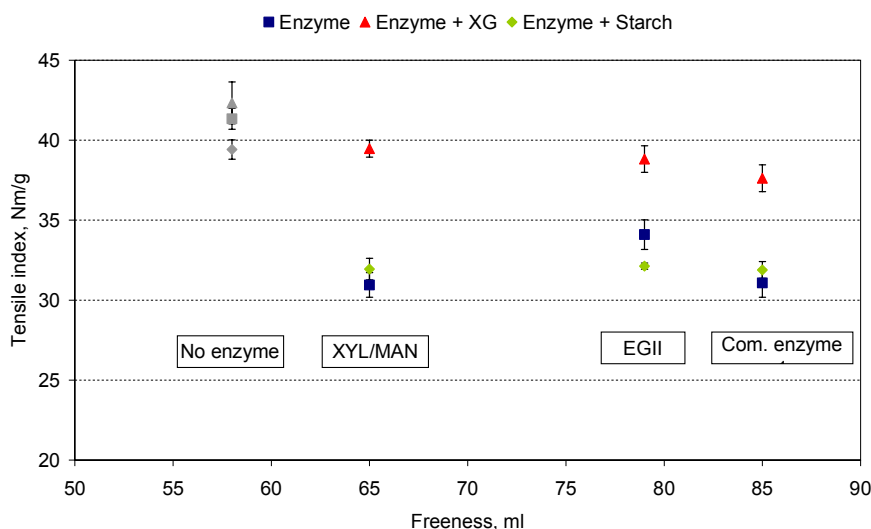


Fig 35. Influence of spraying wet laboratory sheets made of enzymatic treated TMP with XG and starch (Raisamyl 135), 2% of the dry weight. Carbohydrates solubilised from TMP in treatments with purified *T. reesei* cellulases and hemicellulases (EG II = endoglucanase II, MAN=mannanase, XYL=xylanase) and with a commercial enzyme preparation (Ecostone L900). Standard treatment conditions were 50°C, 0.5 mg/g dosage for 24 hrs except for XYL+MAN whose mixture dosage was 0.1 mg/g + 0.1 mg/g. See tables 3 and 4 in publication I. Error bars show the 95% confidence interval of the mean of the measured values.

## 6 Furnish stratification

In this section, the potential of furnish stratification to improve paper production efficiency and end product quality is explored. The results and methods of furnish stratification are described in more detail in publications VI and VII.

Differences in the dewatering and bonding characteristics, surface properties and optical properties of furnishes can be exploited more efficiently by stratification (Hägglom-Ahnger 1998, Leskelä 2004) than with conventional one-layer forming of paper. The forming of separate furnish plies and combining them in the former section enables the manufacturing of clearly layered structures. This technique is utilised in board production. The multilayer headbox concept consists of only one headbox, thus the investment costs are smaller than of machines that have many headboxes. However, the multilayer headbox technique has not become common in paper mills due to challenges in the production of high quality board with pure layers of furnishes. The multilayer headbox structure and the related papermaking process parameters have been widely explored (Lloyd and Norman 1998; Lloyd and Norman 1999; Puurtinen and Oksanen 2003). In printing paper, additive stratification has been found to be less critical for small inter-layer mixing, while the mixing of fibres between layers is not acceptable. Therefore, the multilayer headbox has until now been utilised merely for stratification of additives, such as fillers (Kinnunen et al. 1998; Lloyd 1999). Because of innovations such as 'aqua vanes' (Söderberg 2007; Söderberg 2008) related to fibre stratification interest in layered paper structures may increase in the future.

A hypothesis of this work was that stratification of different furnishes can enhance the papermaking efficiency and at same time the end product quality. It is known that many properties are developed non-linearly as a function of the ratio of mechanical to chemical pulp in the furnish (Retulainen 1992). The effect of furnish layering on the tensile and other quality properties of dry paper has been studied by Hägglom-Ahnger (1998), and less attention has been given to the effect of layering on the mechanical properties and runnability of wet web. For example, mechanical pulp typically has a higher wet web stiffness and stress level than chemical pulp after a given draw. The wet web stiffness



and high stress level are probably the reasons for the high production efficiency of wood containing paper grades (LWC, SC, News). Typically, papers that contain mechanical pulp have lower material costs, better dimensional stability and lower grammage than wood-free paper grades. The main downsides of using mechanical pulp are diminished surface smoothness and brightness (Kouko, Kekko 2006), whereas the presence of fillers in paper improves its optical properties such as brightness and opacity. Other quality properties of paper such as smoothness and ink receptivity, can also be improved with fillers. Filler distribution in the thickness direction of paper is known to influence its printability (Fordsmand et al. 2006). In addition, the economic benefits of using fillers are significant as they are less expensive than pulp (Krogerus 1999). However, an increase in the filler content is generally known to reduce the tensile strength of paper due to the lowered grammage, and density of the fibre network, relative bonded area (RBA) and strength of the bonds (Scott 1987).

The objective of this study was to clarify whether the stratification of fillers and different furnishes can be used to enhance the wet and dry strength properties and quality of paper, or to increase the filler content. Stratification of furnishes may enable a reduction of basis weight and thus enhance the material efficiency of the fibre material. Stratification of furnishes (mechanical and chemical pulp and fillers) with a multilayer handsheet former is described in section 2.6.

### 6.1 Wet strength properties

In the paper machine, the wet strength properties after wet pressing of the web are related to the runnability of the web at the beginning of the drying section, where a large proportion of the web breaks occur. However, high tensile strength of the wet web does not necessarily mean good runnability in the paper machine. The tension holding ability of the wet web has been found to be critical for the web breaks (Kurki et al. 2004). In this research, the viscoelastic behaviour of the wet web was estimated by measuring the residual tension of the samples as a function of wet web strain and time.

The tensile strength of wet samples (at 50% dryness) is shown in *Fig. 36A*. By increasing the amount of the TMP fraction in the pulp, a significantly higher wet tensile strength was obtained (publication VI). Improvement in the tensile strength was also significant when softwood was replaced by TMP. Mixing TMP into pulp gave a higher tensile strength than stratifying. The increase of wet web tensile strength can be explained particularly by increase of fines (de Oliveira 2008) and of the fraction of medium-size fibres (Salminen 2010). Fines and the fraction of medium-size particles fill the inter-fibre spaces during sheet dewatering, and increase the amount of fibre-air-water interactions (Bristow 1986). This may explain why the more evenly distributed TMP content had a greater effect on the wet web tensile strength. However, it has also been proposed that the friction caused by fibre entanglement is responsible for the strength of wet paper instead of capillary forces (de Oliveira 2008).

Even greater differences in the residual tension of wet webs made of chemical and mechanical were observed than in their tensile strength (*Fig. 36B*). The stiff mechanical pulp fibres have been reported to improve the tension holding ability of the wet web (Salminen 2010). By stratifying only 10% of TMP, the residual tension of the wet paper sample was increased by 30%, as shown in *Fig. 36B*. When replacing softwood completely (40% of the total amount of pulp) by TMP, the residual tension increased by 100%. This means that by increasing the TMP fraction in the furnish, the strain induced in the web by transforming it from the pressing to the drying section can be decreased significantly. By decreasing the strain, a lower porosity and higher strain of the final product can be achieved.

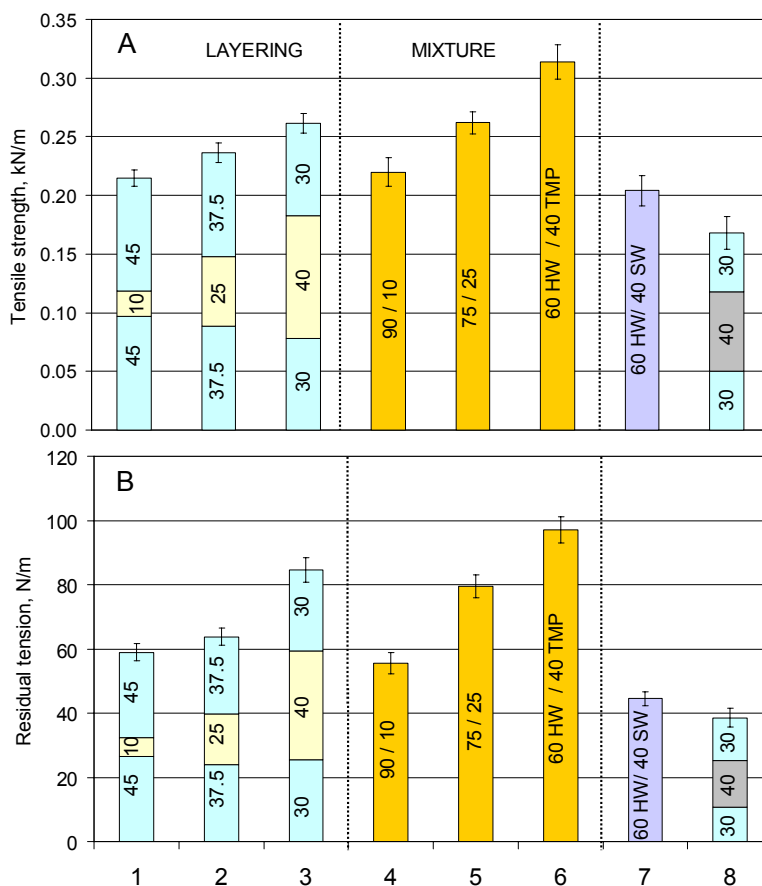


Fig 36. (A) Tensile strength and (B) residual tension of wet paper (dry grammage 60 g/m<sup>2</sup>) for 50% initial dry solids content. Results are linearly interpolated to a dryness level of 50%. In the layering trial points there was 10%, 25% or 40% TMP of the dry weight stratified into the middle layer, while the HW pulp was stratified into surface layers. In the mixture trial points, the same TMP and HW pulp proportions were blended homogeneously in the structure. Two reference trial points: mixture of 60% HW and 40% SW, 40% SW in the middle layer and 30% HW stratified into both surface layers. HW = hardwood, SW = softwood, TMP = thermomechanical pulp. Error bars show the 95% confidence interval of the mean of the measured values.

In publication VII, it was found that pure TMP and a blend of chemical pulps with no fillers had roughly the same wet web tensile strength (Fig. 37A). Mixing 20% PCC with the chemical pulp decreased the tensile strength by 60% at a dryness level of 55%. In the case of TMP pulp, the reduction at this dryness level was on the tensile strength significantly lower (15%). This suggests that addition of fillers to TMP pulp does not interfere with fibre bonds as much as in the case of chemical pulp. Interaction of fibres and fines in TMP is important, as fines can bind fillers into the fibre network. It has also been stated that small filler aggregates can increase the friction between fibres, and thus the wet web strength (de Oliveira et al. 2009). In contrast, large filler aggregates are easily detached from fibres by shear forces, and such aggregates interfere with fibre entanglement, reducing friction between fibres. Stratifying PCC into the top layers had a small positive effect on the wet tensile strength compared to a non-stratified reference, but lower than that for dry paper samples.

Pure TMP and chemical pulp gave a similar dry (39C) and wet web (37A) tensile strength. However, TMP had almost twice as high residual tension at 2% strain as pure chemical pulp at a constant dryness of 55% (Fig. 37B). The addition of 10 or 20% TMP to chemical pulp consistently increased the residual tension of the wet web. Mixing 20% PCC with pure TMP had no effect on the wet web residual tension, while a 20% addition of PCC to chemical pulp decreased the residual tension by 40%. Stratification of TMP or PCC had no significant effect on the residual tension of the wet web.

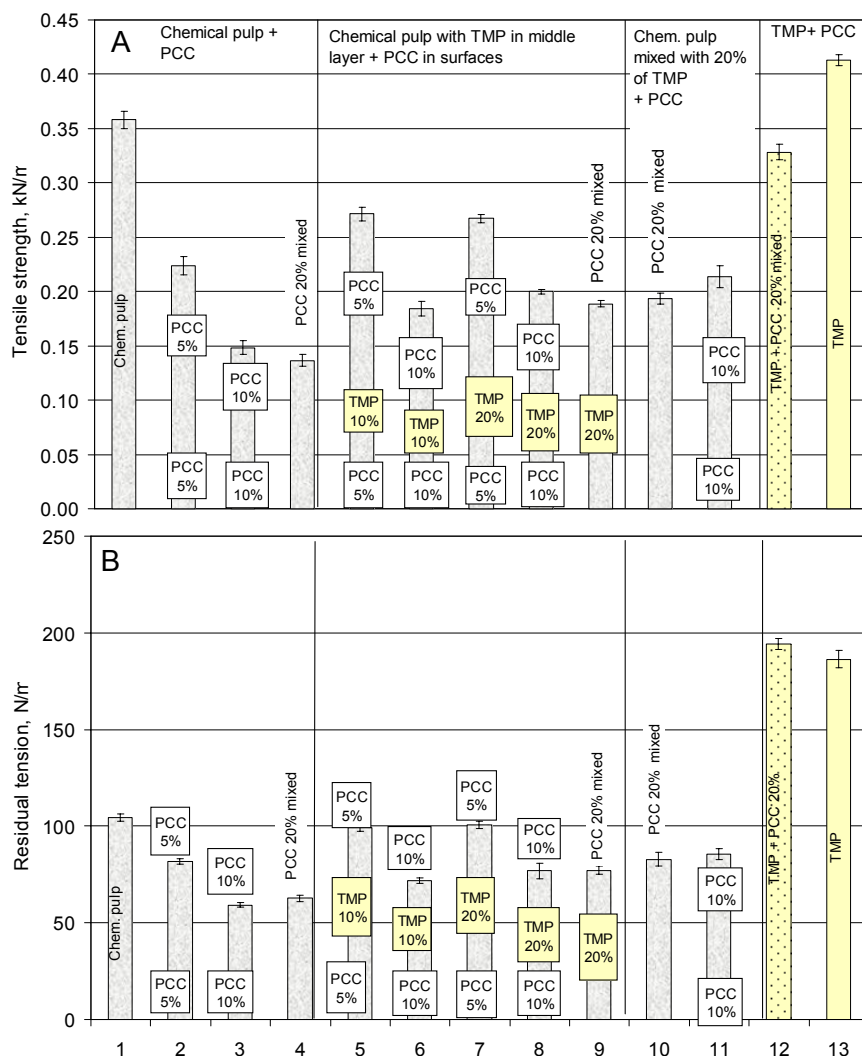


Fig 37. Effect of pulp type and filler on (A) the tensile strength and (B) residual tension at 2% strain of wet multilayer handsheets (results are linearly interpolated to a dryness level of 55%) measured by the impact test rig. The amount (5, 10 or 20%) and location (top, middle or bottom side) of the stratified component (PCC or TMP) is presented in the box above the result bar. Dry grammage of the sheets was 60 g/m<sup>2</sup>. Error bars show the 95% confidence interval of the mean of the measured values.

## 6.2 Dry sheet properties

It was shown that stratification of TMP and chemical pulp had no effect on the dry paper tensile strength. The effect of stratifying and mixing different pulps on the bulk of the trial points is reported in publication VI. Bulk was increased by increasing the amount of TMP. The same bulk was achieved either by a 40% fraction of softwood or by a 10% fraction of TMP. Stratifying and mixing of TMP had a similar effect on the bulk.

The effect of different pulps on the Bendtsen roughness is shown in Fig. 38. The roughness of the samples increased significantly with increasing amount of TMP in the blended pulps. An increase of 40% of TMP in the middle layer had no effect on the roughness of handsheets. This result indicates that a significant amount of TMP can be covered with hardwood.

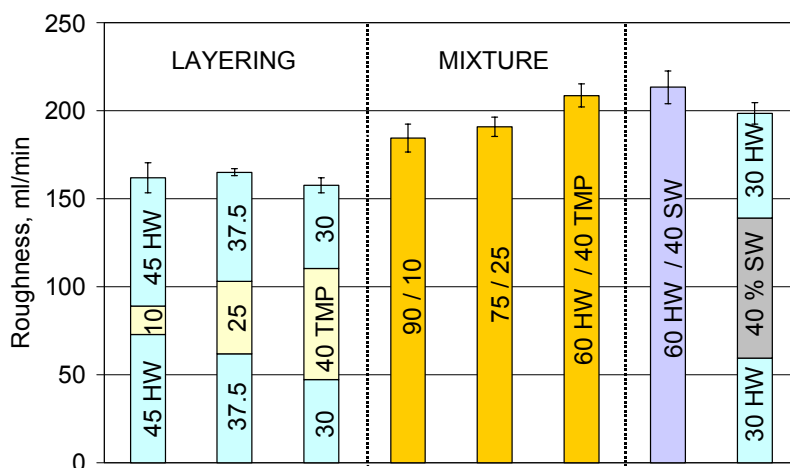


Fig 38. Bendtsen roughness of the samples. The layering trial points were 10%, 25% and 40% TMP of the dry weight stratified into the middle layer while chemical hardwood pulp was stratified into surface layers. In the mixture trial points, the same TMP and HW pulp proportions were blended as in the layering trial points. The two reference trial points were mixture of 60% HW and 40% SW, 40% SW in the middle layer and 30% HW stratified into both surface layers. Error bars show the 95% confidence interval of the mean of the measured values.

Air permeability as a function of bulk is shown in *Fig. 39A* (Publication VII). The chemical pulp had relatively high air permeability, which resulted from the low level of refining. Based on the density and air permeability of pure chemical and TMP sheets, the addition of TMP to the chemical pulp decreased both these quantities. Air permeability decreased by 60% when 20% of the chemical pulp was replaced by TMP. On the other hand, an addition of 10 or 20% PCC of the dry weight to the pure chemical pulp or pulp with 10 or 20% TMP of the dry weight increased bulk and the air permeability. Stratifying 20% PCC in the bottom and top layers of chemical pulp compared with the mixed structure decreased the air permeability by 25%. Mixing PCC with mechanical pulp (TMP) also increased the air permeability, even though the bulk decreased. Stratifying 20% TMP into the middle layer and 20% PCC into the surface layers decreased the air permeability by 20% compared with the results for an unstratified sheet structure.

Stratifying 10 or 20% PCC into the surface layers of sheets made of chemical pulp increased their bulk without significant changes in their roughness, *Fig. 39B*. On the other hand, the addition of PCC into TMP decreased the bulk and roughness. Mixing 20% PCC with chemical pulp gave a 65% higher roughness compared with a trial point, in which PCC was stratified into the surface layers. The addition of TMP into the middle layer or evenly into all the layers decreased the roughness more or less in the same way.

Mixing 20% PCC with pulp reduced the tensile index of handsheets made of a blend of chemical pulp. The consequent reduction in the tensile index was 70%, whereas in the case of TMP pulp the reduction for a similar addition of PCC was only 37% (*Fig. 39C*). This is probably related to the fact that TMP has a significantly higher wet surface area of fibrous material than chemical pulp. In other words, the addition of PCC has a relatively small effect on the surface area of the material that can form bonds in the paper network. Stratifying 20% PCC into the bottom and top layers of sheets made of blend of chemical pulp instead of mixing it into all the layers, increased the tensile strength of the samples by 38%.

The internal bond strengths by Huygen of pure TMP and the blend of chemical pulp were similar (*Fig. 39E*). In the internal bond strength, mixing PCC with chemical pulp also gave a higher reduction than for TMP samples. Stratifying PCC instead of mixing had only a minor effect on the internal bond strength of the samples. One argument against stratifying fillers and fibres has been the belief that layering may dramatically reduce the internal bond strength and therefore cause problems in printing, for example.

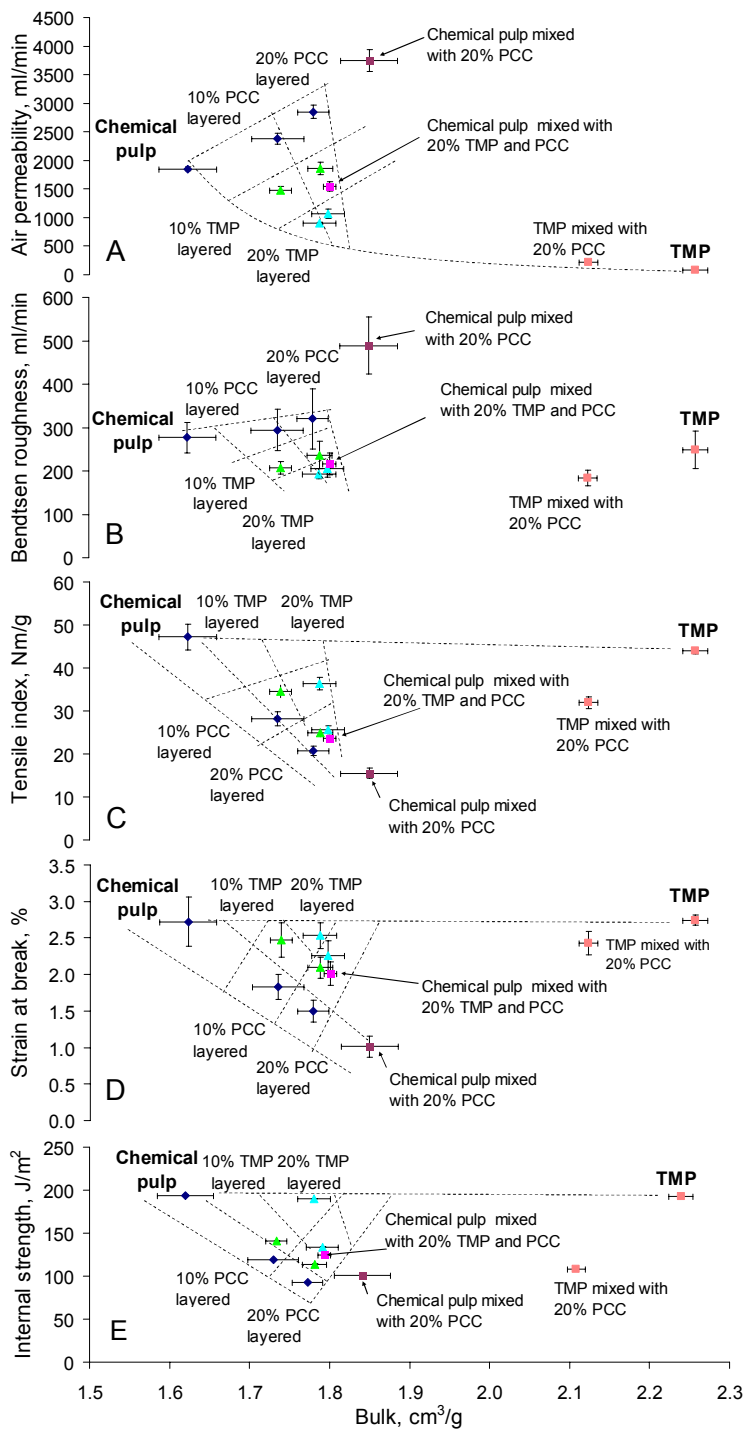


Fig 39. (A) Air permeability, (B) Bendtsen roughness, (C) tensile index, (D) strain at break and (E) internal bond strength by Huygen as a function of bulk. The wet press used was 3.5 bar (Lorentzen & Wettre). Error bars show the 95% confidence interval of the mean of the measured values.

### 6.3 Summary

The effects of stratification of PCC and TMP on the quality and mechanical properties of dry and wet (fine) paper were studied. The results of this study indicated that replacing softwood pulp with stratified TMP in the middle layer of the sheet enables a higher bulk, opacity and surface smoothness of the final product. Even a minor addition of TMP pulp into bleached hardwood pulp improved the tensile and relaxation properties of the wet web. The effect was slightly higher when TMP was homogeneously mixed with the chemical pulp instead of being stratified in the middle layer. Increase of the wet web tensile strength and improved relaxation properties enable an increase in the production speed of the paper machine, which leads to higher profitability. By replacing long fibres by TMP, the cost efficiency can be improved significantly through improved production speed, but also through lower raw material costs.

The filler content had a significant effect on all the mechanical properties of the dry and wet web. By stratifying PCC into the surface layers of paper, the tensile properties of dry samples were significantly increased, but only a minor negative effect on the wet web tensile strength and relaxation properties was observed. The mechanical properties of paper containing TMP were significantly less affected by an increased PCC content compared to paper made of only chemical pulp. The residual tension of wet pure TMP sheets was significantly higher than that sheets made of chemical pulp at a similar dry strength. An addition of 10...20% TMP into the middle layer of the sheets made of chemical pulp enabled a 10% addition of filler in the paper without any effect on the wet web tension holding ability at a constant dryness level. Graphical representation of these findings can be found in *Table 12*.

Table 12. Effect of various stratified structures on some papermaking characteristics and paper properties of sheets made of chemical pulps and TMP. Explanation for signs: ↑ increase, ↓ decrease and — no change in the measured value. X indicates that measurement was not carried out. The nature of changes is colour coded such that green is positive, red is negative and grey is positive or negative change.

		Non-stratified structures		Stratified structures (compared to non-stratified structures).	
		Addition of TMP to HW pulp.	Addition of PCC to SW/HW pulp blend	TMP in the middle and HW in the top layers	PCC in the top layers of SW/HW pulp blend
Dry sheet	Density	↓↓↓	↓↓↓	—	↑↑
	Roughness	↑↑↑	↑↑↑	↓↓↓	—
	Air permeability	X	↑↑↑	X	↑↑↑
	Tensile index	—	↓↓↓	—	↑↑↑
	Internal strength	X	↓↓↓	X	—
Wet	Wet strength	↑↑↑↑	↓↓↓	↓	—
	Res. Tension	↑↑↑↑	↓↓↓	↓	—

Stratification allows the use of TMP and high filler content in paper without loss of runnability of the wet web in the paper machine or deterioration of the end product quality. In addition, a layered structure may enable a decrease in the basis weight or the utilisation of low quality highly recycled pulp in the paper.

## 7 Conclusions

The objective of this thesis was to modify the surface chemistry of fibres and z-directional paper structure in order to find tools to improve the material efficiency of the fibres in the papermaking process. Selective removal of carbohydrates by enzymatic treatments, spray application of various biopolymers, and furnish stratification were evaluated as the strategies for increasing the material efficiency in the context of the modern papermaking process. The effects of the aforementioned treatments were evaluated by complex studies of dewatering characteristics, wet and dry strength properties, basic properties of paper, and permeability of the resulting paper samples. In addition, two new z-directional paper analysis methods were developed so as to characterise the layered furnish structures of paper. In general, several factors were found to have potential to improve the material efficiency of furnishes. Enzyme treatments of furnishes were found to enhance dewatering through whole paper machine, when spraying of chemicals was found to effectively improve wet and dry web strength and stratification of furnishes influenced positively on bulk, smoothness and dry strength

properties of the paper. Further, utilisation of these techniques separately and especially together can enable savings in raw material consumption (decreased grammage of paper grades), in raw material costs (increase of low-cost filler content in the paper). Also, these techniques can contribute positively to production efficiency in the paper machine (less web breaks or higher speed). The improved recyclability of fibres due to chemical treatments can be significant in the future as the recycling times of the fibres continues to grow.

Improved dewatering could be achieved several paper machine sections by surface modification of the fibre by enzymatic actions. Results indicate that hydrolysis of the colloidal polysaccharide layer on the fibres surfaces has an influence on the drainage properties of the pulp. It was also noted that degradation-specific carbohydrates of the TMP fibre increase the dry sheet bulk (but not with the chemical hardwood pulp), which further enables a higher wet pressing load and thus water removal in the press section.

Modification of this gel layer on the fibre surface by enzymes was observed to generally decrease the tension holding ability of the wet web, and thus the runnability potential of the furnish. On the other hand, application of enzymes can increase the dry solids content of the web after wet pressing, which improves the wet web runnability in the paper machine. Enzymatic modification of fibres was also found to enhance the drying rate of the wet web. Thus, improved production speed and thus increased production capacity could be possibly achieved by enzymatic treatment of the furnish. Dewatering characteristics can be improved by an optimal enzyme type and dosage, but strength losses of the paper cannot be avoided. Another aspect of enzyme utilisation is that enzymatic actions could possibly be used to replace refining or decrease the refining energy of unrefined chemical pulp in the paper mill environment. It is critical that enzymatic treatment of the furnish is optimised so that material loss remains at an acceptable level. Recovery of the dissolved sugars from process waters for another chemical application, in paper or for fuel production in a biorefinery mill could enable a high hydrolysis level of carbohydrates. The price of enzyme and its performance under process conditions also influences the profitability of the enzymatic application. In order to become commonly accepted, enzymatic utilisation has to be convenient and reliable.

Paper machine runnability and the strength properties of the end product are typically modified by several chemical additives. Based on this research, many of these chemicals could be replaced by xyloglucan-based chemicals alone. This can contribute to savings in the expenditure on chemicals and to more simplified and stable wet-end chemistry. Due to non-charged nature of xyloglucan it does not disturb the white water system of papermaking. Results also indicate that non-charged polysaccharides like xyloglucan are potential additives for improving the recyclability of pulps. As a consequence of improved fibre bonding, the need for refining decreases, which further improves the recyclability of fibres. Xyloglucan-based treatments could be applied at the pulp mill for enhancing bonding and extending the lifetime of fibre materials of never-dried pulp, or alternatively at the paper/board mill to enhance the runnability of virgin or recovered pulp and strength properties of the end product. Interestingly, the emerged enzymatic treatment of pulp and spray addition of XG in the paper mill could enable good drainage, runnability and end product quality at the same time.

Stratification of furnishes can have a significant effect on the material efficiency due to the enhanced quality, strength and runnability potential of paper. For example, in contrast to conventional papermaking, furnish stratification enables production of paper with high bulk and smooth surfaces. Moreover, savings in raw material costs can be achieved with stratified and high filler structures, without deterioration in the production efficiency or paper quality. However, new investments are necessary in the utilisation of stratification techniques in the mill. Despite a number of unresolved problems, stratification is a potential way of improving paper quality, making savings in raw material costs or improving the runnability of furnishes.

Enzymatic methods seem to have potential to intensify the water removal processes. But the surface chemical modifications also have potential to improve the strength of wet and dry paper, which is an essential requirement for reducing the raw material costs, either by reducing basis weight or by increasing the filler content. Stratification brings further freedom to tailor the surface properties independently of the central layer properties. Overall, these studies indicate that when aiming at reduced material and energy consumption, no single method is able to fulfil the partly conflicting demands. But by combining several unconventional techniques such as enzymatic treatment, spraying of chemicals and furnish stratification, the material efficiency of fibre could be substantially improved.

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# Enhancing dewatering of thermo-mechanical pulp (TMP) based papermaking through enzymatic treatment

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## Abstract

The aim of this work was to improve the dewatering characteristics of thermo-mechanical pulp (TMP) through enzymatic treatment without any significant reduction of the quality of the end product. The cellulose and hemicellulose content of TMP was altered by means of enzymatic treatments using different purified cellulases and hemicellulases as well as commercial enzyme preparations, in order to clarify the target carbohydrate components affecting the dewatering of TMP. The effects of enzymatic treatments on the properties of the pulp as well as its forming, pressing and drying were studied by lab scale measurements. An increased dewatering rate of TMP was observed in initial drainage, wet pressing and drying laboratory experiments, as a result of various enzymatic treatments. Interestingly, both cellulose and galactoglucomannan components in TMP were found to affect the dewatering properties of the pulp, and a greatest improvement in dewatering could be obtained with a combined treatment with an endoglucanase type of cellulase and mannanase.

**Keywords:** cellulose; dewatering; endoglucanase; enzymatic treatment; glucomannan; paper machine; runnability; thermo-mechanical pulp (TMP); wet strength; xylan.

## Introduction

The dewatering properties of the pulp greatly affect the energy efficiency of paper machines, and thus the cost efficiency of papermaking. Enhanced water removal in the former and press section enables lower energy consumption in the dryer section or increased production capacity, or alternately a shorter drying section, and thus decreased investment costs. In mechanical pulping, refiners are used to separate and further fibrillate fibres. The share of short fibre fractions and fibrils is increased during refining. An increase in small particles decreases drainage of wet web in the paper machine. Furthermore, it has been shown that fibrillar small particles have dewatering characteristics very different from flake-like

particles (Luukko and Paulapuro 1999). Conventionally, dewatering is improved in the paper machine by means of drainage aids in the former section or more intense wet pressing in the press section. Drainage aids can, however, worsen formation (Caram et al. 1996), and high wet press levels reduces the bulk of the end product. For this reason, new pulp modification and dewatering innovations are required with new high capacity paper machines (King et al. 1998).

The application of enzymes in the pulp and paper industry has been reviewed by Viikari et al. (2009). Recently, thermo-mechanical pulps (TMP) were activated by laccases (Lähdele et al. 2009), specific refining energy in alkaline peroxide mechanical pulping was reduced by enzyme impregnation (Hart et al. 2009), the influence of mannanase and endoglucanase treatment on CTMP was investigated by Strey et al. (2009), and the effects of cellobiohydrolyse on properties of hardwood pulps were reported by Suchy et al. (2009). Dewatering of different paper and board grades was also improved as a result of enzymatic treatment. Drainage improvement of up to 26% measured as SR value was observed in highly refined chemical pulps modified by various enzymatic treatments (Mansfield et al. 1996; Moran 1996; Kantelinen et al. 1997; Mooney et al. 1999). In mechanical pulps (Mansfield et al. 1996; Wong et al. 2000) and recycled pulps (Pommier et al. 1989; Stork et al. 1995; Caram et al. 1996; Nagarajan and Sarkar 1996) a better drainage has been detected in the paper machine due to enzymatic treatments. With dewatering limited paper machines, machine speed could be increased up to 15% (Pommier et al. 1990; Caram et al. 1996).

Enzyme mixtures containing cellulases and hemicellulases have been advanced as affecting the dewatering by the hydrolysis of fines, resulting in the reduced surface area of the pulp (Richardson et al. 1998) and by the modification of the colloidal polysaccharide layer on the fibre surface (Stork et al. 1995; Kantelinen et al. 1997; Stenius et al. 1996–2000). It has also been suggested that shorter fibres are more susceptible to the enzymatic attack than longer ones, as they are exposed with a larger specific surface area to the enzymes (Pala et al. 2001). Other effects of enzymatic treatments related to improved drainage are the reduction of fibre fibrillation (Stork et al. 1995), the shortening of damaged fibres, and the swelling of the cell wall of broken fibres (Gruber and Gelbrich 1997).

Stork et al. (1995) suggested that endoglucanase treatment is essential to increase dewatering of recovered papers by enzymatic means. Cellobiohydrolase and xylanase treatment can further increase drainage of recycled papers. The effect of enzymatic treatments on drainage improvement of mechanical pulps has been, however, little studied (Mansfield et al. 1996; Wong et al. 2000). The content of galac-

toglucmannan (GGM) and xylan in spruce TMP is about 15–20% and 5–10% of dry pulp, respectively (Stenius 2000). These hemicelluloses can be partially and very specifically hydrolysed from the pulp material by mannanase and xylanase. Endoglucanases can catalyse the hydrolysis of cellulose, but also xylan and GGM from pulp materials. In addition, endoglucanase I (EG I) produced by *Trichoderma reesei* has been shown to act both as a cellulase and xylanase (Suurnäkki et al. 2000). In mechanical pulps, the surface carbohydrates can mainly be attacked by enzymatic hydrolysis. This is due to the limited accessibility of enzymes to the inner fibre wall of mechanical pulp fibres. For this reason, the enzymatic modifications carried out for TMP in this work represent the modifications of the accessible surfaces of pulp material, e.g. fibres and fines.

In this work, the effect of partial removal of pulp cellulose and hemicelluloses, GGM and xylan were elucidated in terms of dewatering and other papermaking properties and technical properties of spruce TMP. Purified endoglucanases, xylanase and mannanase enzymes originate from fungus *Trichoderma reesei* and their mixtures, as well as commercial cellulase preparations, Ecoston L900 and Novozym 476, were applied. The mechanism of enzyme-aided dewatering in mechanical pulp was clarified by studying the correlation between the amount, type and location of carbohydrates modified by the enzymes and the dewatering properties of modified TMP.

## Materials and methods

### Pulp and enzymatic treatments

Unbleached TMP was obtained from a Finnish pulp mill. The freeness value (L&W, App. 30, Type 6-1, Kista, Sverige) of the TMP was 60 ml and length-weighted average fibre length was 1.4 mm, with 40% fines content (L&W FiberMaster STFI, code 910, type 974711, Kista, Sverige). The never-dried pulp was stored in the freezer and melted and disintegrated by SCAN-C 18:65 (Noram, L&W, CA371, Canada) prior to the experiments. Xylanase, mannanase, endoglucanase I (EG I) and endoglucanase II (EG II) originating from fungus *Trichoderma reesei* were produced and purified at VTT as previously described (Tenkanen et al. 1992; Ståbrand et al. 1993; Suurnäkki et al. 2000). Commercial cellulase preparations

**Table 1** Enzyme preparations and their characteristics.

Abbreviation of enzyme	Description	Protein cont. (mg ml <sup>-1</sup> )
EG I	<i>T. reesei</i> endoglucanase I, purified	5.1 10.0
EG II	<i>T. reesei</i> endoglucanase II, purified	
MAN	<i>T. reesei</i> mannanase, purified	4.4
XYL	<i>T. reesei</i> xylanase, purified	3.2
Ecoston L900	Commercial EG-rich cellulase and hemicellulase preparation	162
Novozym 476	Commercial monocomponent cellulase preparation	14.8

Ecoston L900 (courtesy of AB Enzymes, Finland) and Novozym 476 (courtesy of Novozymes, Denmark) were also investigated. The protein content of the enzyme preparations is presented in Table 1.

Enzyme dosages were: 0.01, 0.05, 0.1, and 0.5 mg protein g<sup>-1</sup> of the dry pulp. In addition, a dosage of 0.1+0.1 mg protein g<sup>-1</sup> of the dry pulp was applied in combined xylanase + mannanase treatment. Standard conditions of enzyme treatment: 5% pulp consistency, pH 5 adjusted by 0.1 M sulphuric acid, at 50°C and for 2 h, 5 h, or 24 h. Replicates were carried out for each enzymatic treatment. After enzymatic treatment, the pulp was filtered twice, then a filtrate sample was taken, and finally the pulp was washed with ion exchanged water prior to testing for papermaking properties. The reference treatments were performed as described above, but without addition of enzymes.

### Analyses

Carbohydrates solubilised in the enzymatic treatments were analysed as monomers after secondary enzymatic hydrolysis by HPLC, as previously described (Buchert et al. 1993). The coefficient of variation in high-performance liquid chromatography (HPLC) analysis was under 5%.

The drainage properties of pulp samples were analysed by WRV measurement and by a vacuum-assisted sheet former designed by VTT in co-operation with Metsä Paper. With the vacuum-assisted sheet former 20 kPa and 30 kPa vacuum levels were utilised to form a 60 g m<sup>-2</sup> sheet of area 320×220 mm<sup>2</sup>. A commercial paper machine fabric was used as a forming fabric, as the sheet forming consistency was between 0.02–0.04%. During drainage, the surface level was monitored with an ultrasonic detector, and the vacuum level with pressure sensors. Drainage data were computer collected and plotted as dewatering curves of each pulp sample.

Hand sheets of enzyme-treated TMP were prepared with a laboratory sheet mould to 60 g m<sup>-2</sup> basis weight according to SCAN-C 26:76. In order to achieve two sheet density levels, half of the laboratory sheets were wet pressed at 0.5 bar and the other half at 3.5 bar level in a laboratory sheet wet press (Lorentzen & Wettre). Table 2 presents the standards used in the determination of paper-technical properties of paper and pulp samples. Sheet samples were stored and tested in an air-conditioned laboratory where the relative humidity is 50% and the temperature 23°C.

Dynamic tensile strength and relaxation properties of samples were measured with an impact, fast tensile strength testing rig (Kurki et al. 1999, 2004). The average straining velocity was 1 m s<sup>-1</sup> (while standard tensile strength test velocity is 22 mm min<sup>-1</sup> = 0.00037 m s<sup>-1</sup>). The relaxation properties after a certain relaxation time were measured at a strain of 1% for dry samples and wet samples. The relaxation time was 0.475 s for wet samples. Tensile properties were also measured for dry and wet samples.

**Table 2** Standards for testing of pulp and paper.

Procedure	Standard
Bendtsen air permeability	SCAN-P 26:78
Bendtsen roughness	SCAN-P 84:01
Disintegration (cold and hot)	SCAN-C 18:65
Fibre length (L&W FiberMaster STFI)	ISO/DIS 16065-2
Freeness	SCAN-C 21:65
Grammage	SCAN-P 6:75
Tensile strength	SCAN-P 38:30
Scott Bond	TAPPI T 403
Thickness	SCAN-P 7:75

In order to measure drying time and forces, an impingement drying unit (Hartnett and Irvine 1977) was applied to a standard tensile tester with infrared on-line dry content measurement. Testing parameters: temperature of drying air 110°C, distance between sample holding chaws 100 mm, width of sample 70 mm, pre-load of sample 1 N.

Surface composition of the pulps: electron spectroscopy for chemical analysis (ESCA) according to Koljonen et al. (2003).

Fines particles of the TMP sample were classified into fibrillar and non-fibrillar material by image analysis (Luukko 1999) and the results are expressed as apparent mass share including the ray cell proportion of the fibrillar material.

## Results and discussion

### Effect of enzymatic treatments on TMP freeness and WRV

The effect of the extent and type of enzymatic modification on the water retention of TMP was studied with the aid of both purified *T. reesei* cellulases (EG I, EG II) and hemicellulases (xylanase, mannanase) and two commercial cellulase preparations – Ecostone L900 and Novozym 476 (Table 1). The maximum degree of carbohydrate hydrolysis, about 1.3–1.4% of the dry weight of TMP, was achieved in the extensive EG I and EG II treatments (protein dosage of 0.5 mg g<sup>-1</sup>, Table 3). Interestingly, galactoglucomannan (GGM) was the most accessible component for the purified endoglucanases both at a low and high level of hydrolysis

(Table 3). In addition to GGM, cellulose, and in the case of EG I also xylan, was solubilised from TMP in the endoglucanase treatments. There are specific results in the literature about the performance of purified *T. reesei* cellulases: 1) EG I was active both on xylan, cellulose and, to a minor extent, on GGM if applied for both coarse mechanical pulp and bleached softwood kraft pulp. 2) EG II solubilised mainly cellulose and GGM in the bleached softwood kraft pulp (Pere et al. 2000; Suurnäkki et al. 2000). Mannanase and xylanase treatments of TMP were very specific for the hydrolysis of pulp GGM and xylan, respectively (Table 3). In the most extensive treatments, about 1% of the TMP was solubilised. No synergism in the action of xylanase and mannanase in TMP hydrolysis was observed, as the total amount of hemicellulose solubilisation was 1.3% of the pulp, independently of the separate or common use of the enzymes (Table 3). Treatment of TMP with Ecostone L900, a commercial endoglucanase-rich mixture of cellulases and hemicellulases, affected all the carbohydrate components in the pulp (Table 4). Carbohydrate solubilisation of 1% of the pulp was obtained with a 2-h treatment with a protein dosage of 0.5 mg g<sup>-1</sup> of pulp. The other commercial enzyme preparation used, Novozym 476, was highly specific to cellulose hydrolysis (Table 4). Unlike in the treatment with Ecostone L900, the degree of hydrolysis remained at the moderate level of 0.8% of the TMP even in the case of the most extensive Novozym 476 treatment.

The effects of the specific and partial enzymatic removal of carbohydrates from TMP by the enzymes on the water

**Table 3** Carbohydrates solubilised from TMP in treatments with purified *T. reesei* cellulases and hemicellulases. Standard treatment conditions were (50°C, 2 h or in the case of 0.5 mg/g dosage 5 h\* or 24 h\*\*).

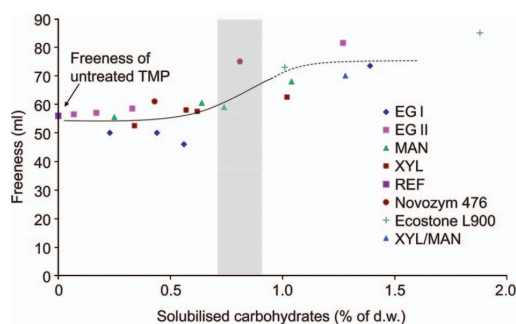
Enzyme	Dosage (mg g <sup>-1</sup> )	Σ of solubil. CH (%)	Composition of solubilised carbohydrates (CH)						Solubilised compounds <sup>1</sup>		
			Glc (%)	Man (%)	Gal (%)	Xyl (%)	Ara (%)	MeGlcA (%)	Cell (%)	GGM (%)	Xylan (%)
EG I	0.01	0.23	0.07	0.12	0.01	0.02	0.01	0	0	0.2	0
	0.05	0.44	0.16	0.20	0.01	0.04	0.02	0.01	0.1	0.3	0.1
	0.1	0.56	0.23	0.23	0.01	0.06	0.02	0.01	0.2	0.3	0.1
	0.5*	1.39	0.67	0.47	0.03	0.17	0.02	0.03	0.5	0.6	0.2
EG II	0.01	0.07	0.01	0.04	0	0.01	0.01	0	0	0.1	0
	0.05	0.17	0.06	0.10	0	0.01	0	0	0	0.1	0
	0.1	0.33	0.11	0.19	0.01	0.01	0.01	0	0.1	0.2	0
	0.5*	1.27	0.72	0.52	0.03	0	0	0	0.5	0.7	0
MAN	0.01	1.31	0.73	0.52	0.03	0.03	0.01	0	0.5	0.7	0
	0.05	0.25	0.05	0.19	0.01	0	0	0	0	0.2	0
	0.1	0.64	0.13	0.48	0.03	0	0	0	0	0.6	0
	0.5*	0.74	0.15	0.55	0.03	0	0.01	0	0	0.7	0
XYL	0.01	1.04	0.23	0.76	0.05	0	0	0	0	0.9	0
	0.05	0.34	0	0	0	0.27	0.03	0.04	0	0	0.3
	0.1	0.57	0	0	0	0.45	0.05	0.07	0	0	0.5
	0.5*	0.62	0	0	0	0.50	0.06	0.08	0	0	0.6
XYL+MAN	0.1+0.1	1.02	0	0.02	0	0.80	0.08	0.12	0	0	0.9
	0.1+0.1**	1.28	0.15	0.56	0.03	0.43	0.05	0.06	0	0.7	0.5
		1.50	0.15	0.50	0.04	0.64	0.06	0.11	0	0.7	0.7

<sup>1</sup>Polysaccharides were calculated from solubilised monosaccharides. The following monosaccharide ratio was used for galactoglucomannan (GGM): galactose:glucose:mannose 0.1:1:4. Xylan includes xylose, methyl glucuronic acid (MeGlcA) and arabinose. EG I, endoglucanase I; EG II, endoglucanase II; MAN, mannanase; XYL, xylanase. Percentages are based on o.d. weight.

**Table 4** Carbohydrates solubilised from TMP in treatments with commercial enzyme preparations Ecostone L900 and Novozym 476. Enzyme dosage 0.5 mg protein g<sup>-1</sup> of TMP (MAN 0.01 mg g<sup>-1</sup>) and standard treatment conditions (see Table 3) were used.

Enzyme treatment	Time (h)	Σ of solubil. CH (%)	Composition of solubilised carbohydrates (CH)						Solubil. compounds <sup>1</sup>		
			Glc (%)	Man (%)	Gal (%)	Xyl (%)	Ara (%)	MeGlcA (%)	Cell (%)	GGM (%)	Xylan (%)
Ecostone L900	2	1.01	0.52	0.30	0.01	0.14	0.03	0	0.40	0.36	0.17
	24	1.88	0.94	0.43	0.03	0.37	0.05	0.06	0.75	0.54	0.42
Novozym 476	2	0.43	0.38	0.05	0	0	0	0	0.33	0.06	0
	24	0.81	0.67	0.11	0.01	0.02	0	0	0.58	0.13	0.02
Novozym 476 +MAN	2	0.89	0.55	0.29	0.02	0.01	0.01	0	0.4	0.4	0

<sup>1</sup>Polysaccharides were calculated from solubilised monosaccharides. The following monosaccharide ratio was used for galactoglucomannan (GGM): galactose:glucose:mannose 0.1:1:4. Xylan includes xylose, methyl glucuronic acid (MeGlcA) and arabinose.



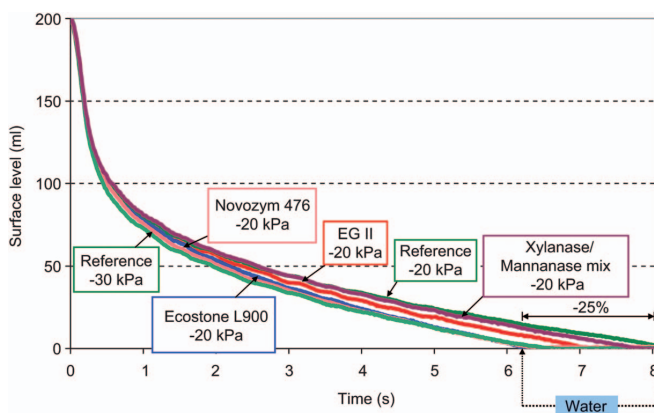
**Figure 1** Freeness vs. the amount of carbohydrates solubilised in the enzyme-treated TMP. Enzymatic treatments as explained in Tables 3 and 4.

removal properties were evaluated by plotting the freeness values of enzymatically modified TMP against the amount of carbohydrates solubilised (Figure 1). In low amounts of carbohydrate solubilisation with EG I and xylanase, about a 10% decrease in the freeness of TMP was observed. To elevate the freeness value of the pulp significantly, 15% or

more, solubilisation of 1% or more of the pulp dry weight was needed (Figure 1). EG II treatments resulted in a greater improvement of freeness than did EG I treatments. The freeness value of TMP was also higher after treatment with mannanase than with xylanase or after a combined xylanase-mannanase treatment. Obviously, the partial removal of xylan from TMP was not beneficial to the freeness improvement. TMP treated extensively with either of the commercial enzyme preparations had more than 15% higher freeness values than the reference TMP. No correlation between water retention value (WRV) and the amount of solubilised carbohydrates was observed (results not shown). Previously, Wong et al. (2000) reported that no substantial increase in freeness was achieved when PRMP (pressurised refiner mechanical pulp) long fibre-rich fraction was hydrolysed by commercial cellulase (Novozyme SP 342, 1.7% solubilisation of carbohydrates).

### Water removal from enzyme-treated TMP

The significance of the freeness increase induced by enzymatic treatments was evaluated: the time needed for dewatering of reference and enzyme-treated pulps was measured



**Figure 2** Dewatering rate of enzyme-treated TMP measured with a vacuum-assisted sheet former. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h.

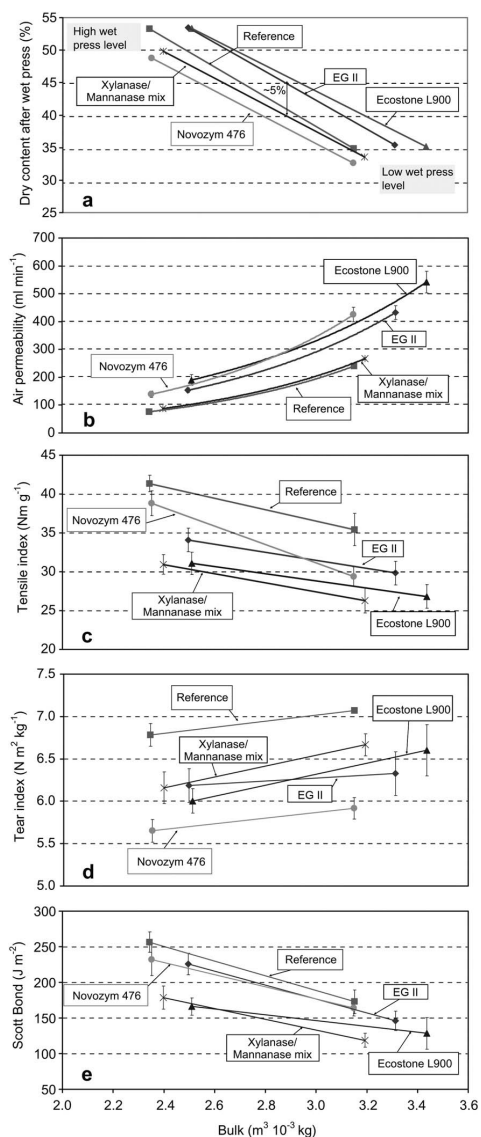


in a vacuum-assisted sheet former (Figure 2). TMP was treated with an enzyme dosage of 0.5 mg protein g<sup>-1</sup> pulp for 2 h, 5 h, or 24 h, resulting in a sufficient hydrolysis level and clear freeness increment (Tables 3 and 4, Figure 1). Treatment of TMP by EG II, Ecostone L900 or Novozym 476 reduced the dewatering time by 25% (Figure 2). TMP treated with Novozym 476 or Ecostone L900 preparation gave the same dewatering time with -20 kPa vacuum level as the untreated reference TMP with -30 kPa vacuum level. The partial hydrolysis of the hemicellulose components from the pulp by combined xylanase-mannanase treatment had only a minor effect on the dewatering time. The role of endo-glucanases in enhancing the drainage of recycled pulp consisting of mechanical pulp has previously been reported by Stork et al. (1995). Nagarajan and Sarkar (1996) measured the reduction in filtration resistance of recycled pulp resulting from enzyme treatment with cellulolytic enzyme by Genecor (Pergalase A-40).

The effect of enzymatic treatments (Tables 3 and 4) on water removal in wet pressing was measured by analysing the dry solids content of a hand sheet after wet press. TMP treated with Ecostone L900 or with EG II solubilising both cellulose and GGGM from the pulp gave the highest dry solids content after wet press in a given dry sheet bulk (Figure 3a). Treatment with Ecostone L900 raised the dry solids content of TMP by 5% after wet press as compared with reference-treated TMP (Figure 3a). After wet press section, 5% higher dry solids content signifies substantial energy savings in the dryer section, as drying energy can be reduced or alternatively production capacity increased (Moran 1996). Degradation of hemicellulose alone by combined xylanase-mannanase treatment or cellulose by Novozym 476 treatment did not result in an increase in the dry content of a hand sheet after wet press (Figure 3a). Based on these results, it seems that both cellulose and glucomannan needs to be degraded (or modified) in TMP in order to achieve the enhanced water removal in sheet pressing.

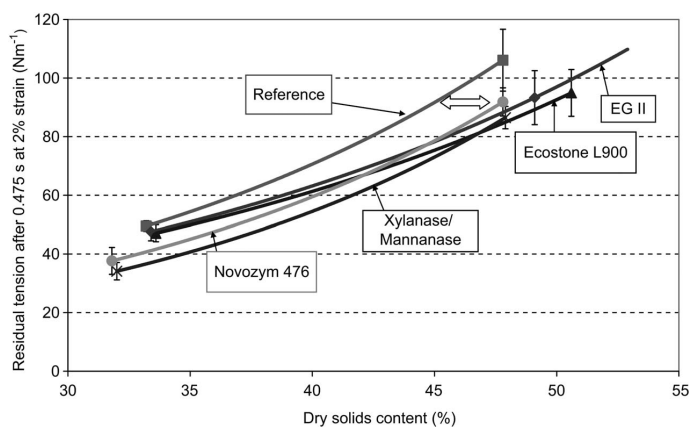
Wet paper tension holding capacity was decreased with all the enzyme treatments in a given dry solids content (Figure 4). On the other hand, increased dry solids content with EG II and Ecostone L900 treated TMP (Figure 3a) is expected to enhance wet paper tension holding capacity and thus paper machine runnability. In the case of TMP treated with mixture of xylanase and mannanase or Novozym 476, reduced tension holding capacity cannot, however, be compensated by increased dry content after wet press without a loss of bulk compared to untreated TMP (Figures 3a and 4). At mill scale, the influence of enzymatic treatments on the wet strength of web has been also observed. Rutledge-Cropey et al. (1998) have reported an increase in wet web strength in press section due to cellulase treatment of recovered paper in a paper mill.

The influence of the Ecostone L900 treatment of TMP on the drying time of paper sheet was studied (Figure 5). The drying rate of sheet samples was increased by 20% due to enzymatic treatment. There is a probable relationship between increased air permeability and drying rate with impingement drying due to cellulase treatment. All enzyme

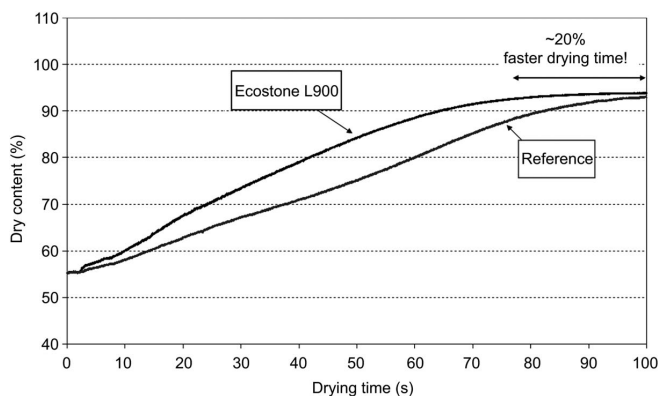


**Figure 3** Dry content after wet press (a), air permeability (b), tensile index (c), tear index (d) and Scott Bond (e) of enzyme-treated TMP vs. dry sheet bulk. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h.

treatments on TMP reduced drying-induced shrinkage of sheet (Table 5). In particular, degradation of hemicelluloses, xylan and GGGM by combined xylanase-mannanase and Ecostone L900 treatment reduced shrinkage significantly by 20% in laboratory sheets. The charge of fibre has an influence on fibre swelling (WRV) (Schönberg et al. 2001) and thus on sheet shrinkage; furthermore, hemicellulose content



**Figure 4** Residual tension of wet web after strain as a function of dry solids content. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h.



**Figure 5** Drying time of TMP enzyme-treated wet sheets with Ecostone L900. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h. On-line IR-measurement of dry content during hot-air drying of wet-pressed sheets.

has a correlation with the anionicity of fibre (Stenius et al. 2000; Schönberg et al. 2001).

#### Physical properties of TMP handsheets

The bulk of laboratory sheet increased 5–10% due to TMP treatment with Ecostone L900 and EG II hydrolysing hemi-

cellulose and the cellulose part of fibre (Tables 3, 4 and 5). Partial hydrolysis of hemicelluloses alone in combined xylanase-mannanase treatment or cellulose in Novozym 476 treatment of TMP (Tables 3 and 4) did not influence dry sheet bulk (Table 5). Figure 6 shows cross-directional images of paper sheet made of Ecostone L900 treated with TMP and untreated reference. The increase in sheet bulk probably orig-

**Table 5** Technical properties of paper prepared from enzyme-treated TMP as a function of handsheet bulk.

TMP treatment	Bulk (m <sup>3</sup> 10 <sup>-3</sup> kg) at		Air permeability (ml min <sup>-1</sup> ) at		Shrinkage (%)
	0.5 bar	3.5 bar	0.5 bar	3.5 bar	
Reference	3.15	2.34	241±3	77±5	2.3±0.14
EG II	3.31	2.50	433±24	154±9	2.0±0.08
Ecostone L900	3.44	2.51	542±39	190±20	1.8±0.07
Novozym 476	3.15	2.35	425±26	139±12	2.1±0.04
XYL+MAN	3.19	2.40	267±4	88±3	1.9±0.02

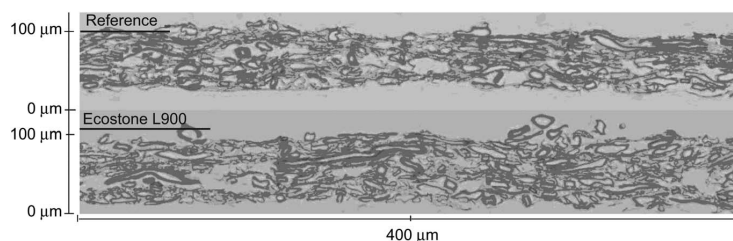
inated from the more intense initial dewatering and reduced web shrinkage due to enzyme treatments. Partial hydrolysis of cellulose from TMP increased air permeability of sheets, whereas modification of hemicellulose did not have an influence on the porosity of fibre network (Tables 3, 4, and 5, Figure 3b). These results correlate with Mansfield et al. (1996), who also reported increased bulk and air permeability resulting from the enzymatic treatment of mechanical pulp.

All enzyme treatments of TMP reduced the tensile index, tear index and Scott Bond (Figure 3c, d and e) of sheets. Partial hydrolysis of pulp hemicelluloses corresponding to hydrolysis of 1.3/1.5% of the dry weight of TMP by Ecoston L900 or combined xylanase-mannanase treatment reduced tensile and tear strength by 20–30% and Scott Bond by 30% in a given bulk. Hydrolysis of the cellulose part of pulp by EG II or Novozym 476 treatment corresponding to hydrolysis of 1.3% or 0.8% of the dry weight of TMP, respectively, reduced tensile and tear strength by 10–20%, whereas the Scott Bond was retained at a high level, decreasing by only 10% as compared with that of reference pulp. In general, changes in structural (Figure 3b, Table 5) and strength (Figure 3) sheet properties due to enzymatic treatments were relevant based on the scale of deviation errors of the results. Reductions in the strength of fibres and thus fibre networks due to enzymatic treatments are widely documented (Pere et al. 1995; Stork et al. 1995; Oksanen et al. 2000; Seo et al. 2000).

### Fines and surface composition of TMP

The partial hydrolysis of fines and/or polysaccharide gel present on the fibre surface has been proposed as the reason for the drainage improvement in recycled and virgin kraft pulp furnishes (Pommier et al. 1990; Kantelinen et al. 1997). The effect of enzymatic treatments in focus of this work was analysed concerning the content of fibrillar fines and ray cells in TMP fines. In the reference TMP, the apparent fibrillar fines and ray cells represented 44% and 4% of the total fines, respectively (Table 6). The changes in apparent fibrillar fines content due to enzymatic treatments were small. All enzymatic treatments other than those with Novozym 476 slightly reduced the amount of fibrillar fines. Treatment with Novozym 476 together with mannanase was the only one to cause a slight reduction in the ray cell proportion in the fines. Apparently, the action of Novozym 476 on pulp fines differed from that of the other enzymes tested in the work. No clear correlation between the effect of enzymatic treatment on the type of fines and on water removal could, however, be found.

The effect of the enzymatic treatments on the chemical composition of the pulp outer surfaces was analysed by ESCA from the handsheets prepared from the enzymatically modified TMP. An increase in aliphatic carbon bonds (C-C), indicating an exposure of lignin and/or extractives on the pulp surfaces, was observed in EG II and Ecoston L900-treated samples (Table 7). The content of carbon-oxygen (C-



**Figure 6** Microtome pictures of paper sheets made of Ecoston L900 treated TMP and untreated reference. Laboratory sheet wet press level was 3.5 bar. 200 $\times$  magnification. Treatment dosage and time: 0.5 mg protein g<sup>-1</sup> dry pulp, 24 h.

**Table 6** Apparent fibrillar content of TMP treated with various purified and commercial enzyme preparations (treatments as in Table 4).

Enzyme treatment		Fibrillar material (%)	Ray cell mass (%)
Enzyme	Dosage, time		
–	24 h	44	4
EG II	0.5 mg g <sup>-1</sup> , 24 h	43	6
Ecoston L900	0.5 mg g <sup>-1</sup> , 24 h	43	5
Novozym 476	0.5 mg g <sup>-1</sup> , 2 h	46	5
Novozym 476	0.5 mg g <sup>-1</sup> , 24 h	45	5
Novozym 476+MAN	0.5+0.01 mg g <sup>-1</sup> , 2 h	46	3
MAN	0.01 mg g <sup>-1</sup> , 2 h	43	6
XYL+MAN	0.1+0.1 mg g <sup>-1</sup> , 24 h	43	5

**Table 7** ESCA analysis of the handsheets prepared from TMP samples treated with various purified and commercial enzyme preparations (std. treatment conditions). The units in ESCA analysis indicate the relative amount of carbons in different oxidation levels (rel. % of C).

Enzyme treatment of TMP		Data of ESCA analysis			
Enzyme	Dosage, time	C-C	C-O	C=O	O-C=O
–	24 h	44.0±0.1	44.4±0.4	8.6±0.4	3.1±0.1
EG II	0.5 mg g <sup>-1</sup> , 24 h	45.4±0.7	44.0±0.6	8.1±0.3	2.5±0.3
Ecoston L900	0.5 mg g <sup>-1</sup> , 24 h	47.2±0.5	43.1±0.3	7.8±0.2	2.0±0
Novozym 476	0.5 mg g <sup>-1</sup> , 2 h	40.4±0.5	48.0±0.3	9.0±0.1	2.7±0.2
Novozym 476	0.5 mg g <sup>-1</sup> , 24 h	38.0±0.5	50.5±0.4	8.9±0.2	2.5±0.2
Novozym 476+MAN	0.5+0.01 mg g <sup>-1</sup> , 2 h	40.7±0.5	47.9±0.2	8.9±0.2	2.5±0
MAN	0.01 mg g <sup>-1</sup> , 2 h	43.1±0.2	45.6±0.4	8.9±0.3	2.5±0.3
XYL+MAN	0.1+0.1 mg g <sup>-1</sup> , 24 h	45.0±0.9	45.2±0.5	7.8±0.2	2.0±0.2

O) bonds, indicating the reduction of carbohydrates on the pulp surfaces, was clearly observed in an Ecoston L900-treated sample, which also had the highest level of hydrolysis, 1.9% of d.w. (Table 4). Treatment of TMP with Novozym 476 as such or together with mannanase resulted in a reduction in aliphatic carbon-containing structures and an increase in C-O bond related to carbohydrates (Table 7). The limited hydrolysis of cellulose from TMP with Novozym 476 (Table 4) seems therefore to remove lignin and/or extractives from the fibre surface, resulting in fibre surfaces with a higher carbohydrate content. Combined xylanase-mannanase treatment had no effect on the carbohydrate or aromatic group coverage on the pulp surfaces (Table 7). Ecoston L900 and combined xylanase-mannanase treatments, removing xylan from the pulp, reduced the carboxylic acid content of the fibre surface. The changes in the surface coverage of carbohydrates by enzymatic treatments seem to correlate with the effect of the treatments on water removal by pressing (Table 7, Figure 3a).

## Conclusions

In order to increase the freeness value of TMP, the solubilisation of ~1% of carbohydrates were needed. The freeness of TMP increased at best from 60 ml to ~80 ml due to cellulase treatments with Ecoston L900, Novozym 476 and EG II. The dewatering time in a vacuum-assisted sheet former decreased by 25%. Hydrolysis of hemicelluloses alone had only minor effects on initial dewatering. Dry solids content increased by 5% after wet press for a given dry sheet bulk with Ecoston L900 and EG II treatments. Results indicated that both the cellulose and hemicellulose (glucomanan) parts of the fibre had to be modified in order to increase the dry solids content after wet press. The tension holding ability of wet web was reduced with both cellulase and hemicellulase-treated TMP. But then, enzymatic treatments with Ecoston L900 and EG II increased dry solids content after wet press in certain dry sheet bulk, which enhances paper machine runnability. Increased dry solids content after press section means a saving in drying energy or alternately increased production. Also, a slight increase in the drying rate was observed with enzyme Ecoston L900. The probable

explanation for an increased drying rate is a more bulky and porous fibre network with enzymatic treated pulp. Reduced shrinkage forces due to hydrolysis of fines and surface hemicelluloses are a probable explanation for the increase in bulk with enzymatic treated mechanical pulps. As expected, dry sheet strength properties decreased due to hydrolysis of carbohydrates. Hydrolysis of the cellulose part of fibre reduced the tensile index by 10–20%. The degradation of hemicelluloses reduced the strength of the fibre network, as tensile index was reduced by 20–30%. The influence of the hydrolysis of cellulose on Scott Bond was limited, whereas the modification of hemicelluloses induced a substantial decrease in Scott Bond. In general, enzymatic treatments had an influence on all dewatering phases of papermaking. What is more, end product quality was affected by enzymatic treatments.

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# Improving Papermaking Process by Controlled Modification of Pulp Carbohydrates

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## ABSTRACT

Effects of carbohydrate composition on flocculation, drainage, wet web tension, drying rate, and end-product quality of bleached birch kraft pulps were examined by laboratory handsheets and in pilot former trials. Carbohydrate composition of unrefined and refined never-dried birch pulps were modified with cellulases and hemicellulases. Dewatering, wet web tension, and drying characteristics of the modified pulps were analysed using versatile analytical instruments. Pilot former enabled on-line monitoring of chemical and physical state of the process. Flocculation of fibre suspension was measured on-line with CCD cameras from the headbox of the pilot former. Flocculation results were accompanied by dry sheet formation measurements. Enhanced initial dewatering by modification of carbohydrates was observed in pilot former. Depending on the modified carbohydrate, i.e., xylan or cellulose, and the extent of the enzymatic treatment, the tensile strength of wet sheet samples increased or decreased. Drying rate was noticed to increase due to specific modification of carbohydrates. Enhanced dewatering, tensile strength, and sheet smoothness could be simultaneously achieved by controlled modification of carbohydrates. Modification of carbohydrates of bleached birch pulp had significant influences on all paper-making sections of paper machine.

## INTRODUCTION

Dewatering properties of the pulp strongly affects the energy efficiency of paper machine and thus the cost efficiency of papermaking. Enhanced water removal in former, press, and dryer sections enables lower energy consumption or increased production capacity. Alternately, due to improved drainage, a shorter drying section would decrease investments costs. Conventionally, dewatering is increased in a paper machine by using drainage aids in the former section or more intense wet pressing in the press section. Use of drainage aids can worsen formation [1], and high wet press levels decreases the bulk of the end-product. A high dewatering rate is typically inversely related to sheet strength and smoothness. The typical way to enhance dry sheet properties is to increase the refining of pulp and thus reduce the dewatering of pulp. Therefore, novel pulp modification and dewatering innovations are required with a new high capacity paper machine. Dewatering of different paper and board grades has been reported to be improved due to enzymatic treatments. Drainage improvement up to 26 % measured as an SR value has been reported in highly refined chemical pulps by enzymatic treatment [2,3,4,5]. End-product quality has to remain at a good level after dewatering improvement. The objective of this work is to explore the dependency of surface chemistry on dewatering characteristics and critical paper technical properties.

## Material and Methods

ECF (Elemental Chlorine Free) birch pulp in a never-dried form was delivered from a Finnish pulp mill. Pulp was delivered after bleaching at a 15 % consistency. The mean fibre length of pulp was 0.92 mm and fine content was 6 %. Pulp was further refined with the laboratory refiner LR40 at a low intensity of 0.3 J/m to 80 kWh/t energy level. The surface chemistry of birch pulp was modified with enzymatic treatments. *Trichoderma reesei* endoglucanase I and II (EG I and II) were produced and purified at VTT. Commercial cellulase and xylanase preparations, Ecostone L900 and Ecopulp TX 200A from AB Enzymes (Finland), were used in dynamic pilot trials. Enzymatic treatments were carried out in a pulp consistency of 2 %, pH 5, at 50 °C for 1 - 16 h. Liberation of carbohydrate oligosaccharides into treatment liquors was evaluated by HPLC analysis. Dewatering was evaluated as Canadian Standard Freeness (CSF), Water Retention Value (WRV) and in dynamic mini former trials. In mini former dewatering characteristics are measured on-line as water flow through vacuum boxes. Fibre flocculation was measured in a head-box with CCD cameras in pilot former.

The pilot former has been built to study drainage, filtration, and chemical issues related to the paper-making process under well-controlled conditions. Studies can be extended from head-box flow dynamics to web and paper

properties. The pilot former is temperature-controlled, ranging from 20 to 60 °C and well-instrumented from a process chemistry point of view. The basis of the former is a combination of a headbox and a fourdrinier device. The dewatering unit consists of a controllable wire section with four independent vacuum boxes. The sizes of pulp and white water tanks are from 1 m<sup>3</sup> to 0.1 m<sup>3</sup> and the pilot former also includes a filler and retention chemical feed system. The chemical state of the papermaking process is characterized by on-line measurements such as temperature, pH, conductivity, turbidity, redox potential, and flow meter measurements, as well as floc size distribution measurements straight from the headbox and the wire section.



Figure 1. The pilot former for simulation of drainage, filtration, and flocculation.

Wet web strength was measured with a tensile tester in the laboratory [6]. Impingement drying units and infra-red dry content measurement were introduced to a standard tensile tester to measure the drying rate. The end-product quality (bulk, strength, and surface properties) were studied according to standards (see Table I).

Table I. Pulp and paper testing standards

Canadian Standard Freeness (CSF)	ISO 5267-2:2001
Water Retention Value (WRV)	SCAN-C 62:00
Preparation of laboratory sheet	ISO 5269-1:2005
Testing of laboratory sheets	ISO 5270:1998
Grammage	ISO 536:1995
Density	ISO 534:2005
Roughness	SCAN-P 84:01
Tensile strength	ISO 1924:1994

## **Results**

The effects of fibre surface chemistry on the paper-making process were evaluated through basic laboratory measurements and dynamic pilot former trials. First, laboratory studies were carried out with the purified enzymes in which standard paper properties were tested accompanied with wet web strength and drying measurements. Thereafter, dynamic trials were executed in the pilot former using commercial enzymes for pulp modification.

### **Basic Laboratory Studies**

**Influence of enzymatic treatments on fibre surface chemistry.** According to the HPLC analysis, the action of the enzymes was quite specific: almost only xylan was released by the xylanase and EG II modified mostly cellulose (see Figure 2). Endoglucanase I was noticed to degrade both xylan and cellulose. With the low and the high dosage of the enzymes, ~ 0.5 % and 1.7 – 2.0 % of the original pulp dry weight was hydrolysed, respectively.

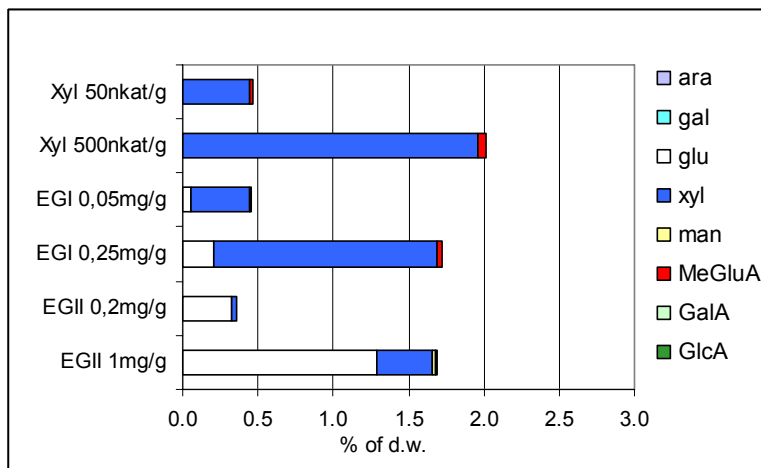


Figure 2. Composition and amount of dissolved sugars released in the enzymatic treatments of the refined birch pulp, as revealed by HPLC analysis.

**Effects of enzymatic treatments on dewatering characteristics of birch pulp.** The effects of specific carbohydrate modifications on the laboratory-measured dewatering characteristics of pulps are presented in Table II. Hydrolysis of cellulose by EG II had a different effect on the unrefined and refined pulps: dewatering of the unrefined pulp was deteriorated whereas dewatering of the fibrillated and net-worked refined pulp was improved. When xylan together with cellulose was hydrolysed to a slight extent by EG I, the highest increase of CSF was detected. At the condition used, EG I acted more as a xylanase than a cellulase, as described earlier [7]. Modifying only the surface xylan of the fibre cell wall with xylanase had only minor effects on CSF, both with the unrefined and refined pulps.

Table II. CSF and WRV values of refined and unrefined pulp after enzymatic treatments. Explanation for abbreviations: Xyl = xylanase, EGI = endoglucanase I, EGII = endoglucanase II. Enzyme dosage unit is nkat/g (activity) / g (pulp) or mg (protein) / g (pulp).

	Unrefined		Refined	
	CSF	WRV	CSF	WRV
Xyl, 50 nkat/g	590	1.65	3.65	1.96
Xyl, 500 nkat/g	595	1.68	380	1.99
EG I, 0.05 mg/g	560	1.72	390	1.98
EG I, 0.25 mg/g	615	1.73	470	1.95
EG II, 0.2 mg/g	535	1.76	435	1.96
EG II, 1 mg/g	565	1.82	455	1.95
Untreated	580	1.68	370	1.98

**Effects of enzymatic treatments on wet strength properties.** The influence of carbohydrate modifications on wet sheet strength is presented in Figure 3. Strength results of the laboratory sheets are presented at a constant 50 % dry content level. Slight hydrolysis of xylan with endoglucanase I increased tensile strength by 12 % compared with the untreated reference. Substantial hydrolysis of cellulose with endoglucanase II reduced tensile strength of wet sheets by 20 %.



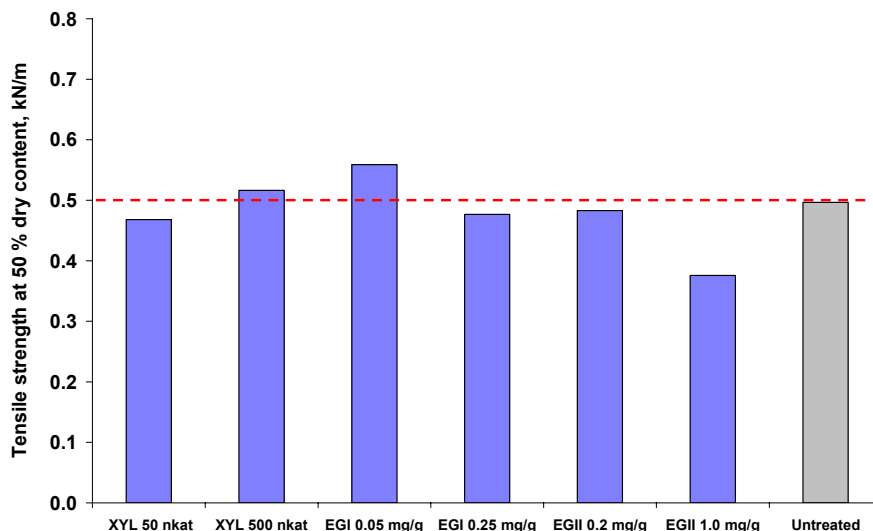


Figure 3. Tensile strength at 50 % dry content of sheet.

**Effects of modification of carbohydrates on drying time of laboratory sheets.** A decrease in drying time for a laboratory sheet was noticed to be accompanied both by xylan and cellulose hydrolysis by EG I or EG II, whereas degradation of xylan by the xylanase did not have a significant influence on drying time. Drying time decreased by 17 % with the high dosage of EG II (1.0 mg protein / g pulp). There is probably a relationship between increased air permeability and drying rate with impingement drying due cellulase treatment of pulp.

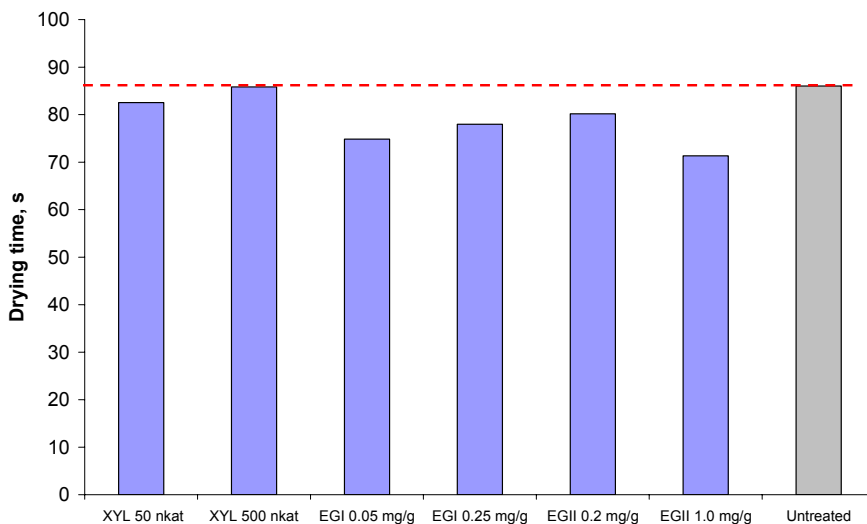


Figure 4. Drying time from a dry solids content of 45 % to 90 % with impingement drying.

**Effects of enzymatic treatments on end-product quality.** The dependency between freeness value (CSF), tensile index, and sheet roughness is presented in Figure 5. Carbohydrate modifications have been made with commercial

xylanase and cellulase preparations (see chapter Material and Methods). According to these results, drainage of highly refined birch pulp can be enhanced by xylanase and cellulase treatments without significant loss of tensile index and roughness.

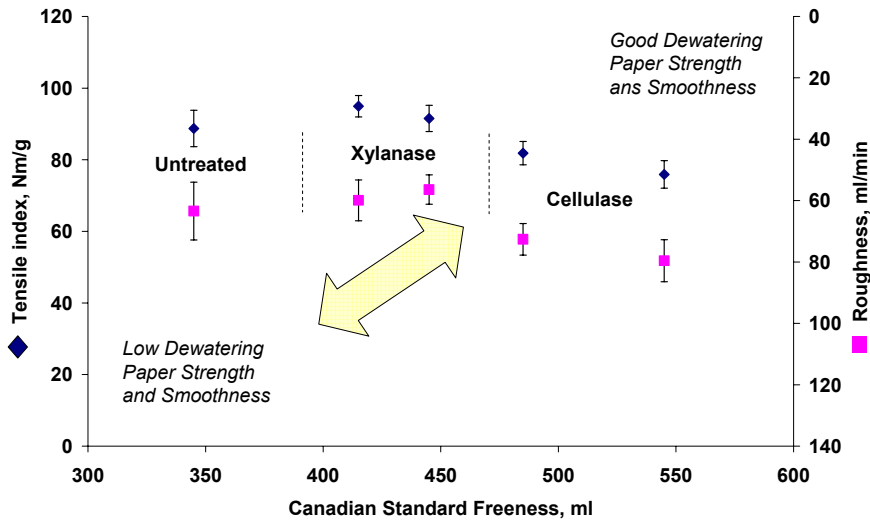


Figure 5. Influence of enzymatic treatments of the refined pulps on CSF, tensile index and roughness.

Figure 6 shows the results of enzymatic treatments with unrefined pulp. Enzymatic treatment increased sheet smoothness at constant drainage and paper-strength level. The highest improvement of sheet smoothness was observed with the xylanase treatments. Results may be connected to increased fibre flexibility due to enzymatic treatment. Results indicate that enzymatic treatment could decrease the refining energy needed to achieve a certain sheet smoothness.

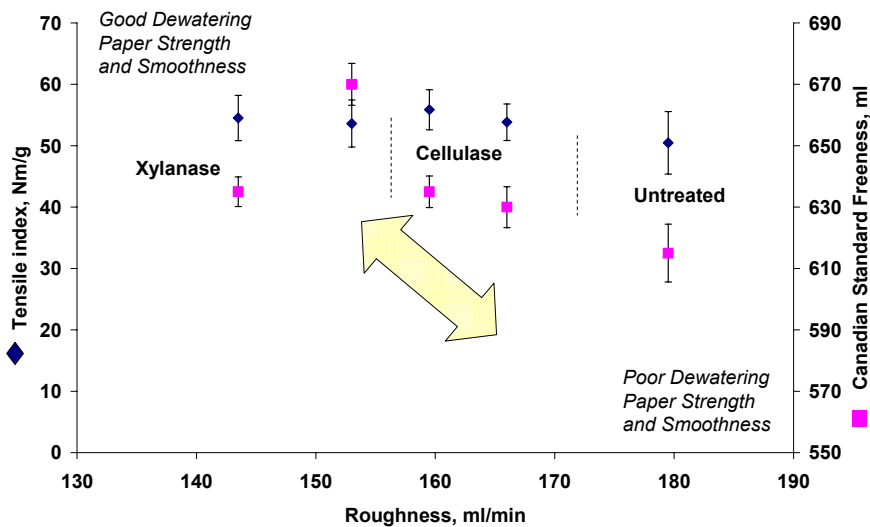


Figure 6. Influence of enzymatic treatments of the unrefined pulp on CSF, tensile index, and roughness.

### Pilot Former Trials

In general, floc size of the unrefined pulp in the pilot former headbox was increased by modification of surface carbohydrates. Especially endoglucanase treatment had an influence on sheet formation. On the other hand, floc size did not increase so much in the case of the refined pulp (see Figure 7). A higher floc size with the refined pulp compared with the unrefined pulp is a result that contradicts common knowledge. As expected, an increase of forming speed from 0.5 m/s to 1.0 m/s decreased floc size with all trial points, as expected.

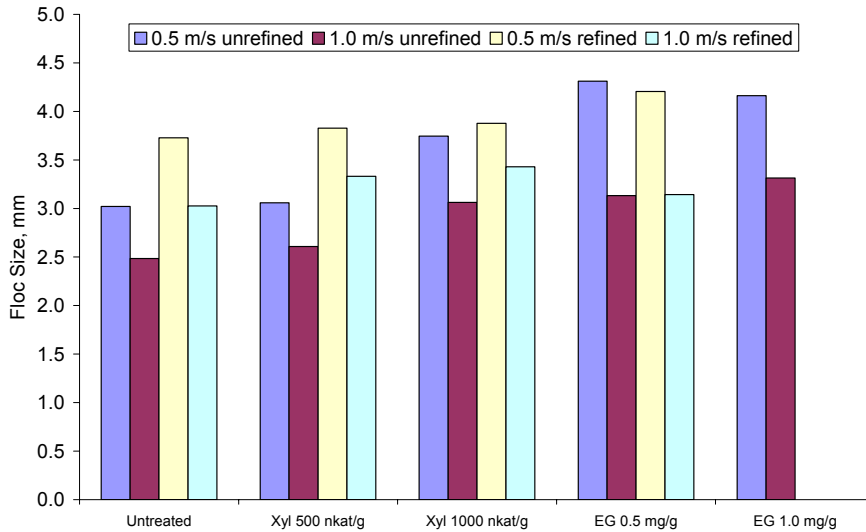


Figure 7. Influence of enzymatic treatments of the unrefined and refined pulp on floc size in pilot former measured from headbox.

Dewatering results of the enzymatic treated pulps are presented in Figure 7. Enzymatic treatments with xylanase (1000 nkat/g) and endoglucanase (0.5 mg / g) increased dewatering ~20 %, especially with a higher (1.0 m/s) forming speed.

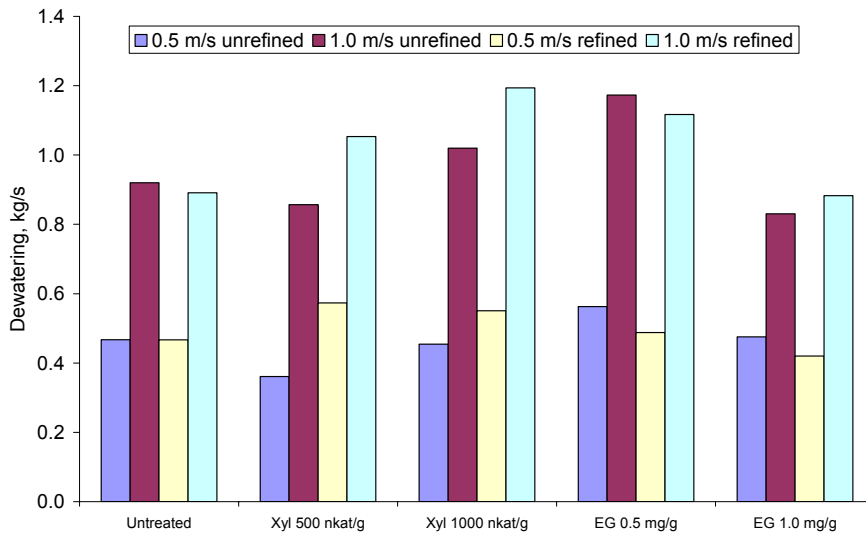


Figure 8. Influence of enzymatic treatments on dewatering of the unrefined and refined pulps in pilot former.

The influence of enzymatic treatments on sheet formation was evaluated from sheet samples taken from pilot former. According to the results presented in Figure 9, carbohydrate hydrolysis to a high extent weakens sheet formation. The results are supported by floc size measurement from the headbox (see Figure 7). Light xylanase treatment did not have a significant influence on sheet formation.

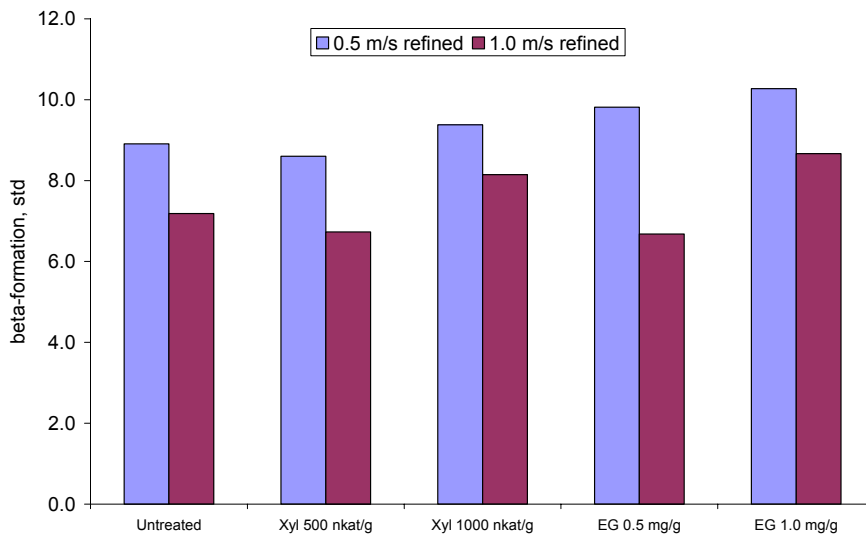


Figure 9. Influence of enzymatic treatments and forming speed on sheet formation.

## CONCLUSIONS

The effects of carbohydrate composition of the bleached birch pulp on flocculation, drainage, wet web tension, drying, and end-product quality were examined in laboratory studies and pilot former trials. The content of cellulose and hemicelluloses of unrefined and refined never-dried birch pulps was modified with specific enzymatic treatments. Special analytical instruments were applied to define dewatering, wet web tension, and drying characteristics of the modified pulps.

Flocculation of fibre suspension was measured on-line with CCD cameras from the headbox in the pilot former. Flocculation increased due to degradation of carbohydrates. The flocculation results were supported by dry sheet formation measurements. According to freeness and filtration device measurements, the dewatering rate of refined pulp was increased after hydrolysis both of xylan and cellulose, whereas modification of only xylan had less influence on the dewatering rate. Enhanced initial dewatering was also observed in pilot former. Depending on the modified carbohydrate and the extent of treatment, enzymatic modifications had both positive and negative effects on the tensile strength of wet sheet samples. Light EG I treatment increased wet strength 10 %, whereas hydrolysis of cellulose with EG II decreased 20 % wet strength of the sheet. The drying rate was noticed to increase due to cellulase treatment. Apparently, cellulase treatments modified the pore structure of the fibre network and fibre cell wall, thus influencing the impingement drying effectiveness. A modification of cellulose decreased more tensile strength than hydrolysis of xylan in a given relative bonded area. Results indicated different response to fibre strength and the fibre-bond strength of the modifications. Through controlled carbohydrate modifications, it was possible to simultaneously enhance dewatering, tensile strength, and sheet smoothness. Overall, results indicate that modification of carbohydrates of the bleached birch pulp had significant influence on all critical paper-making sections on the paper machine.

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# Improving Wet Web Runnability and Paper Quality by an Uncharged Polysaccharide

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The effects of xyloglucan addition on wet web strength, drying tension and end product quality of bleached birch kraft pulps were examined with laboratory trials. Specific xyloglucan dosages were applied onto wet fibre networks by spraying. Laboratory sheets were prepared of never-dried and once-dried birch pulps. Wet sheet strength and drying characteristics were analysed using diverse analytical instruments. Structural, strength and surface properties of dry sheet samples were tested according to standard methods. Wet web strength and tension holding potential of test samples increased with the addition of xyloglucan, which is an indication of better wet web runnability. Xyloglucan also increased the drying tension. Besides enhanced runnability, xyloglucan treatment was also found to improve end product quality by improving smoothness and dry strength properties, and decreasing air permeability. Results indicate that xyloglucan treatment has greater strengthening potential with once-dried chemical pulp, whereas the effect with never-dried pulp was smaller. Never-dried fibre has high natural bonding ability when once-dried fibres re-swelling and thus bonding ability has deteriorated in drying process. Therefore, xyloglucan seems to have potential especially in recovering the strength properties of pulp with hornified cell walls, such as in recycled pulp. In general, these results can be exploited in paper and board machines for tailoring fibre networks for different product grades or special functional products.

**Keywords:** Kraft Birch Pulp, Xyloglucan, Uncharged, Borax, Spraying, Wet Strength, Runnability, Drying Tension, Dry Strength, Hornification, Never-Dried, Once-Dried.

## 1. INTRODUCTION

Due to the high speed of paper production the runnability of the process is always a challenge. The high water content of the web hinders the handling and transfer of it from unit process to another in paper machine. Thus, the runnability of wet web depends on the strength properties including tension and relaxation characteristics.<sup>1</sup> Strength additives are commonly used for improving strength of paper. In addition to well-known benefits, the use of strength additives may also cause unwanted phenomena. For example, they may have negative effects on wet web runnability, because the strength and tension holding ability may deteriorate.<sup>1</sup> The functionality of cationic strength additives is typically disturbed by anionic substances in the process water. It is therefore of great interest to study strength additives which interact with cellulose in a non-charge-mediated manner. One interesting uncharged

strength additive is the plant polysaccharide xyloglucan. In this paper, some of the consequences of applying xyloglucan as an additive in paper making process are evaluated.

Before chemical hydrogen bonds starts to appear (below 50–60% dry solids content of web), the strength of wet web depends on friction between fibres and cohesion due to surface tension.<sup>2</sup> Therefore characteristics that influence the wet web properties in press and drying sections are related to the dry solids content of the web as mechanical friction forces transforms to chemical bonding.

If shrinkage of wet web is prevented during drying, a drying tension is introduced to the paper. Typically, drying tension is first formed slowly but it starts to increase strongly between 60 and 65% of solid content.<sup>2</sup> Drying tension is related to the formation of hydrogen bonds as a function of dry solids content of the paper. The development of drying tension has an influence on the draws needed between dryer groups of paper machine. If drying tension is formed late then the draws in dryer section has to be increased in order to prevent the flutter of the

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web. High draws in dryer section increase the porosity of the web and further influences negatively the quality of coating and printing.

Wet end addition of xyloglucan (XG) has been reported to have positive effects on formation 3, 4 and dry strength properties of paper 5. Ahrenstedt 6 showed that dry tensile strength increases also when xyloglucan is sprayed onto dry sheets. This paper presents novel results of a laboratory study where chemical additives have been introduced by spraying onto wet sheets. Dryness of the sprayed wet sheet samples were in same range than solids content of web after press section in paper machine. Especially, influences of xyloglucan on creation of drying forces and wet and dry strength of the sheets were examined.

## 2. EXPERIMENTS AND METHODS

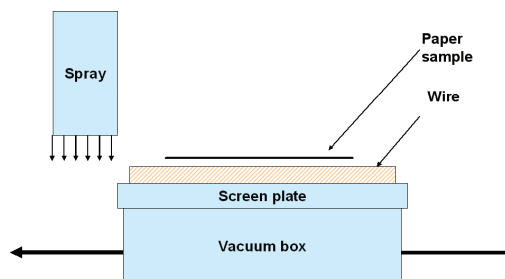
Application of xyloglucan was studied in laboratory scale. Influence of xyloglucan on wet strength and drying characteristics and also on end-product quality were studied. Pulp and sheet properties were tested according to standards (see Table I).

Raw materials used were once-dried and never-dried ECF (Elemental Chlorine Free) unrefined birch pulp from a Finnish pulp mill. Never-dried pulp was collected after bleaching stage in pulp mill at consistency of 13%. Fibre quality was measured by FiberMaster analyser (supplied by Lorentzen and Wettre). Characteristics of the applied pulps are presented in Table II. Hornification of fibre cell wall due to drying of pulp can be seen in Water Retention Value (WRV) of pulp and in width and bendability of fibres. Hornification is generally defined as a loss of fibre ability to swell after drying. WRV is known to correlate with fibre swelling ability. Also, fines content was observed to increase when once-dried samples were re-pulped.

Sheets were prepared onto two different density levels by using either 0.5 bar or 3.5 bar wet pressing pressures. Tamarind xyloglucan<sup>7</sup> (obtained from SweTree Technologies, Umeå), Sweden and cationic starch (Raisamy1 135, degree of substitution 0.035) were introduced either to pulp suspension or onto wet sheets by spraying (see Fig. 1). In this method sheet samples were placed on sledge which passed below the spraying unit. Amount of

**Table II.** Pulp and fibre properties.

	Never-dried	Once-dried
WRV	1.71 ± 0.03	1.07 ± 0.03
Freeness [ml]	535 ± 0	533 ± 0
Length [mm]	0.90 ± 0.007	0.87 ± 0.01
Width [ $\mu$ m]	22.7 ± 0.07	21.4 ± 0.14
Fines [%]	5.5 ± 0.06	8.1 ± 0.18
Shape factor	89.3 ± 0.14	89.1 ± 0.21
Bendability	4.3 ± 0	3.4 ± 0.28



**Fig. 1.** Operation principal of spraying unit.

sprayed chemical was varied by the velocity of the sledge. In spraying the consistency of xyloglucan and starch was 1.0%. Dosages of the strength additives were between 0.8% and 2.0% on dry weight. Highest 2.0% dosage of chemical was applied only with once-dried pulp due to lower bonding ability compared to never-dried pulp.

Wet web strength was measured with a special tensile tester in laboratory.<sup>8</sup> A special feature of the tester is the high 1 m/s (60000 mm/min) strain rate compared to standard testers (e.g., 20 mm/min). Small impingement drying units and infrared moisture detector were connected to a standard tensile tester to measure development of drying tension.

## 3. RESULTS AND DISCUSSION

### 3.1. Wet Sheet Properties

Spraying of xyloglucan (XG) onto never-dried (Fig. 2(A)) or once-dried (Fig. 2(B)) pulp sheets increased wet web strength of samples. XG was found to be more effective wet strength additive than starch. Approximately 0.8% dosage of XG gave same wet strength as 1.4–2.0% addition of starch. Compared to untreated reference chemical treatments increased wet strength from 20–50% depending on the dosage level.

In contrast with the spray application the addition of strength additive to the pulp suspension did not increase wet web strength of sheets. The commercial starch product even decreased wet strength at a given dry solids content compared to reference. An explanation for this result can

**Table I.** Pulp and paper testing standards.

Canadian standard freeness (CSF)	ISO 5267-2:2001
Water retention value (WRV)	SCAN-C 62:00
Preparation of laboratory sheet	ISO 5269-1:2005
Testing of laboratory sheets	ISO 5270:1998
Grammage	ISO 536:1995
Density	ISO 534:2005
Roughness	SCAN-P 84:01
Air permeability	SCAN P-26:78
Tensile strength	ISO 1924:1994

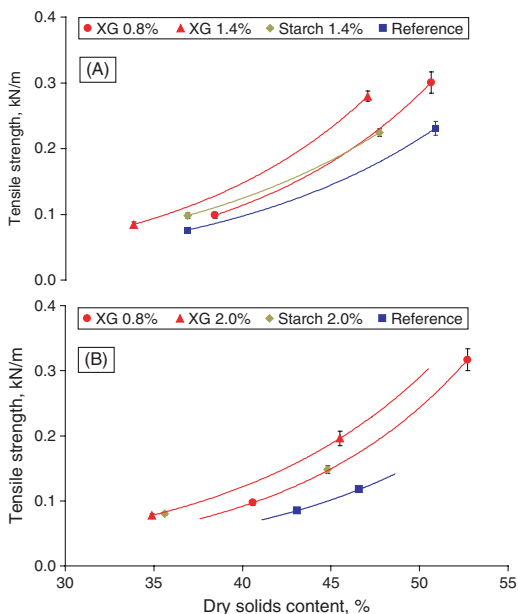


Fig. 2. Wet web strength of never-dried (A) and once-dried (B) pulp samples (spray application).

be that when chemical is added to pulp it easily interferes with high surface area fines material whereas in spray application in to wet sheets chemicals are more likely to be in fibre bonding area. According to drying stress results (Fig. 3), deteriorated wet strength due to starch addition to pulp maybe related to starch working as a lubricant between fibres.

Increased drying tension was noticed when xyloglucan was sprayed onto wet sheets of never-dried (Fig. 4(A)) or once-dried (Fig. 4(B)) pulps. Xyloglucan dosages between 0.8 and 2.0% had almost identical drying tension development as a function of dry solids content. By contrast starch addition delayed the creation of drying tension with both pulps. Increase of Xyloglucan dosage from 0.8 and 2.0% did not further advanced development of drying

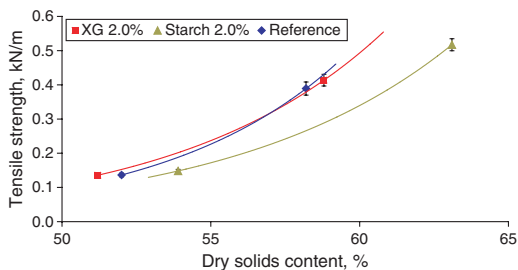


Fig. 3. Influence of strength additive addition to pulp suspension on wet web strength.

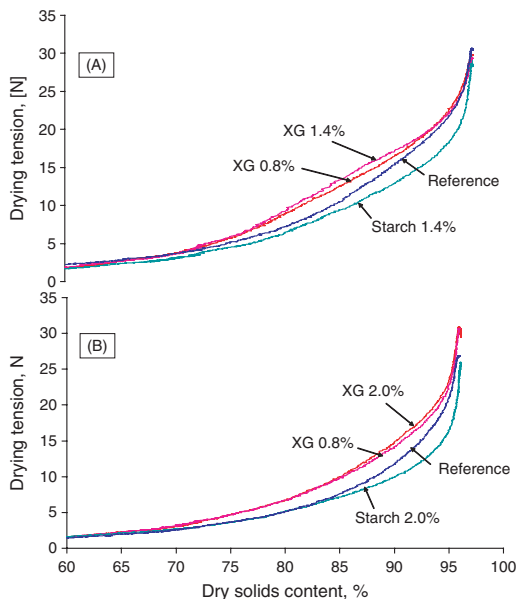


Fig. 4. Formation of drying tension with never-dried (A) and once-dried (B) samples as a function of dry solids content (spray application).

tension. Therefore, xyloglucan dosage below 1% seems to be enough from the runnability perspective of the web in dryer section of paper machine. By contrast starch addition delayed the creation of drying tension with both pulps and have thus negative effect on wet web tension in dryer section. As in case of wet strength, also development of drying stress may be influenced by the fact that chemical has different response when it interacts with fines material (pulp addition) or will be in fibre bonding area (spray application).

### 3.2. Dry Sheet Properties

Applying of xyloglucan and starch onto sheet by spraying enhanced dry strength of samples with never-dried (Fig. 5(A)) and once-dried (Fig. 5(B)) pulp samples. Dry strength improvements are similar as found by other authors.<sup>3,5,6</sup> However, relative tensile index improvement was higher with once-dried pulp sample than with never-dried pulp samples. Starch was found to increase dry tensile strength as much as xyloglucan. Tensile stiffness of dry sheet was found to be higher and breaking strain lower with xyloglucan sample than with starch sample (tensile stiffness and breaking strain results are not shown). Differences in stiffness and breaking strain results between starch and xyloglucan probably are linked to the differences in the tension development during drying.

Spray addition of xyloglucan decreased air permeability (Fig. 6(A)) and sheet roughness (Fig. 6(B)) of



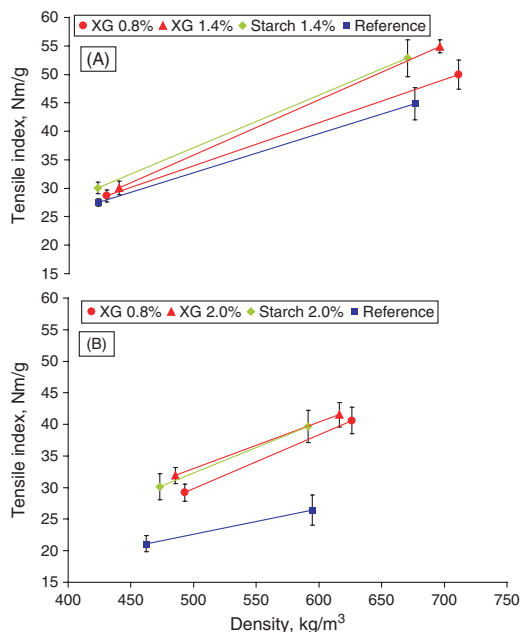


Fig. 5. Dry strength of never-dried (A) and once-dried (B) samples (spray application).

fibre network compared to untreated reference sample. Chemical treatments influenced on air permeability and roughness especially, with never-dried pulp sheets having coarser fibre network than never-dried pulp sheets.

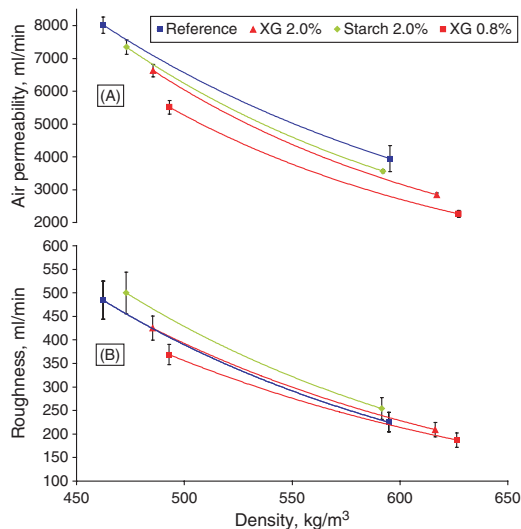


Fig. 6. Air permeability (A) and roughness (B) of once-dried samples (spray application).

Therefore, here is presented only results of once-dried pulp sheets. Reduction of air permeability was slightly higher with xyloglucan than with starch treatments. This result maybe also explained by different film forming, cross-linking characteristics tendencies of xyloglucan and starch.<sup>9</sup> Also Lima<sup>5</sup> observed a reduction in sheet porosity when xyloglucan was introduced as a wet-end additive. Effects of treatments were bigger with smaller 0.8% dosage than with 2.0% dosage on both air permeability and roughness. Spraying of high amount of low concentrate additive may break fibre bonds and thus increase roughness and air permeability. Applying of 2.0% starch dosage by spraying even increased roughness of the sheet.

#### 4. CONCLUSIONS

Possibility to enhance the runnability of wet web in paper machine by chemical treatments was estimated based on laboratory scale trials. Addition of xyloglucan was found to increase wet web strength both with never-dried and once-dried samples. Compared to cationic starch xyloglucan gave higher wet web strength. Wet web strength improvements were higher when chemicals were added by spraying on wet web than added to the pulp suspension. Xyloglucan was also found to promote the creation of drying tension whereas application of starch delayed the formation of shrinkage forces. Advanced drying tension may improve runnability of wet web in dryer section by decreasing fluttering of web.

Additionally, the end product quality was affected by the xyloglucan addition. Tensile index was found to increase in a similar way as with starch when introduced to the fibre network by spraying. Especially with once-dried pulp samples the tensile index was strongly improved. Never-dried pulp has a high natural bonding ability therefore a smaller tensile strength improvement was obtained. Spraying of xyloglucan was also observed to decrease air permeability and roughness.

Xyloglucan, a non-charged polysaccharide, was found to be a potential wet web strength additive for increasing runnability and production of paper or board machines. The obtained results with wet and dry sheet suggest that spray application technique is a very effective way to introduce uncharged chemicals to the web.

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# Improving Recyclability of Chemical Pulp by Introducing Non-charged Cross-linked Polysaccharide on Fiber Surface

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## ABSTRACT

The effect of spray application of xyloglucan on strength and recyclability of bleached chemical pulp was studied. Xyloglucan alone and with a cross-linking chemical was applied on sheets made of unbeaten never-dried and once-dried virgin pulps. Recyclability of these pulps was evaluated based on the tensile strength of wet and dry handsheets. Dry strength measurements showed that the spray application reduces the loss of strength and bonding ability in recycling. The use of cross-linking chemical was found to be essential in enhancing both the wet and dry strength of the virgin and recycled pulps. The chemical application was efficient with both never-dried and once-dried pulps.

Wet web strength results indicate that the amount of web breaks could be decreased in paper and board machines using recovered fibers by having cross-linked xyloglucan layer on fiber surface. Spray application was found to be an effective way to introduce non-charged chemicals into fiber network.

As a consequence of improved fiber bonding the need of refining decreases which further improves the recyclability of fibers. In addition to xyloglucan also other polysaccharides, for example those provided by chemical or mechanical pulp mills, could be used for improving the recyclability and extending the lifetime of fiber material.

## INTRODUCTION

As use of recovered fibers increases in paper and board production the raw material quality becomes critical. During recycling the chemical pulp fibers undergo hornification and lose bonding ability. Hornification typically refers to the loss of swelling ability of fibers due to drying and re-wetting cycles [1, 2]. The loss in fiber swelling caused by recycling can be at least partly restored by refining [3]. Besides decreased re-swelling, hornification is also related to reduced fibre stiffness, conformability and bonding ability [4]. Chemical composition of fiber has been reported to have influence on hornification of fiber. According to literature hemicelluloses content (xylan or glucomannan) of fiber has significant role in hornification by decreasing the aggregation of fibrils [5, 6, 7, 8] whereas lignin has a smaller effect on fiber hornification [8]. Chemicals with different properties (e.g. molecular size, structure and charge) have been tested for reducing fiber hornification. For example, cationic starch has been reported to enhance strength properties of paper and board even when the paper is recycled [9, 10].

The functionality of cationic strength additives is typically disturbed by anionic substances in the process water. Therefore, utilization of non-charge low cost additives as xyloglucan (purified from tamarind kernel powder) introduces interesting possibility to influence the bonding properties of fibers without disturbing white water system. The special feature of xyloglucan is the strong adsorption onto cellulose that makes it a very attractive additive for increasing recyclability of fibers [11]. It has been shown that xyloglucan stands the effect of refining and improves the strength of refined pulp [12]. Additionally, bonding strength of xyloglucan can be further substantially strengthened by elemental cross-linking chemistry with borate [13]. In order to overcome the low wet-end retention of non-charged chemicals xyloglucan can be sprayed onto wet fiber network. Additive applied by spraying is more likely to end up onto fiber surfaces whereas the addition to pulp suspension prefers the adsorption onto high specific area fines. Recyclability of fiber comprises also of runnability potential of fiber material in paper or board machine. Probability of web breaks is known to be related to wet web strength which can be determined in laboratory scale test.

In this study the aim was to determine the potential of a non-charged polysaccharide, xyloglucan for retaining the bonding ability of fibers in recycling.

## Material and Methods

The Influence of chemical additives on the properties of wet and dry sheet was explored in laboratory scale.

Never-dried and once-dried ECF (Elemental Chlorine Free) unrefined birch pulps from pulp mill were used as raw material. Never-dried pulp was collected after bleaching stage in pulp mill at consistency of ~13 %. Standard handsheets with basis weight of 60 g/m<sup>2</sup> were made. Purified xyloglucan sample was obtained from KTH, Sweden and borate sample from VWR Chemicals. Native corn starch was used as a reference polysaccharide. Xyloglucan was applied onto wet sheets by spraying (see Figure 1). In spraying the xyloglucan dosage was 1.0 % on dry weight in all trial points. Borate was mixed with xyloglucan in ratios 1:1 and 1:5 on dry weight. After spraying the sheets were pressed onto two different density levels by using either 0.5 bar or 3.5 bar wet pressing pressures.

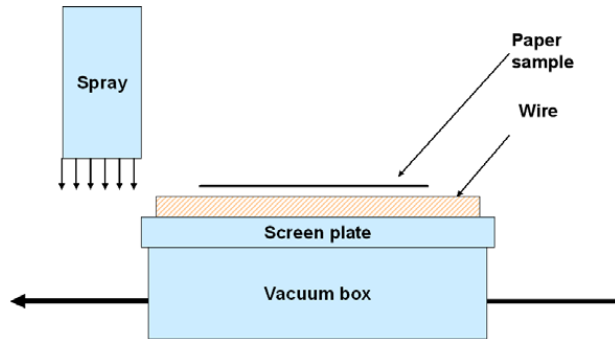


Figure 1. Applying of xyloglucan into wet sheets.

Wet web strength was measured with a tensile tester in laboratory [14]. A special feature of the tester is the high 1 m/s strain rate compared to standard testers (e.g. 20 mm/min). Wet sheets were air dried (shrinkage prevented) in air conditioned laboratory (23 °C, RH 50). Dry paper samples were tested according to the standards shown in Table I.

Table I. Pulp and paper testing standards.

Water Retention Value (WRV)	SCAN-C 62:00
Preparation of laboratory sheet	ISO 5269-1:2005
Testing of laboratory sheets	ISO 5270:1998
Grammage	ISO 536:1995
Density	ISO 534:2005
Air permeability	SCAN P-26:78
Tensile strength	ISO 1924:1994

After testings and storage in laboratory over 3 weeks sheet samples were further repulped for recycling tests. Wet and dry sheet properties were tested from recycled samples.

## **Results**

Effects of xyloglucan based modification of wet fiber network (by spraying) on wet and dry paper characteristics were evaluated through laboratory measurements.

### **Pulp and fiber properties**

Characteristics of the used pulps are presented in Table II. Water retention value is an often used measure for the hornification of fiber cell wall due to drying [2]. In addition to the reduction in WRV the drying of the virgin pulp has also reduced the average fibre width.

Table II. Pulp and fiber properties.

	Never-dried	Once-dried
WRV [g/g]	1.71 ± 0.03	0.9 ± 0.03
Freeness [ml]	535 ± 0	533 ± 0
Length [mm]	0.90 ± 0.007	0.87 ± 0.01
Width [μm]	22.7 ± 0.07	21.4 ± 0.14

Water retention value of never-dried pulp decreased from 1.7 g/g to 1.1 g/g when it was recycled twice whereas the WRV of once-dried sample was not significantly changed in recycling.

### Initial wet strength

**Unrecycled samples.** At same dry solids constant level the sheets made of never-dried pulp had higher wet tensile strength than those made of once-dried pulp (see Figure 2 and 3). Also other authors have found that never dried pulp gives a higher wet strength at constant dry solids content than once-dried pulp [15, 16]. On the other hand, after constant wet pressing conditions the once-dried samples had higher dry solids content than never-dried after wet pressing which decreased the difference in wet strengths. Differences in dry solids content after constant wet pressing with never-dried and once-dried has been also reported by other authors in dynamic paper machine trials [15]. Higher solids content after press section signifies also savings in drying energy of paper or board. Spraying of xyloglucan (XG) or native corn starch onto never-dried or once-dried pulp wet sheets increased the initial wet strength of pulps (see Figures 2 and 3). Addition of borate enhanced further the initial wet strength of xyloglucan containing sample when no synergism was observed with starch.

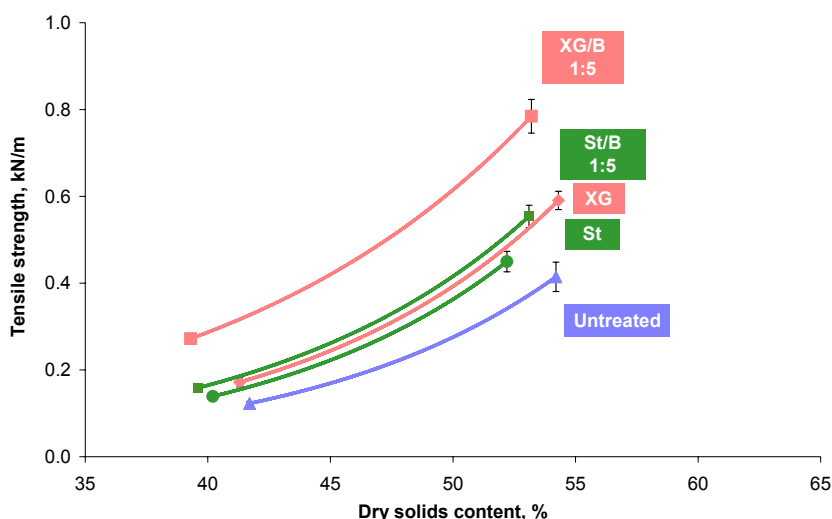


Figure 2. Initial wet strength of sheets made of never-dried pulp. Sheets were treated with xyloglucan (1 % on dry weight) (XG), with xyloglucan combined with borate (XG/B), with native corn starch (St) and with native corn starch combined with borate (St/B).

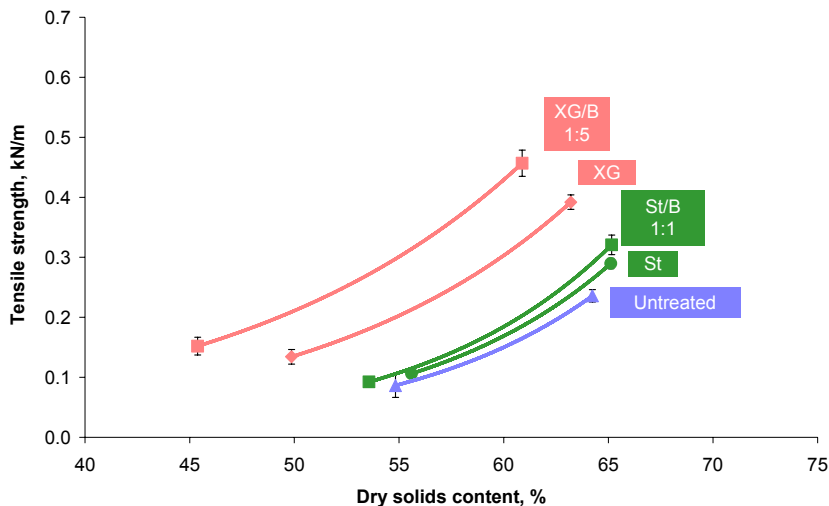


Figure 3. Initial wet strength of sheets made of once-dried pulp. Sheets were treated with xyloglucan (1 % of dry weight) (XG), with xyloglucan combined with borate (XG/B), with native corn starch (St), with native corn starch combined with borate (St/B).

**Recycled samples.** In figures 4 and 5 are shown the initial wet strength of sheets made of recycled never-dried and once-dried pulps. At constant dry content level the initial wet strength decreased in recycling the never-dried and once-dried pulps. On the other hand, recycled samples had higher dry solids content after wet pressing than the virgin, not recycled samples which has a positive effect on the initial wet strength. Compared to not recycled and untreated reference the addition of xyloglucan with borate before recycling compensated for almost all the wet strength lost due to recycling.

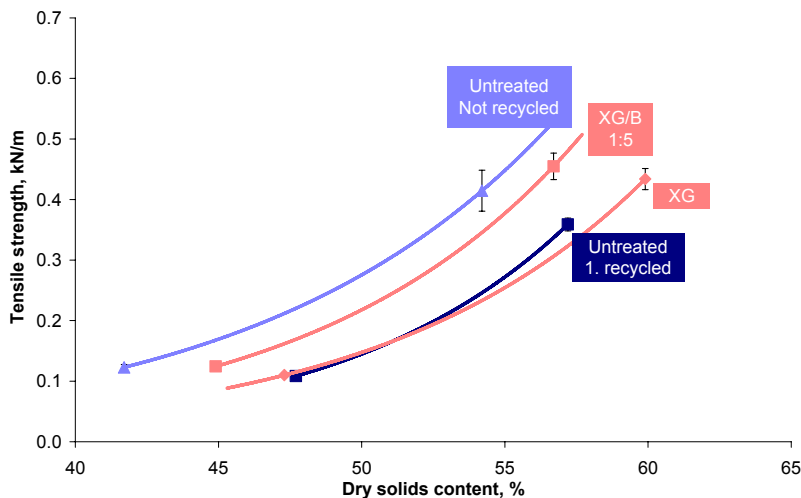


Figure 4. Initial wet strength of sheets made of once recycled samples of originally never-dried pulp. Sheets were treated with xyloglucan (1 % on dry weight) (XG) or with xyloglucan with borate (XG/B).

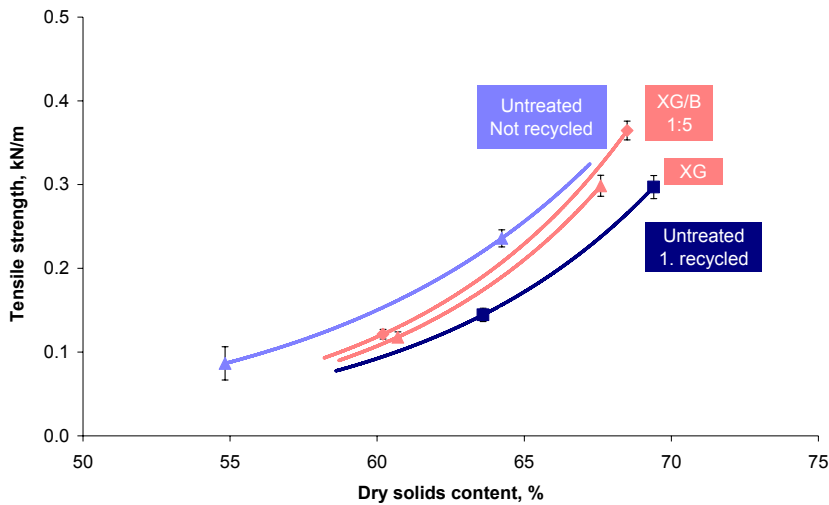


Figure 5. Initial wet strength of sheets made of once recycled samples of originally once-dried pulp. Sheets were treated with xyloglucan (1 % on dry weight) (XG) or with xyloglucan with borate (XG/B).

### Properties of dry sheets

Recycling of sheets prepared from originally never-dried pulp increased the bulk from 1.4 to 1.7. Spraying of xyloglucan or xyloglucan-borate complex decreased slightly the bulk of not recycled and recycled sheets.

Table III. Bulk of recycled never-dried pulp hand sheets ( $\text{m}^3/\text{kg} \cdot 1000$ ).

	Not recycled	1. Recycled	2. Recycled
Untreated	$1.42 \pm 0.005$	$1.55 \pm 0.012$	$1.73 \pm 0.014$
Xyloglucan	$1.37 \pm 0.012$	$1.52 \pm 0.005$	$1.70 \pm 0.019$
XG-Borate (1:1)	$1.40 \pm 0.012$	$1.51 \pm 0.011$	$1.69 \pm 0.014$
XG-Borate (1:5)	$1.36 \pm 0.004$	$1.49 \pm 0.008$	$1.68 \pm 0.008$

Recycling of originally never-dried pulp samples decreased the dry strength of sheets (see Figure 6). Before and after recycling the highest tensile strength was observed with xyloglucan and borate complex (XG-borate ratio 1:5). Increase of dry tensile strength due to xyloglucane-borate complex addition to fiber network has been reported also earlier [13]. Tensile index difference between xyloglucan and xyloglucan-borate complex decreases with recycling times. Based on tensile index results xyloglucan stays firmly on the fiber surfaces also when paper is repulped. This has been observed also by other authors [11, 12]. According to literature dry strength additives do not typically affect mechanical changes in fiber properties associated with the drying and recycling of kraft fibers [17]. However the treatment of fibers with chemicals such as xyloglucan mainly improves the hydrogen bonding ability of recycled cellulose material [17].

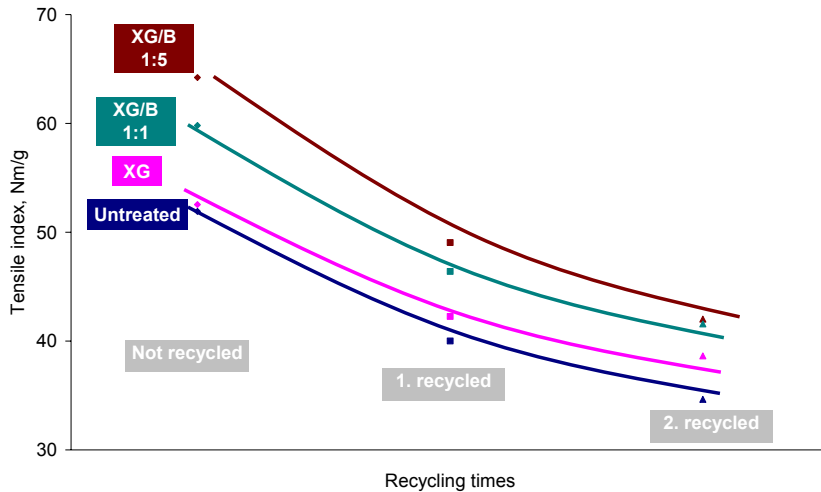


Figure 6. Influence of recycling on the dry tensile index of sheets made of originally never-dried pulps. The wet sheets made of virgin pulp were sprayed before recycling with xyloglucan 1 % of dry weight (XG) or with xyloglucan with borate (XG/B).

Spraying of xyloglucan or xyloglucan-borate complex onto surface of handsheets made of virgin, once-dried pulp increased the dry tensile index of recycled paper in the same way as with the sheets made of virgin, never-dried pulp. Highest growth in tensile index was achieved with xyloglucan-borate complex (blend ratio 1 to 5). With non-recycled pulps the spraying of merely xyloglucan gave higher increase of tensile index with once-dried pulp than with never-dried pulp. After recycling influence of borate on tensile index was found to be negligible. Synergism between xyloglucan and borate was also found to decrease after one recycling cycle of the sheets made of originally once-dried pulp. This behaviour is different from that found with never-dried pulp. As xyloglucan has been found to remain on the surface of cellulose, part of the borate may be lost during the recycling process. This could be compensated for by adding more borate onto reformed fiber network during the recycling process in order to refresh the cross-linkage matrix of xyloglucan and cellulose enabled by borate molecules.

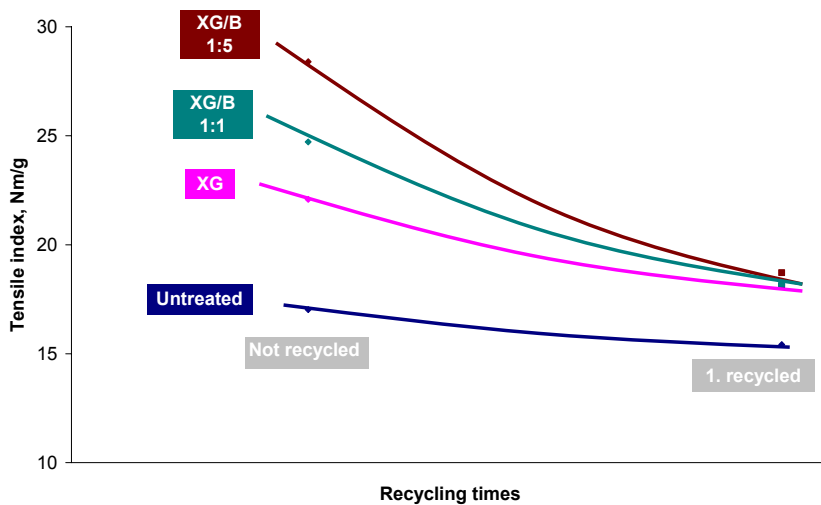




Figure 7. Influence of recycling on the dry tensile index of sheets made of originally once-dried pulp. Wet sheets were sprayed with xyloglucan (1 % on dry weight) (XG) or with xyloglucan with borate (XG/B).

Recycling of sheet prepared from originally never-dried pulp increased the air permeability. This can be explained by the increase of sheet bulk (see Table III) due to increased stiffness of fibres. Spraying of xyloglucan or xyloglucan-borate complex reduced the air permeability of never-dried samples. Decrease of air permeability was observed also after recycling. Decrease of air permeability due to chemical treatments cannot be explained by decrease of sheet bulk (see Table III).

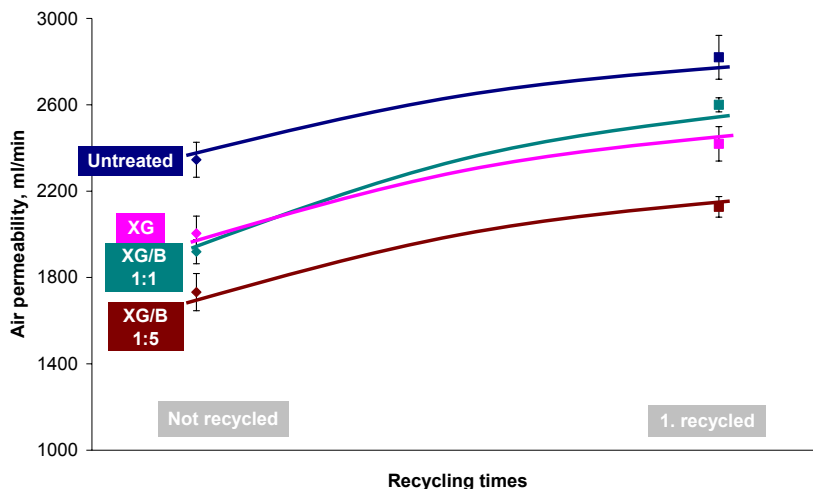


Figure 8. Influence of recycling on air permeability of never-dried samples. Wet sheets sprayed once with xyloglucan 1 % of dry weight (XG) or with xyloglucan with borate (XG/B).

## CONCLUSIONS

The effects of non-charged polysaccharide xyloglucan and its borate cross-linked complex on wet and dry paper properties were explored before and after recycling cycles in laboratory trials. Xyloglucan or xyloglucan and borate complex were applied onto wet fiber network by spraying after sheet forming. Influences of chemical treatments on the recyclability of paper made of never-dried and once dried pulp were examined.

Initial wet strength of paper samples was increased when xyloglucan and especially xyloglucan and borate complex was sprayed onto fiber network. Enhanced wet strength was observed with never-dried and once-dried pulp due to the chemical treatments. Native corn starch increased also wet strength, but no synergism with borate was noticed. Also after recycling improved initial wet strength was also observed with xyloglucan and xyloglucan-borate treated samples compared to untreated recycled samples. Xyloglucan-borate complex treatment compensated almost entirely for the wet strength loss caused by one recycling cycle. It did not matter whether the pulp was originally never-dried or once-dried.

Dry tensile index of samples was increased due to xyloglucan and xyloglucan-borate treatments of sheets made of virgin pulp. Cross-linkage of xyloglucan and cellulose with borate enhanced the tensile index of recycled samples made of originally never-dried pulp. With recycled samples made of originally once-dried pulp the tensile index was increased by xyloglucan treatments whereas borate did not enhance tensile strength further.

Results indicate that non-charged polysaccharides like xyloglucan are potential additives for improving recyclability of both never-dried and once-dried pulps. Xyloglucan has strong natural affinity to cellulose and it

forms complexes with borate which further strengthen the fiber network. Xyloglucan and borate could be applied at pulp mill for enhancing strength and recyclability of never-dried pulp or, alternatively at paper/board mill to enhance runnability of virgin and recovered pulp and strength properties of end product. Spraying was found to be an effective method to introduce low amounts of non-charged strength additives onto fiber network.

## ACKNOWLEDGMENTS

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## Non-charge polysaccharides

# Effects on runnability of wet web and efficiency of fibre material

By A. Oksanen, E. Retulainen, J. Kataja-aho, M. Somerkallio, C. Xu und H. Brumer

**Downtime minimisation is the key determinant of paper machine production efficiency [1]. However, the high width and speed of modern paper machines puts pressure on process stability and furnish quality [2]. The probability of web breaks is known to be closely related to wet web strength and web tension profiles [3, 4, 5].**

There are many known additives for improving the dry strength of the end product, such as starch. In contrast, though, the existing range of chemicals for enhancing initial wet web strength in paper production is limited. G-PAM, used for a number of paper grades, is one of the few known paper machine runnability additives [6, 7]. The utilization of non-charge low cost additives, such as xyloglucan, offers interesting potential for influencing the bonding properties of fibres without disturbing the white water system.

Use of guar gum and xyloglucan as process additives in papermaking can improve paper properties [8, 9]. The dry bonding strength of xyloglucan can be substantially further strengthened by elemental cross-linking using borate [8]. It is also known that chemicals consisting of aldehyde groups can enhance the wet strength of the fibre network [10]. Galactose oxidase selectively catalyzes the oxidation of galactose without degrading the polymer chain compared to conventional chemical oxidation [11]. In order to overcome the low wet-end retention of non-charged chemicals, e.g. xyloglucan can be sprayed onto the wet fibre network.

### Materials & methods

Raw materials used were once-dried ECF (Elemental Chlorine Free) unrefined birch pulp (SR 21) from a Finnish pulp mill in laboratory trials, and in pilot trials eucalyptus pulp (SR 30). Xyloglucan (purity >95%) and de-oiled tamarind kernel powder (containing ca. 60% xyloglucan) were obtained from SweTree Technologies, Umeå, Sweden for laboratory and pilot trials. Native potato starch (Raisamyl 00021) was delivered by Chemigate, Finland and guar gum from MP Biomedicals (Cat No. 105008). The borax (di-natriumtetraborate decahydrate) sample was supplied by Merck KGaA, 64271 Darmstadt, Germany.

Preparation of xyloglucan fractions and molecular weight determination: Xyloglucan with lowered molar mass was prepared from purified xyloglucan via par-

tial digestion with the endo-xyloglucanase Xgl from *Chrysosporium lucknowense* [12] obtained from Dyadic NL, Netherlands. The molecular weight of different XG fractions was determined by gel permeation chromatography (GPC) measurements.

Oxidation of xyloglucan by galactose oxidase: *Fusarium graminearum* galactose oxidase was produced recombinantly in *Pichia pastoris* according to the protocol described by Spadiut et al. [13, 14]. Optimized xyloglucan oxidation conditions were as follows: to a 10 mL XG aqueous solution, catalase (Cat.), horseradish peroxidase (H.R.P.), and GalOx were added.

Pulp and dry paper measurements: Pulp and paper samples were prepared and tested according to pulp and paper testing standards (Tab. 1) in an air-conditioned laboratory environment (RH 50, 23 °C).

Shopper-Riegler	SCAN-C 19:65
Preparation of laboratory sheet	ISO 5269-1:2005
Testing of laboratory sheet	ISO 5270:1998
Grammage	ISO 536:1995
Density	ISO 534:2005
Air permeability	SCAN P-26:78
Tensile strength	ISO 1924:1994

Tab 1: Pulp and paper testing standards

The effects of chemical application on wet and dry strength properties of the web were studied in laboratory and pilot scale trials. Laboratory sheets were prepared at two different dryness and density levels by using either 0.5 bar or 3.5 bar wet pressing pressures. Chemicals were introduced onto the wet sheets by spraying device in laboratory [15]. Wet web strength was measured in the laboratory using a special tensile tester [16]. In the method used, the wet web was first strained to 2%, and the residual tension (N/m) of the wet web was measured after 0.475 s. Residual tension value has been found to correlate with pulp runnability potential in several mill case studies.

### Trials on a VTT pilot machine

The effects on end product properties of spraying non-charged chemicals onto the wet web were tested on a VTT pilot paper machine (built in 2010). The pilot machine consists of a convertible former (gap or hybrid)

and wet pressing sections. Roll samples are taken after the wet press unit and dried in the laboratory. The pilot machine's press section uses a shoe press (1-nip geometry). The operating speed in the trials was 500 m/min, and a hybrid forming section was used. Chemical spraying was carried out at the end of the former section. The chemical dosage in spraying was varied according to the consistency of the chemical and the pumping capacity. A fine paper furnish (80 g/m<sup>2</sup>) comprising eucalyptus pulp with 15% PCC (Omya Syncarb S-PCC) content was used. Sprayed chemicals in pilot trials were tamarind kernel powder (TKP), native potato starch and guar gum.

On-line measurement of wet web runnability potential is based on the determination of strain at break during transfer of the web from press section to drier section. The wet web draw is increased (typically between 2 to 5%) until web break occurs. The fracture lines are analysed using videos and images captured by high speed camera (Fig. 1a and Fig. 1b).

### Results of laboratory-scale trials

The effects of XG molecular weight and crosslinking of xyloglucan using borax on tensile strength and residual tension are presented in Figure 2. Spraying of unmodified xyloglucan or xyloglucan of reduced molecular weight (50 kDa and 15 kDa) alone brought about a slight increase in tensile strength and residual tension of the wet web. However, the tensile strength and residual tension of wet samples were increased substantially by cross-linkage of unmodified xyloglucan with borax. The positive effect was higher for wet tensile strength than residual tension. Conversely, this synergism benefit of xyloglucan with borax was not seen in same extent with xyloglucan samples of decreased molecular weight.

The effects of xyloglucan-based fibre network treatments on the tensile index of dry samples are presented in Figure 3. Addition of unmodified xyloglucan or decreased molecular weight xyloglucan (15 kDa

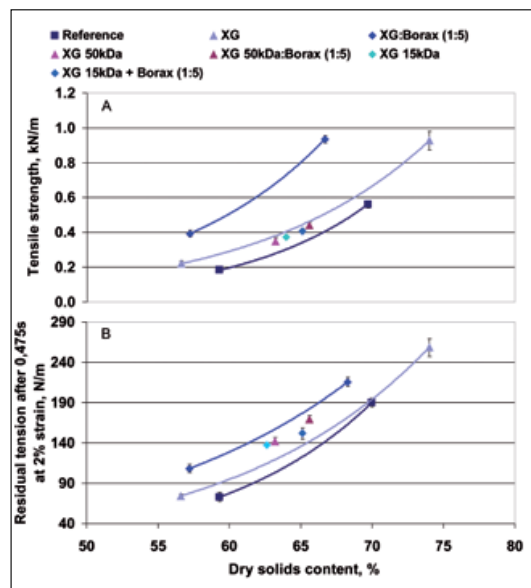


Fig. 2: Influence of crosslinking of xyloglucan (0.5% of d.w.) with borax (mixed to a ratio of 1:5) and modification of molecular weight (unmodified xyloglucan 1,000 kDa, 50 kDa and 15 kDa Mw) on wet tensile strength (A) and residual tension (B) as a function of sheet dry solids content

or 50 kDa) improved the tensile index of the samples at a constant sheet density. The highest tensile index increase, 10 units, was observed with the xyloglucan and borax complex. As in the case of wet strength properties, also with dry strength the synergism between xyloglucan and borax was decreased when the molecular weight of xyloglucan was reduced.

The effects of unmodified xyloglucan, oxidised (introduction of aldehyde groups) xyloglucan and crosslinking of xyloglucan with borax on wet tensile strength and residual tension are presented in Figure 4. Spraying

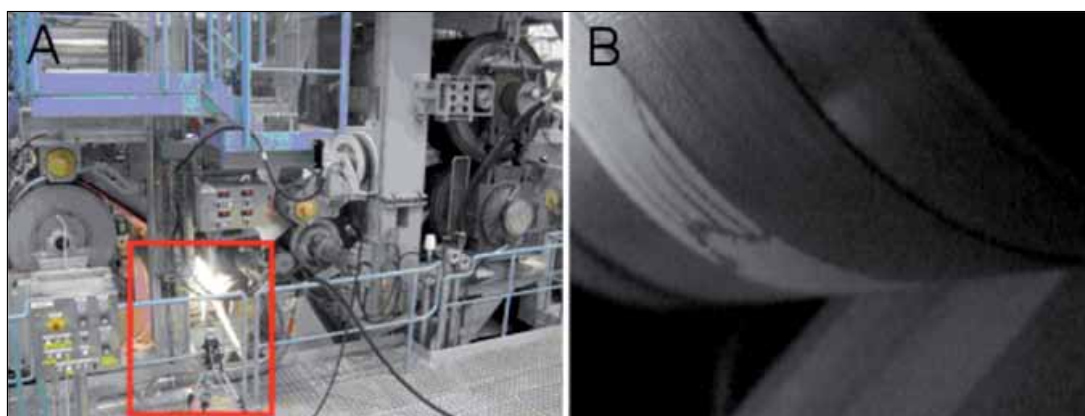


Fig. 1: Capture of web break images by high speed camera at wet web transfer from press section to drier section (a). A web break fracture line is shown in image (b)

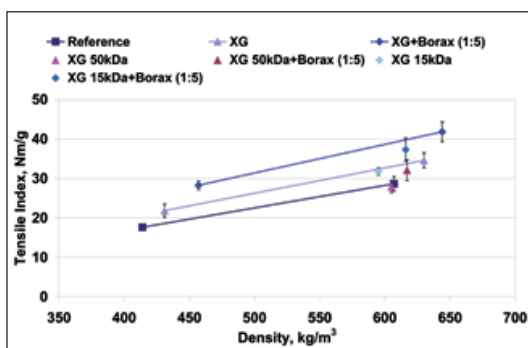


Fig. 3: Influence of cross-linking of xyloglucan (0.5% of d.w.) with borax (mixed to a ratio of 1:5) and modification of molecular weight (unmodified xyloglucan 1,000 kDa, 50 kDa and 15 kDa Mw) on dry tensile index as a function of dry sheet density

of unmodified xyloglucan at dosages of 0.5 or 1.0% of dry weight produced a slight increase in wet tensile strength and residual tension. As with the previous results, xyloglucan synergism with borax significantly increased the tensile strength and residual tension of the wet sheet samples. The highest wet strength properties were found with oxidised xyloglucan. Over 100% increases in tensile strength and residual tension values were measured with dosages between 0.5 and 1.0% of oxidised xyloglucan. Addition of oxidised xyloglucan at a dosage of 0.5% of dry weight enhanced wet tensile strength and residual tension by approximately same degree as the addition of xyloglucan (0.5% of d.w.) and borax mixed to a ratio of 1:5.

The effects of unmodified xyloglucan, oxidised xyloglucan and cross-linked xyloglucan with borax on tensile index are presented in Figure 5. The addition of unmodified xyloglucan at a dosage of 0.5 or 1.0% of dry weight produced a slight increase in tensile index. Tensile index was improved by 25% when xyloglucan was mixed with borax. Oxidation of xyloglucan enhanced the dry strength of the samples considerably. Spraying xyloglucan at a dosage of 0.5% and 1.0% of dry weight increased the tensile index by 30% and ~60%, respectively.

### Introduction of chemicals

In the pilot trials, the chemicals were introduced to the wet fibre network by spraying at the end part of the former section. Spraying of the chemicals at the former section was found to have no significant influence on the dry content of the web after the press section compared to unsprayed samples. The wet pressing load was either 600 kN/m or 1200 kN/m in the trials. Different wet web draws (0.5 to 2.0%) were tested at transfer of the wet web from the press section to the drier section.

The results of the pilot on-line measurement of wet web strain at break as a function of sprayed chemical dosage are presented in Figure 6. Native potato starch produced

a slight increase in strain at break when sprayed on base paper with no filler. Introduction of native xyloglucan (tamarind kernel powder, containing 60% xyloglucan) and especially native guar gum significantly enhanced the strain at break value of base papers with 15% PCC. According to the results, spraying guar gum at a dosage of 0.3% enables addition of 15% PCC without loss in wet web strain at break value.

Figure 7 shows the tensile index results as a function of sheet density measured from pilot machine samples. As expected, tensile strength increases as a function of sheet density. At a constant sheet density level, spraying of native potato starch and native guar gum enhanced the tensile index compared to the unsprayed reference. The guar gum dosage required to reach a given tensile

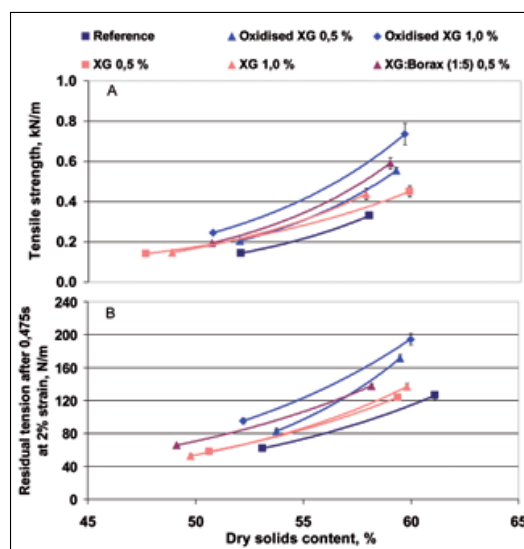


Fig. 4: Influence of oxidation and crosslinking of xyloglucan (0.5% or 1.0% of d.w.) with borax (mixed to a ratio of 1:5) on wet tensile strength (a) and residual tension (b) as a function of sheet solids content

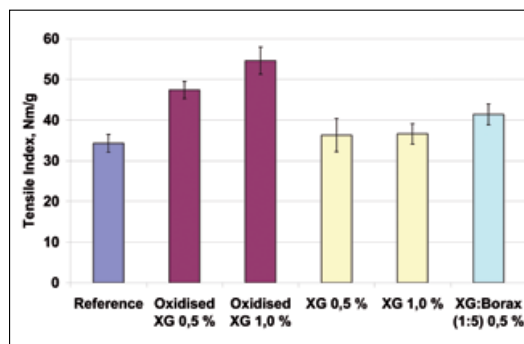


Fig. 5: Influence of oxidation and cross-linking xyloglucan (0.5% or 1.0% of d.w.) with borax (mixed to a ratio of 1:5) on the dry tensile index as a function of dry sheet density

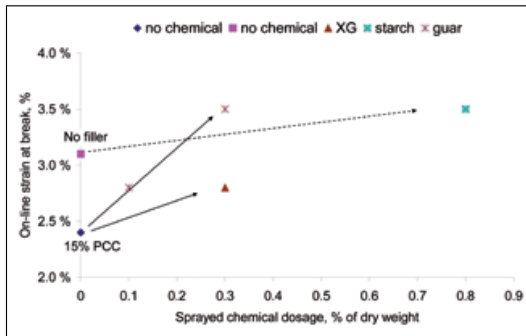


Fig. 6: Influence of chemical spraying on on-line measured wet web strain at break on the pilot machine

index value was found to be less than half that of starch. Addition of native xyloglucan without synergism with borax or aldehyde groups did not influence the tensile index of the pilot sample.

### Discussion

The wet and dry strength of paper samples increased when xyloglucan and, especially, xyloglucan with borax was introduced to the fibre network. Xyloglucan synergism with borax was not observed with decreased molecular weight xyloglucan. These results indicate that when cross-linked by borax, long bridging polymers are needed for improving the adhesive forces between fibres in the wet web and in the creation of strong fibre bonds and a large bonding area in drying. Due to the low solids content (50 to 60 %) after wet pressing, minimal hydrogen bonding occurs in the web at this stage and, therefore, the creation of covalent bonds, e.g. by a xyloglucan-borax complex or by introducing aldehyde groups to xyloglucan, can play an important role in strengthening the wet fibre network. This theory was supported by xyloglucan oxidation results which showed that aldehyde groups strongly enhanced wet and dry strength properties. The effect of oxidised xyloglucan on dry tensile strength was much higher than with the xyloglucan borax complex.

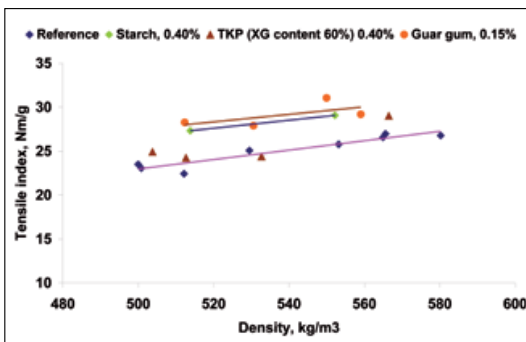


Fig. 7: Influence of chemical spraying on the pilot machine on the off-line measured dry tensile index as a function of dry sheet density

In the pilot trials, the application of xyloglucan, guar gum or starch to the wet fibre network by spraying at the forming section of the pilot machine did not influence the dry content of the web after the press section. This may be due to fact that free water introduced to the fibre network by spraying is relatively easily dewa-

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tered at the end section of the former and in wet pressing. According to the on-line wet strain results from the pilot machine, the application of guar gum may enable increased filler content without loss of runnability or dry sheet strength properties.

Paper machine runnability and end product strength properties are typically modified by means of several different chemical additives. Based on this research, many of these chemicals could be replaced by oxidised xyloglucan or guar gum alone. This can contribute to achieving chemical savings and more simplified and stable wet end chemistry. ■



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## Enhanced quality, strength and cost efficiency by means of layering

### Keywords

Stratifying, runnability, relaxation, residual tension, wet paper, strength.

### Abstract

The effect of adding thermo-mechanical pulp (TMP) in the middle layer of fine paper was studied. Bleached hardwood pulp made of birch (BHW) was stratified in top and bottom layers, while TMP was layered in the middle layer of hand sheets. The amount of TMP in the middle layer was varied from 10 to 40 percent of grammage. Chemical pulps were beaten with a Valley laboratory beater so that they had the same tensile index of dry paper as that of TMP. In addition to standard paper, technical properties, tensile and relaxation properties of dry and wet paper at high strain rate were studied. Decrease in brightness when replacing part of chemical pulp with TMP was evaluated for the layered structure. In addition, a new method based on Kubelka & Munk equations was developed to characterize the success of stratifying.

Layering of TMP in the middle enhanced surface smoothness significantly compared to trials points, where pulps were mixed and homogenous. Adding of 40% of TMP pulp in the middle layer had no effect on surface properties of hand sheets. Addition of TMP increased the bulk of uncalendered hand sheets significantly. Increase in TMP or stratifying the pulps had no effect on the tensile properties of dry paper. Tensile strength and residual tension, i.e. tension holding capacity of wet web, increased significantly when increasing TMP in furnish. Mixing TMP in pulps instead of stratifying resulted in higher tensile and residual tension values for wet samples. A theoretical study showed that addition of TMP decreases brightness significantly also with layered structure.

### Tiivistelmä

#### Kuitukerrostuksella parempi paperin laatu, lujuus ja kustannustehokkuus

Tässä työssä selvitettiin termomekaanisen massan (TMP) käyttöä hienopaperin keskikerroksessa. Valkaistua koivusellua ker-

rostettiin käsiarkkien ala- ja yläpintaan ja TMP kerrostettiin keskikerrokseen. TMP:n osuus keskikerroksessa vaihteli välillä 10 ja 40 % neliömassasta. Kemiaaliset massat jauhettiin Valley-laboratoriojauhimella samaan kuivavetolujuustasoon TMP:n kanssa. Tunnettujen paperiteknisten määrittysten lisäksi tehtiin kuiville ja märille näytteille vetolujuus- ja relaksaatiomittaukset nopeassa vedossa. TMP:n kerrostamisen vaikutusta hienopaperin vaaleuteen arvioitiin eri neliömassoilla ja TMP:n osuuksilla. Kerrosrakteiden puhtauden selvittämiseksi kehitettiin uusi optiseen mittaukseen perustuva menetelmä. Menetelmässä hyödynnettiin paperin valmistajille hyvin tuttuja Kubelka&Munk -yhtälöitä.

Kerrostamalla TMP keskikerrokseen saatiin arkin sileyks pysymään koivusellun tasolla. Jopa 40 % TMP:n osuus keskikerroksessa ei laskenut arkin sileyttä. Odotetusti TMP käyttö lisäsi huomattavasti kalanteroimattoman näytteen bulkkia. Kuivien näytteiden vetolujuuteen ei TMP:n lisäämisellä ollut vaikutusta. Sen sijaan märkien arkkiin vetolujuuteen ja kireydenpitokykyyn oli TMP:n lisäyksellä suuri vaikutus. Seosrakteella saatiin parempi märän rainan vetolujuus ja kireydenpitokyky kuin kerrosrakteella. Teoreettinen tarkastelu osoitti, että TMP:n käyttö massaseoksessa laskee huomattavasti paperin vaaleutta. Tämä havaittiin myös kerrostetuilla näytteillä.

### Introduction

The average annual increase in top PM production speed has been 30–40 m/min during the last decade, depending on the paper grade. The development of PM speed is mainly limited by mechanical properties of wet web. In the press-to-dryer section web transfer, the dry solids content of paper ranges typically 40–50 %. At this state the tensile strength of the web is only 10–15% of the corresponding value of dry paper /1–3/. Surprisingly, paper grades of low grammage, high filler content and low dry paper tensile and tear strength are produced with the highest production speeds (LWC, SC and News), whereas, paper grades of high tensile properties of dry paper are

produced with lowest production capacities (fine papers).

In order to achieve a sufficient tension that stabilizes the wet web in the open draw and on the dryer section, a certain strain is needed. The tension created in the open draw is rapidly decreased by the plastic and viscoelastic properties of the wet web. With low residual tension the probability of bagging, fluttering, etc., runnability problems will increase significantly. It is evident that by increasing the residual tension of wet web (minimizing the relaxation) the PM production speed can be increased. It has been shown that papers made from mechanical pulp have significantly higher residual tension and tensile strength than wood-free paper grades /4/. This is one of the main reasons, why modern paper machines producing wood-free paper grades have significantly lower production speeds compared with those producing wood-containing ones.

Stratifying of different furnishes and chemicals have been studied earlier. The effect of layering on dry paper tensile and quality properties has been published /5/. Less attention has been given to the effect of layering on wet web mechanical properties. The aim of this study was to clarify the effect of stratifying mechanical pulp in wood-free pulps. Special attention was paid to tensile and relaxation properties of wet web. In addition, surface and optical properties of samples were studied.

### Materials and methods

#### Hand sheets

Multilayered hand sheets of 60 g/m<sup>2</sup> were prepared with a special laboratory sheet former. The pulps used in forming were bleached softwood pulp (CSF 620 ml, fibre length 2.20 mm), bleached hardwood pulp (CSF 450 ml, fibre length 0.88 mm) and bleached TMP (CSF 60 ml, fibre length 1.86 mm). Sheets were wet-pressed on two

1. Oksanen, A., Salminen, K., Kouko, J., VTT Technical Research Centre of Finland, VTT, PO Box 1603, FI-40101 Jyväskylä, Finland.

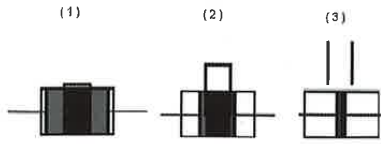


Fig. 1. Principle of multilayer sheet forming.

different excess pressure levels (50 kPa and 350 kPa) in order to reach two different levels of dry solids content.

A special feature of this multilayer sheet former is its two-sided water removal. The principle of multilayer sheet forming is shown in Fig. 1. The pulp and chemicals were added into chambers (Fig. 1, part 1). The pulps were mixed with air before the actual sheet forming, where the fabrics were pushed pneumatically towards each other (Fig. 1, part 2). When the fabrics were moved close to the dividing plates, the plates dividing different chambers were removed by vertical cylinders (Fig. 1, part 3) /6/.

### Impact -fast tensile test rig

Dynamic tensile strength and relaxation properties of samples were measured with an Impact, fast tensile strength testing rig /1/. Average straining velocity was 1 m/s (while standard tensile strength test velocity is 22 mm/min = 0.00037 m/s).

The relaxation properties after certain relaxation time were measured at a strain of 1% for dry samples and wet samples. The relaxation time was 0.475 s for wet samples. Tensile properties were also measured for dry and wet samples. The principle of relaxation test is shown in Fig. 2. An example of tensile strength measurement is shown in Fig. 3.

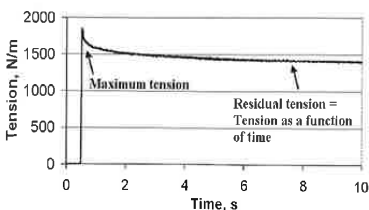


Fig. 2. Dry paper relaxation test curve at 1% straining by Impact test rig.

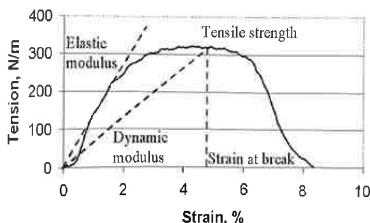


Fig. 3. Tension test curve by Impact.

### Method of layer purity measurements

A method was developed to evaluate the layer purity of stratified paper samples. High layer purity means that there is only little mixing of stratified pulps in the thickness direction of papers. The method was based on differences in the light scattering and absorption properties of various kinds of pulp. Scattering and absorption coefficients ( $s_{560}$ ,  $k_{560}$ ) were determined with spectrophotometry for tape-stripped layers of samples using black and white backgrounds /7/.

$$a = \frac{1}{2} \cdot \frac{(R_{gv} - R_{gs})(1 + R_w R_s) - (R_w - R_s)(1 + R_{gs} R_{gv})}{R_s R_{gv} - R_w R_{gs}} \quad (1)$$

$$R_w = a - \sqrt{a^2 - 1} \quad (2)$$

$$s = \frac{1}{w \left( \frac{1}{R_w} - R_w \right)} \cdot \ln \frac{(1 - R_w R_s)(R_w - R_{gs})}{(1 - R_w R_{gs})(R_w - R_s)} \quad (3)$$

$$k = \frac{s \cdot (1 - R_w)^2}{2 \cdot R_w} \quad (4)$$

where

- $R_w$  = reflectance factor of sample measured over white background
- $R_s$  = reflectance factor of sample measured over black background
- $R_{gs}$  = reflectance factor of white background
- $R_{gv}$  = reflectance factor of black background
- $s$  = light scattering
- $k$  = light absorption

Tape stripping was found to be the main source of error. The stripped layer should be even and contain fibres enough for reliable optical measurement. Other sources of error were the effect of tape and the limitations of Kubelka & Munk theories for low grammages /8,9/. Weaknesses of Kubelka & Munk theories for very low grammages were found to be indomitable if there is a significant difference (>0.2 m<sup>2</sup>/kg) in absorption coefficients between the layers. A tape of high transparency was selected to minimize the effect of tape on the measurement. Hence, the layered structure of tape and paper sample was not considered in the measurement and calculation. Additive rule for homogenous structure was used to compensate the effect of tape on the absorption coefficient /7/.

$$k_{paper} = \frac{k_{paper+tape} - k_{tape}(1 - X_{paper})}{X_{paper}} \quad (5)$$

where

- $k_{paper}$  = absorption coefficient of paper,
- $k_{paper+tape}$  = absorption coefficient of paper and tape,
- $k_{tape}$  = absorption coefficient of tape,
- $X_{paper}$  = mass share of paper in tape stripped layer.

### Paper technical properties

The paper-technical properties of paper and pulp samples were determined according to SCAN standards. Tensile and relaxation tests with the Impact fast tensile test rig, and hand sheet preparing with the multilayer sheet former were performed with own methods and standards.

### Experimental

Hand sheets containing 10%, 25% and 40% of TMP pulp in the middle layer and the same amount uniformly distributed with BHW were formed. These trial points were compared to those of hand sheets containing 40% of softwood (stratified to middle layer and uniformly distributed). The trial points are shown in Table 1.

### Results and discussion

Distribution of TMP in sample's thickness direction was optically measured from tape strips (Fig. 4). At trial points where TMP was rationed to the middle layer, TMP spread only little toward surfaces. For example, when rationing 10% of TMP in the middle layer it spread to 20% of total grammage. Respectively, when rationing 40% of TMP in the middle layer it spread to 50% of total grammage. Therefore, the total mixed boundary layer area with three-layer structure was about 10% of total grammage. This can be seen in Fig. 4 where measured TMP distribution (solid line) and theoretical TMP distribution (dashed line) are presented in sample's thickness direction. Theoretical TMP distribution curves are based on pulp dosages in different layers and  $k_{560}$  values of pure hardwood and TMP samples. Trial point of 10% TMP in the middle layer gave lower values of absorption coefficient. This was due to mixing of boundary layers. Minor mixing in boundary layers is desired to achieve a proper internal strength with three-layer structure. Overall stratifying of TMP and chemical pulps succeeded excellently.

The effect of stratifying and mixing different pulps on bulk values of trial points is shown in Fig. 5. The same bulk value (1.54 cm<sup>3</sup>/g) was achieved either by 40% share of softwood or by 10% of TMP. The bulk was increased by increasing the amount of TMP. An increase of 10 to 40% in the

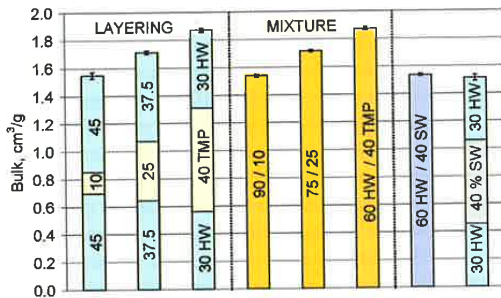
**Table 1. Percentage of pulp component and pulp type in the layers of trial points.**

Trial point	Top layer, %	Middle layer, %	Bottom layer, %
1	45% [HW]	10% [TMP]	45% [HW]
2	37.5% [HW]	25% [TMP]	37.5% [HW]
3	30% [HW]	40% [TMP]	30% [HW]
4	90% [HW] + 10% [TMP] evenly in all layers		
5	75% [HW] + 25% [TMP] evenly in all layers		
6	60% [HW] + 40% [TMP] evenly in all layers		
7	60% [HW] + 40% [SW] evenly in all layers		
8	30% [HW]	40% [SW]	30% [HW]

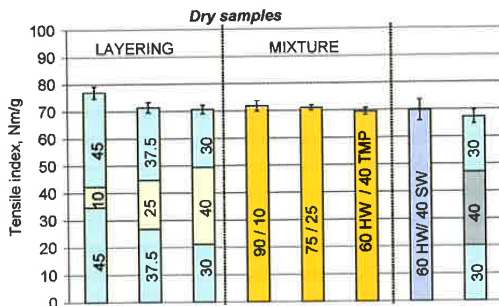
TMP content improved the bulk approximately by 20%. Stratifying and mixing of TMP had a similar effect on bulk.

The effect of different pulps on Bendtsen roughness is shown in Fig. 6. The roughness values of the samples increased significantly with the increasing amount of TMP when the pulps were blended. An increase of 40% in TMP on the middle layer had no effect on the roughness of hand sheets. This result indicates that a significant amount of TMP can be covered with hardwood.

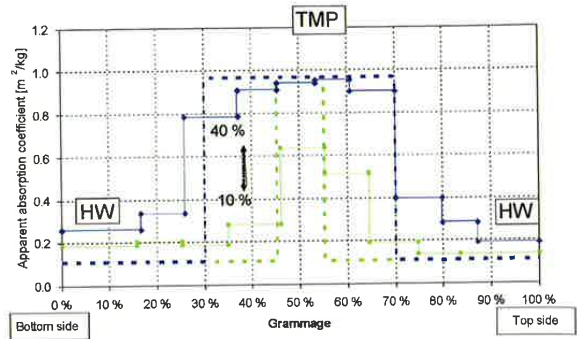
Tensile index of dry paper samples is shown in Fig. 7. The target of tensile index was 70 Nm/g in order to compare mechanical and quality properties for the same tensile strength of dry paper. As can be seen from Fig. 6, there were only minor differences between tensile strength values of the samples. Fig. 7 also shows that stratifying of pulps had no effect on dry paper tensile strength.



**Fig. 5. The bulk values of the trial points.**



**Fig. 7. Tensile index of dry samples measured by fast tensile test rig Impact.**



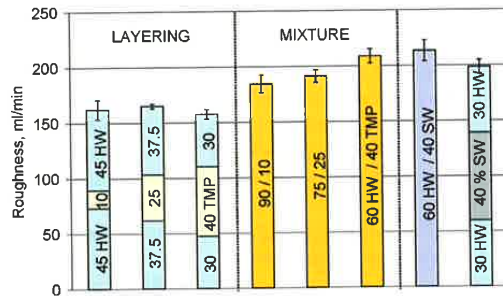
**Fig. 4. Determination of layer purity for stratified samples in thickness direction by measuring absorption coefficient from tape stripped layers. Solid lines represent measured data when dashed lines are theoretical curves for 10% and 40% TMP content in middle layer.**

The tensile index of wet samples (dryness 50%) is shown in Fig. 8. By increasing the amount of TMP share in the pulp, a significantly higher wet tensile strength was gained. Improvement in tensile strength was also significant when softwood was replaced with TMP. Mixing TMP in pulp gave higher tensile strength values than stratifying. The increment of wet web tensile properties can be explained especially by increment of fines and middle fraction proportion in wet web. Wet web is held together by friction between fibres and fibre-fibre interactions. Fines and middle fraction particles fill interfibre space during sheet dewatering and increase the amount of fibre-air-water interactions [8]. This also explains why the

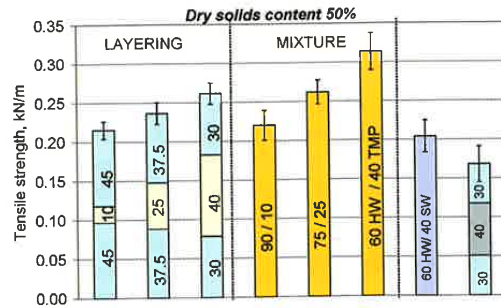
more evenly distributed TMP content had a greater effect on wet web tensile strength.

By stratifying only 10% of TMP, the residual tension was increased by 30% as shown in Fig. 9. When replacing softwood completely (40% of total amount of pulp) with TMP the residual tension increased approximately by 100%. This means that by increasing TMP to furnish, the strain from the press-to-dryer section can be decreased significantly. By decreasing the strain, a lower porosity and higher strain of the final product can be achieved.

Top layers have a great influence on brightness when stratifying TMP to the middle layer. Covering of 'dark' TMP with 'bright' bleached hardwood is more efficient



**Fig. 6. Bendtsen roughness of samples.**



**Fig. 8. Tensile strength of wet paper at 50% initial dry solids content.**

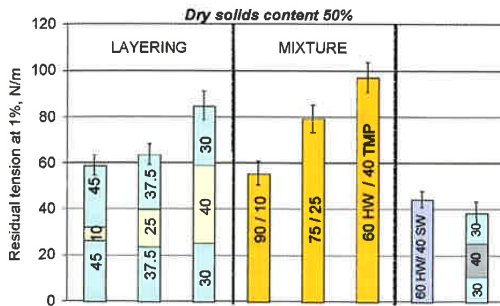


Fig. 9. Residual tension of wet paper at 50% initial dry solids content.

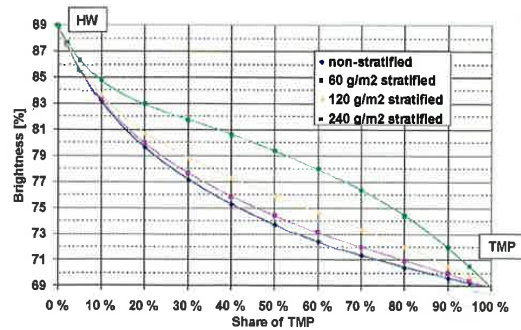


Fig. 10. Theoretical effect of TMP share on calculated brightness of three-layer hand sheets with different grammages.

with higher paper grammages. In Fig. 10, the theoretical development of brightness is shown as a function of total grammage and TMP share in the middle layer. These curves are only suggestive because no measurements of three layer samples were used in these theoretical brightness curves. The scattering ( $S_{457}$ ) and absorption ( $k_{457}$ ) coefficients measured for pure hardwood and TMP samples and equations for three-layer constructions were used to calculate curves shown in Fig. 9 /7,11–12/.

$$R_{\infty ABC} = \frac{1 + R_{0ABC} R_{0CBA} - T_{ABC}^2}{2R_{0CBA}}$$

$$\sqrt{\left( \frac{1 + R_{0ABC} R_{0CBA} - T_{ABC}^2}{2R_{0CBA}} \right) - \frac{R_{0ABC}}{R_{0CBA}}} \quad (6)$$

where

- $R_{\infty ABC}$  = reflectance factor of three-layer construction ABC over pad,
- $R_{0ABC}$  = reflectance factor of three layer construction ABC over black background,
- $R_{0CBA}$  = reflectance factor of three-layer construction CBA over black background,
- $T_{ABC}$  = transmittance of three layer construction ABC.

The high grammage in Fig. 10 means thick 'bright' hardwood layers in the bottom and top side of sheets. Brightness drops very steeply even with a very low amount of TMP. According to these curves it is obvious that brightness cannot be retained at a high level when covering TMP with hardwood. An explanation for this is low scattering coefficient,  $S_{457}$ , of hardwood /7/. Brightness can be improved by layering high brightness fillers or optical brightener on the bottom and top layers. Coating of paper is an efficient way of improving brightness. Stratified base paper enhances the brightness of the final coated product compared to a non-

stratified product. Brightness curves would obviously be different for other pulp types. For example, CTMP with higher brightness in the middle layer would be easier to cover with chemical pulp.

### Conclusion

The potential of adding thermomechanical pulp (TMP) in the middle layer of fine paper was studied. The success of stratifying (layer purity) with a multilayer sheet former was estimated by a new method. It was shown that stratifying of TMP on with multilayer former was successful.

The results of this study indicated that replacing softwood pulp with stratified TMP in middle layer enables higher gain of bulk, opacity and surface smoothness of final product. No significant changes on tensile properties of dry paper were found.

Even a minor increment of TMP pulp in bleached hardwood improved the tensile and relaxation properties of wet web. This effect was slightly higher when TMP was mixed in fine paper in stead of stratified in the middle layer. The increase of wet web tensile and relaxation properties enables increase of production speed at paper machine which leads to higher profitability.

Theoretical study indicated that increase in TMP content in furnish decreases the brightness of hand sheets significantly. The study also showed that the brightness loss can be reduced by stratifying pulps of high grammage. On the other hand, increased wet web mechanical properties might enable higher amount of fillers in paper at similar production speed. The use of TMP in low grammage fine papers, that have demands for high brightness, might be unlikely in the future, but the use of CTMP (having higher brightness) might be possible even in those grades.

By replacing long fibres with TMP, the cost efficiency can be improved significantly by improved production speed but also by lowered raw material costs. Increasing price

of energy might lower the benefit in material costs when replacing chemical pulp with TMP. Additionally, new investments are necessary in order to stratify furnishes. For example, multilayer headbox and two different short circulations might be required. Despite some unsolved problems, stratifying was found to be a potential way of improving paper quality and runnability potential of furnishes in the future.

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# The effects of TMP and filler stratifying on wet web runnability and end product quality of fine paper

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**KEYWORDS:** Times New Roman (normal) 10 pt, Stratifying, Chemical pulp, TMP, PCC, Wet strength, Dry strength, runnability

**SUMMARY:** Increase of filler content in paper improves quality of the final product and reduces raw material costs. However, this is often accompanied by deterioration of paper machine runnability. In this paper the effects of stratifying PCC (precipitated calcium carbonate) and TMP on fine paper quality and the mechanical properties of dry and wet paper were studied. In addition, a new method was introduced for evaluating the layer purity of pulp and filler stratifying by measuring the fibre length distribution in the thickness direction of the paper. The filler addition reduced the mechanical properties of paper more with chemical than mechanical pulps, with similar dry tensile indices. Stratifying filler onto paper surfaces gave higher dry tensile strength properties than samples with mixed structures, whereas only a small positive effect was detected for wet tensile and relaxation properties as a result of stratifying. Stratifying fillers only had a small negative effect on the internal bond strength. Stratifying or mixing TMP with a chemical pulp blend was shown to enable an increase in the filler content of 10% without significant changes in the residual tension (tension after 0.475 s of relaxation) or tensile index of wet samples. Based on layer purity analysis, stratifying TMP and filler was found to be successful in these trials.

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The presence of fillers in paper improves the optical properties of paper, such as brightness and opacity. Other quality properties of paper such as smoothness and ink receptivity can also be obtained using fillers. The economic benefits of using fillers are significant as they are less expensive than pulps (Krogerus 1999). An increase in filler content is generally known to reduce the tensile strength of dry paper due to the lowered grammage and density of the fibre network, the relative bonded area (RBA) and the strength of the bonds (Scott 1987). Aggregates of fillers, fines and fibres cover the fibre-fibre crossings in the web structure, preventing the development of hydrogen bonds between the

fibres. Due to intensive flocculation, poor formation leads to uneven stress distribution during straining and therefore decreases the tensile strength of dry paper (Brown 1990).

Fine papers with filler contents of 15-25% are common in the paper industry. An increase in the filler content typically leads to sheets with low wet web strength and thus to increased amount of web breaks on paper machines (especially in the open draw between the press and the dryer section), or reduced production speed (Güldenbergh et al. 2004; de Oliveira et al. 2009). After the open draw, the velocity of the web remains constant for a considerable time. During this time, the tension created in the open draw does not remain constant but decreases rapidly, i.e., tension relaxation occurs. Of the tension created during straining, 50-60% is typically lost during the 0.5 s relaxation time (Kurki et al. 2004). Lowered tension due to relaxation may lead to slackening of the wet paper. This causes wrinkling, bagging, fluttering and weaving of the web, which can lead to web breaks. An increase in straining generates higher tension in the open draw and after relaxation (residual tension). Increased straining is accompanied by negative effects on the mechanical properties and quality of the final product however. For example, strain at break, porosity and z-directional (thickness directional) delamination energy of the final dry paper are greatly dependent on the straining the paper undergoes during manufacturing in the paper machine line. For this reason, the straining of paper in paper machines is often minimised (Grön 2003). The relaxation characteristics of wet paper are therefore of great importance.

Mechanical pulps typically have higher wet web stiffness and higher stress levels than chemical pulps after a similar draw. These are essential reasons for high production efficiency of wood containing paper grades (LWC, SC, News). Papers containing mechanical pulps have lower material costs, better dimensional stability and lower grammage than wood-free paper grades. The main downsides of mechanical pulp use are diminished surface smoothness and brightness (Kouko, Kekko 2006).

In addition, a novel method of analysing the layer purity of paper is introduced. Fibre length and filler

distributions in the thickness direction of paper are known to have a correlation with many of the technical properties of paper (Hägglom-Ahnger 1998). For coating and printing quality, particle distribution is essential in the z-direction of the paper. For example, uneven fines distribution may induce paper curl and reduce the internal strength of the paper. There are only a few methods to define particle size distribution in the thickness direction of the paper. These methods are typically quite inaccurate, time-consuming and may need expensive equipment. The Micro Tome technique is a well-known method to characterise fibre and filler distributions in the thickness direction. In this method, the paper sample is first chemically treated to obtain a high contrast between the fillers and fibres. A small sample is cut from the stiffened resin capsule for microscopic examination. The proportions of fibre, filler and void volume are calculated using image analysis. The basic disadvantages of this method are the limited information from the very small sample area and that it is time-consuming. Besides light waves, the sample can be illuminated by electrons. Scanning Electron Microscope (SEM) images have a much higher magnification than those of a light microscope. The disadvantages are the small measurement area and high price of the microscope. SEM is used in the paper making industry, e.g., in the structural analysis of coated paper. With X-ray Microtomography (XMT), it is possible to form a three-dimensional image by focusing X-rays from different angles onto the sample. The resolution of XMT is between 1 and 5  $\mu\text{m}$ . SEM also enables examination of density and pore size distributions in the thickness direction of the paper (Roux et al 2008; Turpeinen 2005). With the Beloit Sheet Splitter (Tappi UM-576 Method), it is possible to strip the sample into layers in the thickness direction of the sheet. In this method, the wet paper sample is introduced into the nip of the stainless steel splitting rolls. These rolls are cooled to a point below  $0^{\circ}\text{C}$ . The sample is split internally on the outgoing side of the nip. The split sections are doctored from the rolls. The method can be used, e.g., to determine the ink or coating penetration into base paper. Different layers of paper samples can also be revealed by grinding (Beckman, Plucker 1973). The advantages of this method are ease and large sample area. The disadvantage is that the layers come from different samples, as ground dust cannot be exploited. Another way to split the paper sample into layers is to use the tape stripping method (Erkkilä 1995). The tape stripping technique is generally used in determining filler distribution and fibre orientation in the thickness direction of the paper sample. With

tape splitting, a large number of layers can be produced. The area of the layer sample can even be of A3 size, thus the splitting of the paper with this method is very uniform. Oksanen et al. 2007 introduced a method based on tape splitting of the paper sample. In this article, optical differences in pulp samples were used to define distributions of pulp samples in the thickness direction of the paper samples. Layer purity was also optically defined from the tape strips in the thesis of Puurtinen 2003. In this study, the optical difference between pulps was prepared by colouring part of the furnish.

The objective of this work is to clarify if stratifying fillers and different furnishes can be used to enhance the strength properties and quality of paper or to increase the amount of filler content. Additionally, the aim was to develop and use a novel method to characterize filler and fibre distributions in thickness direction of stratified paper sheets.

## Materials and Methods

### Pulp samples

Mechanical and chemical pulp samples were provided by Finnish pulp mills. The studied furnishes consisted of chemical pulp mix and TMP. The chemical pulp mix consisted of 60% bleached birch kraft pulp and 40% bleached pine kraft pulp. Once-dried chemical pulp sheets were beaten with ProLab refiner (at 4% consistency) to the same dry tensile index level (48 Nm/g, birch CSF 350 ml, pine CSF 610 ml) as TMP (CSF 60 ml) in order to make the comparison of the different samples more valid. The cationic retention aid (cationic polyacrylamide) by Ciba (Percol 47) was used at all the trial points. The filler used was precipitated calcium carbonate (PCC) provided by Specialty Minerals Inc. (Albacar LO).

### Multilayer handsheets and testing standards

Wet and dry laboratory handsheets of  $60\text{ g/m}^2$  were formed with a multilayer sheet former. The device enables three-layer handsheets to be made. Another special feature of this multilayer sheet former is two-sided water removal in sheet preparation. The principle of multilayer sheet forming was introduced in the publication by Puurtinen et al. 2003.

In order to achieve two-sheet dryness levels for wet strength measurement, half of the laboratory sheets were wet pressed at 50 kPa and the other half at 350 kPa level in a laboratory sheet wet press (Lorentzen & Wettre). Table 1 presents the standards used in the determination of paper-technical properties of paper and pulp samples. Sheet samples were stored and tested in an air-

conditioned laboratory where the relative humidity was 50% and the temperature 23°C.

Table 1. Standards for testing pulp and paper quality.

Procedure	Standard
Bendtsen air permeability	SCAN-P 26:78
Bendtsen roughness	SCAN-P 84:01
Disintegration (cold and hot)	SCAN-C 18:65
Fibre length (L&W FiberMaster STFI)	ISO/DIS 16065-2
Freeness	SCAN-C 21:65
Grammage	SCAN-P 6:75
Tensile strength	SCAN-P 38:30
Internal bond strength by Huygen	TAPPI T 403
Thickness	SCAN-P 7:75

### Measurement of filler content and fibre dimension distributions in the thickness direction of a paper sample

In this study, the determination of the filler and fibre content and fractions in the thickness direction of the paper samples were based on the tape stripping technique. The tape stripping technique (Erkkilä 1995) enables representative samples from the bottom to the top layer, and it is easy to operate. In the filler distribution method, the tape stripped layer samples of paper consisting carbonate (e.g., PCC) are combusted at a temperature of 500°C. The fibre and tape material is burned off from the sample leaving ash intact. The oven ash content of the layers was determined by weighting the samples before and after combustion and reducing the results.

It was very challenging to determine the fibre dimension distribution in the thickness direction to a good level of accuracy. This paper presented a fibre dimension analysis in the thickness direction of paper based on three main steps:

1. Tape stripping of the paper sample into layers (*Fig 1*)
2. Dissolution of fibres from tape glue
3. Fibre dimension analysis of pulp samples

In this method tapes are placed on both sides of the paper sample (the tape strip area was 14.1 cm x 14.2 cm) before lamination of the sample with Ibeco IL-12HR. Laminated sample is stripped to two layers. The layers are further stripped until they reach basis weight from 3 to 15 g/m<sup>2</sup>. A paper sample of basis weight 60 g/m<sup>2</sup> can be stripped from 9 to 12 layers. The quantitative demand of fibre samples for fibre dimension analysis sets a minimum for the tape strip area or tape strip thickness respectively.

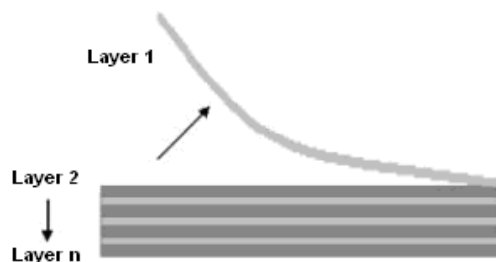


Fig 1. Principle of tape stripping of paper samples. The paper tape lamination device (Ibeco IL-12HR) and tape (Scotch Brand 9308) are used in this method.

The main aim of this research was to find a way to release fibres from the glue of the tape without causing any significant change in amount of fines or defects to the fibres. While developing the method, various kinds of materials and procedures were studied. The optimised method parameters were tape and solvent type and the dissolution conditions. Following procedure was developed in this work in order to release fibres from the tape. Tape strips are first sprayed twice with solvent (Label off 50, CRC industries Europe). Second treatment with solvent is done 2 min after first spraying. After 5 min of first spraying, the fibres and glue are scraped off from the tape and blended with 80 ml of water. In this point suspension contains still glue which have to be removed. Because glue floats in the water, suspension is mixed for more than 30 s with blender bar when most of the glue will separate on to surface of the suspension where it can be removed with spatula and pipette. Finally, residual glue is separated on to surface of the suspension by centrifugation of the suspension 10 min with intensity 4100 r/min. Probably, some glue will stay in the suspension after treatments, but this residual glue was not noticed to influence on the results of fibre dimension analysis.

After releasing fibres from the tape, the fibre dimensions can be measured further with a conventional fibre dimension analyser. Although, the influence of residual glue in the suspension on fibre dimension analyser with narrow flow capillaries is not known. In this study used fibre dimension analyser L&W FiberMaster STFI has large flow channels compared to many other analysers.

It was observed that fines were also released from the glue of the tape quite effectively because the total amount of fines decreased only slightly compared to fines content of the initial reference pulp.

## Tensile and relaxation measurements

A fast tensile test rig was applied to the paper tensile strength and relaxation tests. The strain rate used in this study was 1 m/s. The relaxation characteristics (tension after 0.475 s relaxation, i.e., residual tension) of wet paper have been suggested as an indicator for the runnability of wet paper at the beginning of the dryer section (Kurki et al. 2004; Kouko et al. 2007). In this study, the residual tension of wet paper was estimated from wet paper samples at two dryness levels after fast straining to 2% elongation followed by 0.475 seconds of relaxation.

## Results and discussion

The trial points of the stratifying study are presented in Table 2. The chemical pulp mixture consisted of 60% bleached hardwood (HW) and 40% bleached softwood (SW). Thermo-mechanical pulp (TMP) was introduced into different layers of 10, 20 or 100% of dry weight, on its own or mixed with chemical pulp slurry. The proportions of pulp and filler (PCC) were adjusted so that the grammage of the sheet samples was 60 g/m<sup>2</sup> at all the trial points. The total proportion of the dry matter of fibres (chemical and mechanical pulps together) was kept even in all three layers when the proportion of filler was 0, 10 or 20% of the layers. A constant 0.02% cationic retention aid dry weight dosage (Ciba, Percol 47) was added

evenly in all the layers and at the trial points.

Table 2. Trial points of filler and pulp stratifying into three layers with the multilayer sheet former. HW = hardwood, SW = softwood.

Trial point	Filler content			Fibre share		
	bottom [%]	middle [%]	top [%]	bottom [%]	middle [%]	top [%]
1	0	0	0	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW
2	5	0	5	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW
3	10	0	10	mix 60HW/40SW	mix 60HW/40SW	mix 60HW/40SW
4	tot. 20% evenly to all layers			mix 60 HW/40SW	mix 60HW/40SW	mix 60HW/40SW
5	5	0	5	45(60HW/40SW)	10TMP	45(60HW/40SW)
6	10	0	10	45(60HW/40SW)	10TMP	45(60HW/40SW)
7	5	0	5	40(60HW/40SW)	20TMP	40(60HW/40SW)
8	10	0	10	40(60HW/40SW)	20TMP	40(60HW/40SW)
9	tot. 20% evenly to all layers			40(60HW/40SW)	20TMP	40(60HW/40SW)
10	tot. 20% evenly to all layers			mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP
11	10	0	10	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP	mix 80(60HW/40SW)/20TMP
12	tot. 20% evenly to all layers			TMP	TMP	TMP
13	0	0	0	TMP	TMP	TMP

## Results from handsheet preparation

The filler distributions at three stratifying trial points (2, 3 and 4) are shown in Fig 2. The non-

symmetric shape of the distributions is derived mainly from the slight unevenness of the tape stripping. The layered structures are usually more difficult to strip into even layers than the mixed structures because of the high density variation in the thickness direction. Stratifying the filler was found to be successful according to the clear differences in filler distributions. Influence of stratifying of 10% PCC into the bottom and top layers (Fig 2A) induced U-shape filler distribution. As expected, U-shape filler distribution was steeper when 20% PCC was stratified into surface layers (Fig 2B). Stratifying PCC evenly into all three gave almost flat filler distribution (Fig 2C). Slight U-shape curve derives from two sided water removal of multilayer sheet former.

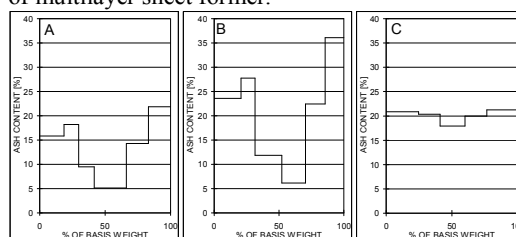


Fig 2. Filler distributions in the thickness direction determined by oven ash from tape strips at a combustion temperature of 500°C. Ash content in the thickness direction of the samples: (A) trial point 2, 10% PCC of the dry weight, stratified into the bottom and top layers, (B) trial point 3, 20% PCC of the dry weight stratified into the bottom and top layers, (C) trial point 4, 20% PCC of the dry weight stratified evenly into all three layers. A chemical pulp mixture of 60% HW and 40% SW was used in all three layers.

As the average fibre lengths of the TMP and chemical pulp mixtures (60% HW and 40% SW) were the same (length of weighted fibre length ~1.4 mm), the stratifying, evaluated by the fibre length fraction proportions in layers, was a success. The

fibre fraction distributions in the thickness direction of the layered structures are shown in Fig 3A (trial point 5) and Fig 3B (trial point 7). The addition of TMP into the middle layer of 10 or 20% can be seen as a bend in the curves in the middle layers in the



figures. The increase in TMP content from 10 to 20% of the total dry weight can be observed as a higher fines content and decrease of 0.5-1.2 mm in the proportion of fibre fraction in the middle layer. The fibre length fraction of 0.0-0.2 mm is considered to be the fines fraction.

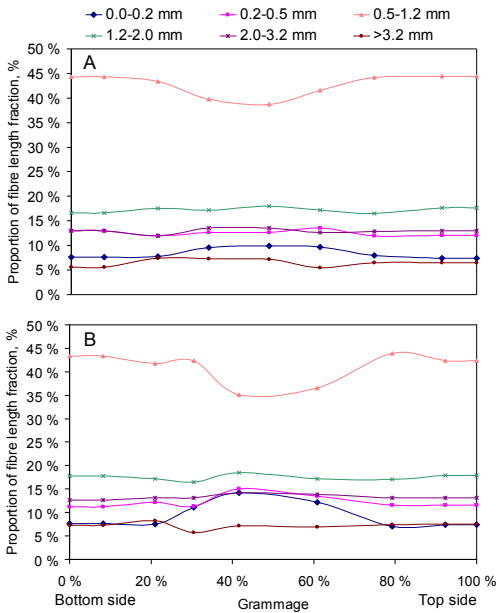


Fig 3. Fibre fraction distributions in the thickness direction of fine paper samples when stratified by (A) 10% TMP (trial point 5) and (B) 20% TMP (trial point 7) into the middle layer of fine paper. The preparation of fibre samples in the thickness direction of the paper was based on the tape stripping technique. The fibre fraction distributions were determined with the L&W FiberMaster STFI fibre quality analyser from fibre samples released from tape strips.

Looking at the fines content distribution, the stratifying was a success when evaluated more closely (Fig 4). As expected, a 20% higher dosage of TMP into the middle layer increased the fines content in the middle layer compared with a 10% addition of TMP. The boundary layer (mixed area) width is estimated at about 10% of the total grammage. According to Fig. 4, the layer purity is more or less the same for a 10 and a 20% TMP addition of total dry weight. A wider boundary layer means that more mixing has occurred between the layers. The theoretical sites of the boundary layers are located at the points 33% and 66% of the x-axis (marked in Fig 4). The grammage proportion of the individual tape strip affects the fines distribution curve of the sheet. In order to define the boundary layers with high accuracy, many low grammage tape strip samples need to be prepared. The resolution of the fibre quality analyser also sets a limit for how

many of the small particles, under 0.2 mm in length, are recognised.

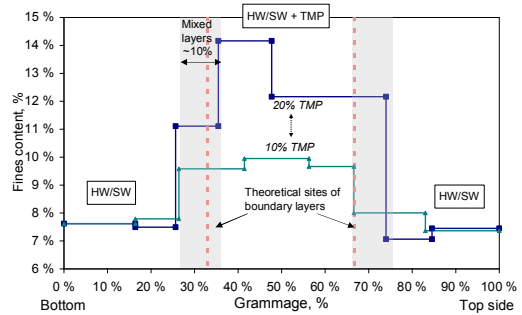


Fig 4. Distribution of fines content in the thickness direction of handsheets made with the multilayer handsheet former. The fines content is 0.0-0.2 mm particle fraction in pulp measured by the fibre quality analyser (FiberMaster). In the middle layer of the fine paper, 10% (trial point 5) or 20% (trial point 7) TMP was added.

Air permeability as a function of sheet bulk is presented in Figure 5A. The chemical pulp had high air permeability, which resulted from the low level of refining. Based on the sheet density and air permeability values of pure chemical and TMP sheets, the addition of TMP to the chemical pulp decreased the sheet density and air permeability. Air permeability decreased by 60% when 20% of the chemical pulp was replaced with TMP. On the contrary, an addition of 10 or 20% PCC of dry weight to the pure chemical pulp or pulp with 10 or 20% TMP of dry weight increased bulk and air permeability at the same time. Stratifying 20% PCC in the bottom and top layers of chemical pulp compared with the mixed structure, decreased air permeability by 25%. Mixing PCC with mechanical pulp (TMP) also increased air permeability, even though the sheet bulk decreased. Stratifying 20% TMP into the middle layer and 20% PCC into the surface layers decreased air permeability by 20% of the constant bulk level compared with an unstratified sheet structure.

Stratifying PCC by 10 or 20% into the surface layers of chemical pulp sheet increased sheet bulk without significant changes in sheet roughness (Fig 5B). On the contrary, the addition of PCC into TMP decreased the bulk and roughness. Mixing 20% PCC with chemical pulp gave 65% higher sheet roughness compared with a trial point at which PCC was stratified into the surface layers. The addition of TMP into the middle layer or evenly into all the layers decreased the sheet roughness more or less in the same way.

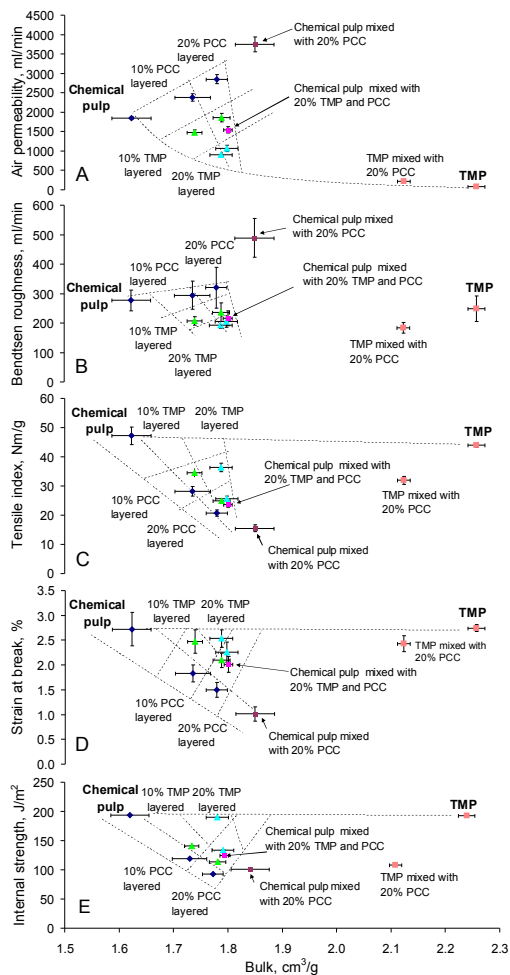


Fig 5. (A) Air permeability, (B) Bendtsen roughness, (C) tensile index, (D) strain at break and (E) internal bond strength by Huygen as a function of sheet bulk. Laboratory sheet wet press level was 3.5 bar (Lorentzen & Wettre).

### Strength properties of dry samples

Mixing 20% PCC with pulp reduced the tensile index of handsheets made from chemical pulp blend. The reduction in the tensile index was 70%, whereas with TMP pulp the reduction with a similar addition of PCC was only 37% (Fig 5C). This is probably related to the fact that TMP has a significantly higher surface area of fibrous material than chemical pulp. In other words, the addition of PCC has a relatively lower effect on the surface area of material that can form bonds in a paper network. Stratifying 20% of PCC into the bottom and top layers with chemical pulp blend instead of mixing it into all the layers increased the tensile strength of samples by 38%.

Mixing 20% of PCC with pure TMP only had a minor effect on the dry paper strain at break values (Fig 5D), whereas with chemical pulp blend the reduction was significant (the decrease was higher than 50%). Stratifying, instead of mixing 20% PCC into the bottom and top layers of the chemical pulp blend, increased strain at break by 37%. Stratifying fillers into surface layers and increasing the TMP content of the chemical pulp blend increased the strain at break values significantly. The dry paper strain at break is known to be important to the dry paper runnability in printing houses (Uesaka 2005).

The internal bond strengths by Huygen (model 1314, Illinois 60014, USA) of pure TMP and chemical pulp blend were similar (Fig 5E). For the internal bond strength, mixing PCC with chemical pulp also gave a higher reduction than for TMP samples. Stratifying PCC instead of mixing only had a minor effect on the internal bond strength of the samples. One argument against stratifying fillers and fibres has been the belief that layering may dramatically reduce the internal bond strength and therefore cause problems in, for example, printing.

### Tensile and relaxation properties of wet samples

Pure TMP and chemical pulp bends with no fillers had similar wet web tensile strength values (Fig 6). Mixing 20% PCC with whole pulp decreased the tensile strength of chemical pulp significantly (60%) at a dryness level of 55%. With TMP pulp, the reduction at this dryness level was significantly lower (15%). This suggests that with TMP pulp containing 20% less fibrous material, filler particles interact between fibres. The result correlates with the findings reported by de Oliveira et al. 2009. They concluded that small filler aggregates can increase friction between fibres and thus wet web strength. In contrast, large filler aggregates are easily detached from fibres due to the shear, and the aggregates interfere with fibre entanglement. As the size of the filler aggregates was not measured during this study, the difference in filler aggregate size between mechanical and chemical pulps cannot be estimated. The addition of TMP to the middle layer of chemical pulp increased the wet web tensile strength of the samples containing filler. Stratifying PCC into the top layers had a small positive effect on the tensile strength of wet paper but lower than for dry paper samples.

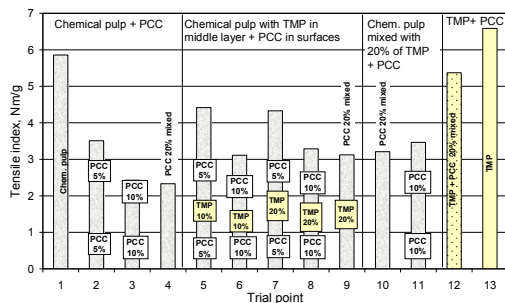


Fig 6. Effect of pulp type, filler content and their addition mode on the tensile index of wet multilayer handsheets (results are linearly interpolated to a dryness level of 55%) measured by the impact test rig at a strain rate of 1 m/s.

Pure TMP and chemical pulps gave similar dry and wet web paper tensile strength values. TMP had almost twice as high residual tension at 2% strain as pure chemical pulp at a constant dryness of 55% however (Fig 7). Mixing 20% PCC with pure TMP had no effect on the wet web residual tension at a constant dryness of 55% while a 20% addition of chemical pulp blend decreased residual tension by 40%. This result indicates that fillers have a higher effect on the interactions between fibres than the readiness of fibre segments to carry load. When stratifying 10% TMP into the middle layer of the chemical pulp blend and 10% PCC into the top layers, the wet web residual tension was not reduced compared with pure chemical pulp blend without any fillers. Stratifying fillers (20%) with pure chemical pulp or chemical pulp mixed with 20% TMP into whole pulp only had a small effect on the residual tension of wet web.

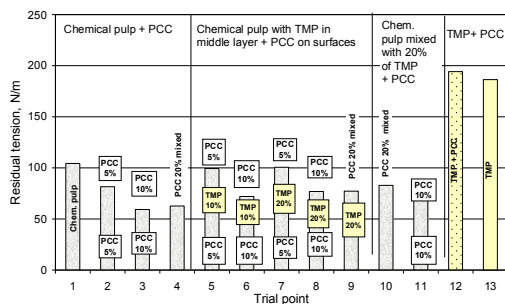


Fig 7. Effect of pulp type, filler content and their addition mode on residual tension at 2% strain of a wet multilayer handsheet (the results are linearly interpolated to a dryness of level 55%) measured by the impact test rig at a strain rate of 1 m/s.

## Conclusions

A new method was introduced to characterise the distribution of fibre dimensions in the thickness direction of the paper sample. Based on the fibre fraction results from the stratified paper samples the development of method was found to be successful. According to the fines distributions in the thickness direction of the sample, the intermixed layers made up ~10% of the total grammage. In order to prevent delamination of the multi layer sheet structure (e.g. in printing), little intermixing between the layers may be desirable.

The effects of stratifying PCC and TMP on fine paper quality and mechanical properties of dry and wet paper were studied. It was found that a high layer of purity in terms of filler content and fibre composition can be achieved with the multilayer sheet former. The filler content had a significant effect on all the mechanical properties of the dry and wet web. By stratifying PCC into the surface layers of paper, the tensile properties of dry samples were significantly increased, but only a minor effect on the wet web tensile and relaxation properties was observed. The mechanical properties of paper containing TMP were significantly less affected by an increased PCC content compared to paper of only chemical pulp. The residual tension of wet pure TMP sheets was significantly higher than that of chemical pulp at a similar dry strength. An addition of 10...20% TMP into the middle layer made of chemical pulp enables a 10% addition of filler in paper without any effect on the wet web tension, holding the ability at a constant dryness level.

The results of this study indicate that stratifying fillers, pulps and possibly chemicals can have a significant effect on the quality, strength and thus runnability potential of paper. Even though the formation of stratified structures in paper machines poses some challenges today, these results encourage further development of stratifying methods.

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