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FibreSurf – New biotechnological tools for wood fibre modification and analysis

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Summary

The objective of this cross-disciplinary research initiative was to unite several unique approaches for the analysis and modification of wood fibres working toward new value-added materials.

In contrast to their degradation to provide monosaccharides, plant cell wall polysaccharides can find added value as strength-building agents in papermaking. XG in particular possesses a uniquely high binding affinity for cellulose fibres, has excellent solubility in water, and is readily available as an agricultural by-product (tamarind kernel powder, TKP). Wet-end addition of native XG added to pulp suspensions improves paper sheet stength properties, while spray application to paper sheets results in significantly greater improvements. In both cases, this can be directly attributed to XG-mediated cross-linking of fibre surfaces but very little is known about the nature of this interaction at the molecular level. Depending on localisation, XG has great potential to affect the nature of interfibre bonds created during drying, and, consequently, the mechanical and rheological paper properties in the wet and dry web. The introduction of XG into fibre wall can also provide a new opportunity to reduce or prevent hornification and related inactivation of fibre surfaces, thereby improving the value of recycled fibre streams. Further, biochemical addition of functional groups to XG using enzymes such as xyloglucan endo-transglycosylase (XET) or galactose oxidase (GalOx) can improve fibre properties further through increased crosslinking.

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1 Introduction

As a consequence of its physiological role as the key crosslinking polysaccharide in the primary cell wall, XG (xlyloglucan) possesses a uniquely high binding affinity for cellulose. Furthermore, unlike GAX (glucuronoarabinoxylan), XG has excellent solubility in water, has Newtonian solution properties, and is also readily available as the agricultural product tamarind kernel powder (TKP).[i] As a consequence, XG has significant potential in cellulose fibre modification, including the topochemical modification of wood pulp. The Royal Institue of Technolgy (KTH) has made significant advances in this area, including initiating the first studies at KTH demonstrating that native XG binds to pulp suspensions and improves paper sheet properties (e.g., strength and formation).[ii] They have demonstrated that, e.g., a *ca.* 20% increase in paper tensile strength can be obtained by the addition of 1% XG to unrefined hard- or softwood chemical pulps, whereas more recent work performed in collaboration with VTT has indicated that spray-coating an equivalent amount of XG onto pre-formed *dry* sheets can double the tensile strength of dry paper. The increase of strength can be attributed to the improved molecular level interaction between fibres and their cellulosic surfaces at fiber crossings that improve the strength of inter-fibre bonding. The location of the XG presumably can be controlled by the method of addition. However at present very little is known about the nature of this interaction at the molecular level. For example, adsorption and spray applications of XG are united by the common feature of XG-cellulose binding and cross-linking, but the spatial localisation of XG on the surface and within the interlamellar pores of the fibre is essentially unknown as a function of, e.g., loading amount and application technique.

It has been shown that XG can modify the surface properties of wet pulp fibres and reduce the surface friction that reduces the flocculation of fibres and improves evenness of paper[iii]. This is an indication of potential to modify surface properties of wet fibres and the interaction of fibres in wet state.

KTH has developed a novel method to introduce a wide variety of chemical functionality to cellulose surfaces through the binding of chemo-enzymatically modified XG in water[iv]. The addition of functional groups to XG using enzymes such as xyloglucan *endo*-transglycosylase (XET)[iv] or galactose oxidase (GalOx)[v] can improve fibre properties further. Additionally, the interaction of wet fibres can be further modified, and the strength of wet fibre network improved by linking XG with suitable groups that are capable to make covalent bonds under wet environment. This would strengthen the interaction of wet fibre network, improve the strength of wet paper and modify the drying stresses and activation of the fibre network during drying resulting in improved runnability and paper strength.

It has been shown that XG of suitable molecule size (M_w 30 000) can also penetrate the surface pores and interstices between lamellas in swollen fibre wall and modify the internal properties of the fibre wall[i]. It is known that removal of hemicelluloses - that have structure similar to XG- from fibre wall during kraft pulping, cause hornification[vi] (i.e. loss of swelling ability), inactivation of cellulosic surfaces and loss of fibre-fibre bond strength[vii] which results in considerable strength reduction in recycling of chemical pulp fibres. The introduction of XG into fibre wall could reduce or prevent the hornificaton and related inactivation of surfaces. An other novel idea is to utilise XG and xyloglucanase in de-inking process. Application of XG coating onto the sheet surface before printing and utilising suitable selective xyloglucanases to remove it could greatly improve the ink removal in de-inking stage.

The above mentioned points show that XG can be absorbed onto fibre surfaces modifying the surface properties of fibres and it probably can also penetrate the interlamellar pores of fibres modifying the fibre wall properties. Depending on the location it can be assumed to have potential to modify the behaviour of fibres in water suspension, in wet fibre mat, during the drying phase and in the final dry fibre network. Additionally the fibre-fibre interactions are modified both in wet and dry fibre network. This means that it poses a great potential in affecting wet and dry paper properties, and the nature of interfibre bonds created during drying, and further the mechanical and rheological properties of paper. The drying phase has a central role in modifying the mechanical and rheological properties of the fibre network, due to the shrinkage stresses that are created during the moisture removal phase. The drying stresses modify both the network structure, the structure of interfibre bonds and the internal structure of fibres.

Thus, we have a potential tools for improving the processing of the papermaking raw material, the strength of wet and dry paper, the structural changes within fibre network and within fibres, and eventually affecting the raw material consumption, recyclability, and energy consumption in papermaking.

2 Goal

The objective of this subproject is to utilise XET/XG based modification methods on wood fibres. The target is to modify the fibre surface and fibre wall properties for improving the material properties and recyclability of paper. The effects on fibre suspension, consolidating and dry fibre network and reduced hornification and improved de-inkability will be examined. The ultimate goal is to contribute to reduced the material and energy consumption, improved runnability and efficiency of the papermaking process and enhanced the environmental sustainability of paper.

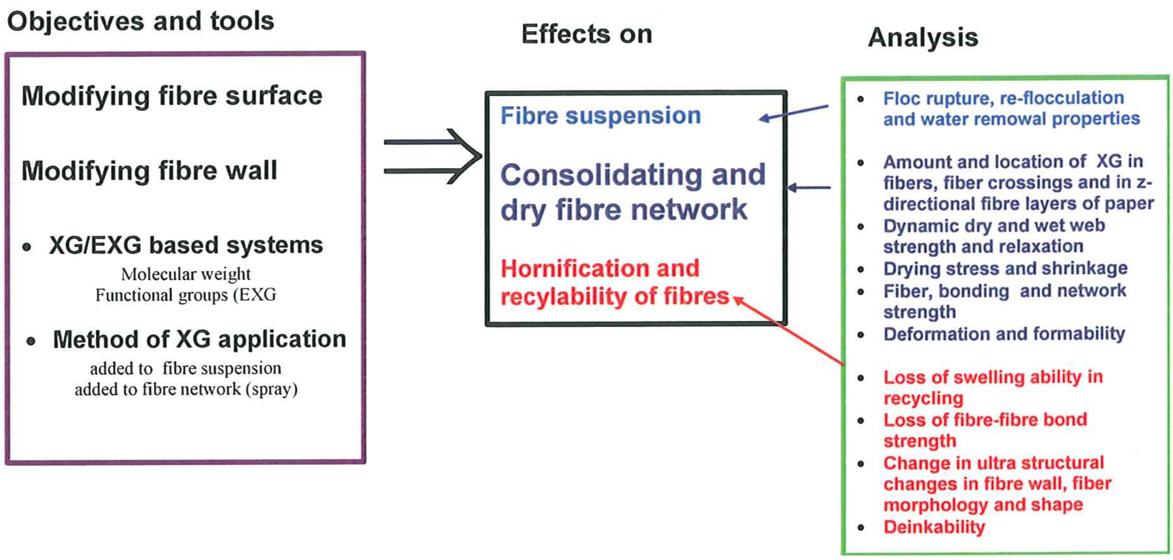

Figure 1 The schematic description of project's objectives, tools and analyses applied.

3 Description

The basic approach of the study is illustrated in the Figure 1. By modifying the fiber surface and internal wall structure with XG based methods we aim for better understanding of it's potential application in improving properties of fibre suspension, consolidating and dry fibre network structure and recyclability.

The study is divided into two main parts that are further divided into two subtasks:

1) XG based modification of wood fibres for improved material properties
a) The effects of native XG based on the properties of consolidating and dry fibre network.
b) The effect of new XG based cross-linking chemistry on the properties of fibre suspension, and on the properties of consolidating and dry fibre network

2) Novel XG- and XG/EXG based systems to maintain or improve the properties of recycled wood fibre
a) Effects of XG on fibre hornification
b) A novel application of XG in de-inking

1) XG based modification of wood fibres for improved material properties

a) The effects of native XG based on the properties of consolidating and dry fiber network

The native XG is applied to wet fibre network by spraying method that in ensures the retention of this non-ionic polymer. The degree of XG penetration is controlled by applied vacuum. The sprayed XG solution is assumed to concentrate at the fibre crossings where it has the strongest effect. The molecular weight of XG and the viscosity of the solution is assumed to play a role here. The location of the XG is analysed using the marking techniques developed by other research partners and the layer splitting method of VTT. The dynamic strength and relaxation properties and drying stress of the wet fibre network are measured, together with the in-plane and out-of-plane mechanical properties of dry paper.

b) The effect of new XG based cross-linking chemistry on the properties of fibre suspension, and on the properties of consolidating and dry fibre network

The XG combined with cross-linking chemistry makes it possible to introduce charged and other functional groups that improve the adsorption of XG on to fibres and strengthen the fibre interaction in wet fibre network. An promising method is to combine XG addition with cross-linking chemistry based upon the oxidation of the polysaccharide with the enzyme galactose oxidase (GalOx). GalOx selectively oxidises the C-6 position of the galactose side chains in XG to introduce aldehyde groups along the polysaccharide. These aldehydes are then capable of forming (hemi)acetals with hydroxyl groups on other XG chains. In solution, this phenomenon leads to the cross linking of XG and subsequent gel formation. To avoid this complication, XG will be first adsorbed (i.e., immobilised) onto chemical pulp fibres in suspension, or spray applied as described above, followed by *in situ* activation of the Gal residues with GalOx.

These modifications are assumed have effect also on the internal stresses created in the fibre network during drying and on the extensional stiffness of the dry network.

2) Novel XG and XG/EXG based systems to maintain and improve the properties of recycled wood fibre

a) Effects of XG on fibre hornification

XG based method are applied to reducing hornification, stiffening and loss of bonding ability of fibres due to repeated drying and recycling. This is received by using polymers of suitable size that can penetrate the fibre wall and surface pores.

The effects on hornification and inactivation of fibre surfaces are tested by using repeated sheet forming- drying - slushing cycles and testing the change in in-plane and out-of-plane mechanical properties. The changes of fibre shape and structure using are tested using Fiber analyser[viii], and fibre wall changes are studied using the special XG labelling methods, microscope analysis and other cell wall ultra structure analysis methods developed by the .

b) A novel application of XG in de-inking

The deinkability will be studied by applying a XG pre-treatment on paper surface before printing and utilising enzymes to remove the XG and detach the printing ink from the fibre surface.

The techniques of the consortium for applying a layer of XG to fibre surfaces together with the enzymological tools and expertise of the partners, paves the way for this new system to potentially facilitate the removal of particles during fibre recycling. Application of XG coating onto the fibre/sheet surface before printing will provide a "protective" layer onto which ink particles will adsorb. Native XG will be spray-coated onto paper sheets, followed by electrophotographic printing. It is expected that cleavage of the XG coating layer will facilitate removal of ink particles by weaking the particle-fibre link mediated by the polysaccharide.
The de-inking research will concentrate in electrophographic printing method and detachment of hard-to-separate toners that degrade the value of recycled paper. Washing de-inking method is applied as the main method.

4 Methods

Two addition methods are applied: spray addition and addition to fibre suspension. The location of the XG is tested by using end labelling technique. Effects of high and low molecular mass XG is explored on paper properties.

The testing methods utilised in determining the special features brought about by the XG include, in addition to the more conventional methods, several unique methods developed at VTT:

- Dynamic strength and relaxation analyse method for wet and dry paper[ix x]
- Determination of development of the uniaxial drying stress and strength with sheet dryness[xi]
- Laboratory scale spray application system[xii]

These test are carried preferably in laboratory scale but VTT also provides a pilot scale testing environment.

5 Results

Results have been disseminated in reports, diploma works, conference presentations and manuscripts in the below.

Non-charged polysaccharides, such as xyloglucan and guar gum, show excellent potential in influencing the papermaking process. However, non-charged chemicals added to pulp suspensions are susceptible to insufficient retention. Spray application offers a means of introducing non-charged chemicals to the fibre network.
In these paper 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. Xyloglucan seems to have potential especially in recovering the strength properties of pulp with hornified cell walls, such as in recycled pulp.

According to these studies, the strength and elongation of the wet web can be considerably improved by introducing non-charged polysaccharides. In addition, tension holding capacity after relaxation increased due to the treatments. The strengthening effect of the fibre network with xyloglucan was enhanced by using borax as a cross-linking agent or by introducing aldehyde groups to the xyloglucan. Reduced molecular weight of xyloglucan was found to decrease the positive wet and dry web strengthening effect of xyloglucan-borax synergism. A xyloglucan layer between the fibre network and ink was also found to contribute to better deinkability in laboratory trials.

In addition to laboratory studies, pilot machine trials were also executed to examine the influences of spray application of chemicals on runnability and the quality potential of fine paper. Spray application at the former section was found to have no significant effect on the dry solids content of the web after wet pressing. The draw after the press section was controllable and the occurrence of web breaks detectable during the trials. Guar gum was found to increase the elongation and tensile energy absorption of the wet web, contributing to better runnability. The extent of the draw and addition of chemicals also had a clear effect on paper quality, for example with respect to tensile strength and porosity.

The results suggest that non-charged polysaccharides, when sprayed on a wet web, can improve both the efficiency of paper production and the material efficiency of fibres. In general, these results can be exploited in paper and board machines for tailoring fibre networks for different product grades or special functional products.

- **Rantanen, A.,,** Bachelor's Thesis, Influences of Xyloglucan application on wet web characteristics and quality of paper. University of applied sciences, School of Engineering and Technology, 2008.

Item: *hornification of fibre, drying stresses, enhanced tension holding ability by XG treatment*

- **Oksanen, A.,** Report of task project "Bulkkinen paperi" of "Raaka-aine" –project coordinated by Antti Grönroos.

Item: *Strengthening of bulky paper structure by spraying of xyloglucan, analysis of XG in the fibre-nework (fluorescence microscopy)*

Figure 2 The tracking of labelled XG in the fibre network with fluorescence microscopy. Picture of paper sample in thickeness direction (XG in white areas).

- **Oksanen, A., Retulainen, E.,** Brumer, H. Can high quality bulky paper be produced by optimizing the use of fibres, fines and chemicals? International Austrian Paper Conference, 19 - 20 May 2010, Graz/AUT

Item: *Strengthening of bulky paper structure by spraying of xyloglucan, analysis of XG in the fibre-nework (fluorescence microscopy)*

- **Retulainen, E, Oksanen, A., Salminen, K., Rantanen, T.,** and Brumer, H., Improving the materials efficiency of fibres by tailored addition of non-charged polysaccharide. PTS Paper Symposium 2010, Munich, Sept 7-9, 2010.
- **Oksanen, A., Retulainen, E., Rantanen,** T., Brumer, H. Improving Recyclability of Chemical Pulp by Introducing Non-charged Cross-linked Polysaccharide on Fiber Surface. 2010 TAPPI PEERS & 9th Research Forum on Recycling, October 17-20, Norfolk, Virginia, USA.

Item: *Preserving of bonding ability of the fibre in recycling by introduction of XG + borax complex in to surface of fibre.*

- **Oksanen, A., Rantanen, T., Retulainen, E.,** Salminen, K., Brumer, H., Improving wet web runnability and paper quality by an uncharged polysaccharide. 4th International Symposium on Emerging Technologies of Pulping and Papermaking, November 8-10, 2010, Guangzhou, China

Item: *hornification of fibre, drying stresses, enhanced tension holding ability by XG treatment*

- **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.

Item: *hornification of fibre, drying stresses, enhanced tension holding ability by XG treatment*

- **Oksanen, Antti**, Brumer, Harry (KTH), WoodWisdom-Net Programme Seminar, FibreSurf: New biotechnological tools for wood fibre modification and analysis, 1-2 of February, 2011 FCBA, Paris, France.

Item: Highlight results of all partners in FibreSurf -project

- **Retulainen**, E., **Salminen, K., Oksanen**, A., and Lindqvist H. Improving the wet web strength and runnability. Appita Annual Conference and Exhibition, 10-13 April, Rotorua, New Zealand.
- **Somerkallio** M., Master of Science Thesis, Spray Application of strength chemicals, Tampere University of Technology, 2011.

Item: *Spraying of XG, starch, borax, boundary conditions of spraying*

- **Oksanen, Elias Retulainen, Janne Kataja-aho** , Manu Somerkallio, Chunlin Xu, Harry Brumer Effects of non-charge polysaccharides on runnability of wet web and efficiency of fibre material, Zellcheming conference 28th - 30th June 2011, Wiesbaden

Item: *Influence of molecular size of XG, XG + borax complex, introduction of aldehyde groups to XG on wet strength (runnability) properties.*

6 Validation of results

While many of the outcomes of the project were fundamental in nature, the VTT was instrumental in developing the application of the polysaccharide xyloglucan as a paper wet-strength additive in laboratory and pilot scale applications. These studies further support the positive impact of XG as an environmetally friendly papermaking chemical and comprise a step toward susequent industrial utilization.

7 Conclusions

The potential use and application methods of XG and similar hemicelluloses that were developed in the project have been presented to several Finnish companies (Botnia, UPM, Stora Enso, Metso, Kemira and Tervakoski Oy) in a separate seminar, and in private
communications raising considerable interest. As the most inventions created in the project need further demonstration in practice, the ideas have been taken to other research projects. Also practical pilot scale demonstrations have been carried out in other projects. The research has also seminated some development work in those private companies, of which little information is obtained.

8 Summary

Xyloglucan (XG) and its enzyme based modification methods (XET and GalOx) were applied in modifying the fibre surface and fibre wall properties for improved material properties and recyclability of paper. It was shown that due to its high affinity to cellulose XG possesses a high potential to improve- not only the dry strength – but also the initial wet strength of fibre network.
Also the stress relaxation rate of the fibre networks was found to reduce and the drying induced stress to increase, both are indications of enhanced fibre-fibre interactions under stress. Only a few polymers have this potential. These results have impact on the runnability of wet and dry web and efficiency of paper machines.
Of practical importance is also the finding that spray application onto wet web before wet pressing was found to be a more efficient than addition to pulp suspension. This suggests that in spraying the chemical will concentrate more to the fibre surface and fibre crossings where the strengthening effect is better than when adsorbed onto fine material. Elemental cross-linking with borax further strengthens the positive effects of XG both with wet and dry fibre network. Also tamarind kernel powder, which contains 60% XG, has a similar positive effect that is proportional to its XG content.
The relative improvement of XG was higher with once-dried chemical pulp fibres than with never-dried fibres. Molecular level interactions are important both in initial wet web strength and dry strength, suggesting that the strong interactions take place between the gel-like layer on fibre surfaces. When the molecular weight of XG was enzymatically reduced the strengthening ability was nearly lost, and even in the presence of borax. As the relative improvement of strength was better with once dried than with never dried fibres, suggested that XG could be used to heal or compensate for the surface hornification of the fibres. Enzymatic galatose oxidation of the XG was used for introducing aldehyde groups to the XG

molecule, which was found to have a considerable improving effect on both the initial wet strength and dry strength of the fibre network.
As the XG absorbs permanently onto cellulose fibres improved strengths can be found also in the reslushed and reformed sheets. This is an indication of improved recyclability. Additionally, XG was found to contribute to better deinkability when combined with enzymes in deinking stage. These may have considerable positive effect on use of recycled fibres.
Generally the results show the high potential of XG and other similar hemicelluloses, as pure, modified, or non-purified technical
chemicals, to increase the material efficiency of fibres. XG can contribute to reduced used of fibre material, i.e. lower basis weights, better wet web runnability, reduced refining need, lower drying energy consumption, bulkier network structure, and better recyclability.

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