Polysaccharide interactions with nanocellulose as a platform for biomimetic modifications

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Abstract
We have studied the interactions of nanofibrillar cellulose with different polysaccharides both in molecular- and macroscopic level in aqueous environment. First, basic properties affecting the interactions with polysaccharides were explored using thin films of NFC and two different high-precision adsorption techniques for ultrathin films of NFC. Furthermore, we extended the study from fundamental to practical scale by preparing films from refined and fluidized nanocellulose gels using a filtration based technique. The effect of selected polysaccharide adsorption on film properties was evaluated.

Introduction
In order to efficiently utilize nanocellulose as raw material in emerging biobased applications the unique properties of cellulose should be retained. Many approaches to increase the low compatibility of cellulose fibrils with other materials due to their strong intrafibrillar aggregation behaviour have been proposed. The problem with direct chemical modifications to cellulose structures, however, is that it often leads to unwanted changes, especially in cellulose strength properties. One proposed way to overcome harsh chemical treatments is to do the compatibilization biomimetically, coating fibrils with material that has natural affinity to cellulose [1], such as polysaccharides. It is known that similar (1→4)-linked β-D -structured backbones of glucose and mannose present in wood cell walls as versatile compounds known as hemicelluloses are known to naturally adhere on cellulose pulps or microcrystalline cellulose [2-5]. Therefore one purpose of this study was to look closer into the interactions of different polysaccharides with nanofibrillated cellulose, after which the chemical modifications and activations of attached polysaccharides, is easier while retaining the important cellulose features.

Materials and Methods
The nanofibrillar cellulose was prepared from hardwood kraft pulp by high-pressure multiple fluidized process and obtained from the Finnish Center for Nanocellulosic Technologies. Ultrathin films were prepared on sensors by utilizing the method developed by Ahola et al [6]. All polysaccharides tested were commercially available water-soluble products and a simple and fast hydrolysis was performed to selected samples to study the effect of molecular weight on adsorption phenomena. A statistical analysis was performed to find the most important factors governing the attachment of polysaccharides on nanofibrillar cellulose. Main techniques to characterize the attachment were quartz crystal with microbalance (QCM-D) (Q-Sense E4, Västrå Frölunda, Sweden) and surface plasmon resonance (SPR, Biacore 100, GE Healthcare, Uppsala, Sweden), combined with atomic force microscopy AFM (Multimode 3000, Digital Instruments, Santa Barbara CA, USA) imaging to verify the nanofibrillar structure before and after treatments. Films were prepared by casting or filtration based techniques.

Results
Selected results are collected in Figure 1. Adsorption on nanocellulose film of polysaccharides having similar molecular weight reveals clearly the major role of polysaccharide backbone structure and charge properties. Neutral polysaccharides adsorbed in greater amount and had the expected dispersing effect on the nanofibril film structure, while especially cationically charged formed a thinner layer with strong initial interaction, illustrated in Figure 1a. These results are discussed in detail and compared to literature values and simulations of polysaccharide structures. Nearly all the tested polysaccharides have strong irreversible attachment towards nanofibrillated cellulose film.
When adsorbed mass results are combined with energy dissipation data acquired simultaneously, viscoelastic properties of adsorbed layers were estimated in relation to adsorbed layer thickness and viscosity. However, due to the high content of coupled water both within cellulose fibril network and the polysaccharide layer complementing techniques are needed. Therefore, Surface Plasmon Resonance (SPR) measurements based on the total internal reflection of light were performed and the attachment of polysaccharides was verified (Figure 1b). By combining results from complementary techniques, the relative amount of bound water per polysaccharide was estimated and utilized when moving from molecular scale studies to macroscale, utilizing the strong innate film forming property observed with nanocellulosic fibrils. Furthermore, the structures of both ultrathin nanofibrillar films and macroscaled structures were studied with various techniques, including AFM imaging (Figure 1c). Finally, films (Figure 1d) were prepared with or without polysaccharide modifications and compared emphasizing the need for further chemical modifications of the polysaccharides.

Figure 1. Selected results combining the adsorption studies of polysaccharides with nanofibrillar cellulose with different techniques together with images of nanofibrillated cellulose as ultathin model film and as macroscopic nanocellulose film.

References cited

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Content of presentation

• Why polysaccharides adsorb on NFC
• Water soluble polysaccharides
• Main characterization techniques:
  – QCM-D (viscoelastic properties)
  – AFM (morphology)
  – AFM combined with DPFM (adhesion and stiffness properties)
• Formation thin polysaccharide layer on nanosized fibril films
Objectives

• To verify the most suitable polysaccharides adsorbing on cellulose and compare the adsorption properties

  ➔ new knowledge of polysaccharide adsorption on nanocellulose

  ➔ important for further adsorption of modified polysaccharides
Background

Plant cell-wall: natural nanocomposite structure

Adapted from Sticklen

TEM

AFM phase

Adapted from Pääkkö et al.
Biomacromolecules 2007, 8, 1934
Motivation

• Nanocellulose surface modification via polysaccharide adsorption

• Why polysaccharides?
  – Biodegradable
  – Natural ability to adsorb on cellulose
  – Modifications possible
  – Have been shown to increase properties such as tensile strength of paper (e.g. Petri Myllytie, PhD-thesis, Dep. Forest Products Technology, TKK 2009)
Experimental

• Most of preliminary work focused on molecular interactions
  – literature review of previous studies with pulps
    most promising ones chosen

  – high precision techniques (QCM-D, AFM, SPR, DPF)

  – ultrathin films prepared from hardwood nanofibrillar cellulose
Model films from cellulose nanofibrils

• Necessary for fundamental studies on molecular level
  – chemistry and morphology

• Preparation: spin-coating of NFC
  (Ahola et al. Biomacromolecules 2008, 9, 1273)

adapted from E. Kontturi
Polysaccharides

- Water-soluble, readily available
- Different backbone structure:
  - Mannans:
    - guar (GG) and locust bean gum (LBG)
  - Cellulose derivatives:
    - methyl cellulose (MC) and carboxymethyl cellulose (CMC)
  - Xylan from birch (XYL)
  - Chitosan (CHI)
- Acid hydrolysis of mannans $\rightarrow$ Mw

Quartz Crystal Microbalance with dissipation (QCM-D)

Fibril model film (AFM image, 2x2µm)

Combined mass and viscoelastic properties

Picture used with permission from Q-Sense
Properties of adsorbed layers on NFC film

pH 4.5, 10 mM NaAc-HAc-buffer, T= 24°C

Irreversible attachment

Backbone structure and available surface area affect adsorption
No direct correlation (statistical analysis)

In the following polysaccharides with similar Mw were chosen
Adsorbed amount as a function of time
Effect of backbone structure and charge

QCM-D

Highest adsorbed amount of neutral polysaccharide-similar backbone as cellulose

Cationic: thin layer

bound water included!
Viscoelastic properties of the adsorbed polysaccharide layer

**Effects:**

- Thick, swollen layer
- Attaches despite electrostatic repulsion
- Thin, rigid layer

![Graph showing the effect of polymers on viscoelastic properties](image)
Estimated results of adsorbed polysaccharide layer mass

Significant amount of bound water attached with polysaccharides!
Comparison of estimated layer properties

Hydrodynamic thickness

Shear viscosity

Dried films after polysaccharide adsorption

ref
cmc
chi

Topography AFM 5x5 µm², z-scale 40 nm

Adsorbed polysaccharides not visible!
DPFM-Digital pulsed force mode-AFM

non-resonant, intermittent contact mode

adhesion

stiffness

Schematic PFM-curve
Digital pulsed force mode – comparison of films

Difference detected!
Conclusions

• Attachment of polysaccharides verified also for nanoscale films
  – layer on top of ultrathin fibril film
  – backbone structure influences most
  – heterogeneous

• Molecular scale:
  – no changes in topography
  – differences in adhesion

• Modifications possible after bi-layer attachment
Future prospects

Transparent&tough nanocellulose film:
Young’s modulus 2.290
Tensile stress 125.1 MPa

New functionalities while retaining excellent strength properties via fibril-fibril interactions!
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Thank you

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