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# Nanocomposite films based on cellulose nanofibrils and water-soluble polysaccharides

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## Abstract

All-polysaccharide composite films were prepared from native, unmodified cellulose nanofibrils (CNF) mixed with various natural water-soluble polysaccharides like carboxymethyl cellulose, galactoglucomannan, xyloglucan and guar gum. Composite films were manufactured by pressurized filtration and hot pressing. The mechanical properties of the films were systematically evaluated in the dry and the wet state. GG was furthermore selectively oxidized using galactose oxidase (EC 1.1.3.9), and the effect of the degree of oxidation on the final composite film properties was shown. It was found that all the tested polysaccharides increased the strength and toughness of the *dry* composite films at 2 weight percent (wt-%) addition to CNF. After soaking the samples for 24h in water, striking differences between the samples were found: already at 2 wt-% CMC the wet strength of the composite films diminished, while the uncharged polysaccharides improved the wet strength. For example, the addition of 2 wt-% GGM increased Young's modulus by a factor of 1.3, the tensile strength by a factor of 2.8, and the toughness by a factor of 3.4. The results are discussed in relation to the amount of water absorbed in the films and possible reasons for the improved properties are suggested.

KEYWORDS: Cellulose nanofibrils, composite film, tensile strength, guar gum, galactoglucomannan

## 1. Introduction

Due to increased environmental awareness and rising oil prices there is a demand to replace petroleum- based materials with materials from renewable resources. However, properties of the

new materials should be as good as or preferably better than the ones that are being replaced. Cellulose nanofibrils (CNF), obtained from biomass through mechanical disintegration [1] have recently gained much attention. Encouraged by the high specific strength of the cellulose crystal and the thermal stability and network forming ability of the fibrils, CNF has been used to produce strong materials like films [2-5], aerogels, foams [3,6,7], and reinforcements for biocomposites [7-9].

There are a few different approaches to the use of CNF in composites. One approach is to reinforce a soft matrix with a small amount of CNF [10]. Improved strength properties are achieved provided there is an affinity between the matrix and the cellulose fibrils. Mikkonen et al. [10] used 5-15 % CNF to reinforce films of spruce O-acetyl galactoglucomannan while Peng et al. [11] and Hansen et al. [12] used CNF to reinforce xylan films. CNF has also been used to reinforce composites based on thermoplastic starch and chitosan [13] an addition of 10-20% CNF improved the composites mechanical properties and thermal stability. More specifically, the tensile strength and Young's modulus increased significantly, but the elongation at break decreased. Another approach is to utilize the excellent strength properties of pure CNF nanopaper and modify the pre-formed CNF film. Recently Sehaqui et al. [14] showed increased hydrophobicity and wet strength through esterification of pre-formed nanopaper. The modification, performed in wet state, decreased the dry strength of the nanopaper, while solely surface treatment usually retains the dry strength of the CNF film [2]. A third approach is to mix CNF with a small amount of soft polymers in order to mimic the structure of natural strong materials. In this biomimetic approach the CNF network gives the material its strength and stiffness while the role of the soft polymer is to hinder crack propagation, thus enhancing the toughness of the material. These approaches ultimately aim at mechanical properties that exceed the individual properties of both materials, which is not possible in conventional composites. Previously, highly anionic CNF has been combined with a cationic block-copolymer and synergistic effects have been observed [15,16]. Nevertheless, the ionic interaction between anionic fibrils and the cationic polymer removed water from the gel, and systems relying on ionic interactions could be susceptible to aggregation. It is important to control the state of dispersion and aggregation of CNF by controlling the interactions between the fibrils in order to achieve high strength and stiffness in cellulose nanopapers [17]. In natural composites like wood, silk, mollusk shells or bone the interactions are nonionic, mainly van der Waals interactions and multiple hydrogen bonds. Thus we recently studied biomimetic composites from CNF and poly(ethylene glycol) grafted carboxymethyl cellulose [18] where the interactions between the polymer and CNF are nonionic. We found that, in this system, the water swollen polymer was able

to lubricate the interface between fibrils during film formation and as a consequence an even and strong film was formed.

Although excellent strength properties have been achieved for dry CNF-based composites there is a dearth of systematic comparisons for CNF systems. Since the properties of CNF, the film formation method, and tensile testing protocol all affect the results, it is not possible to determine the most promising polysaccharide to use in CNF-based composites based only on the existing literature. Moreover, the wet strength of CNF based materials gets less attention although adequate wet strength is important both for surface modification and for applications such as wound dressing, electronics, sensors and packaging [19]. Benítez et al. [17] recently showed that the mechanical properties of CNF films are very sensitive to moisture, and water acts as a plasticizer in the films at humid conditions. However, the film became very weak after swelling with water, which could be due to their high charge - films prepared from highly charged CNF have been found to be more sensitive to water than films from low charged CNF [19]. Recent studies have shown promising enhancement of wet strength through either esterification or crosslinking [14,20]. However, esterification requires solvent exchange and crosslinking restricts the further modification of CMC. It would be beneficial to find simpler ways to improve the wet strength.

In this work we systematically evaluate the effect of various natural polysaccharides on the wet and dry strength of CNF based composites. Water-soluble polysaccharides, like xyloglucan, carboxymethylated cellulose, and galactoglucomannan, that have previously shown promising results in some properties, are compared with polysaccharides that have not previously been used in CNF based material, such as guar galactomannan (guar gum), a widely utilized thickening agent [21]. Furthermore, the effect of selective enzymatic oxidation of guar galactomannan is demonstrated and the reasons for the exceptionally good wet strength of the all-polysaccharide composites films developed are discussed.

## **2 Experimental**

### **2.1 Materials**

#### *2.1.1 CNF (Cellulose nanofibrils)*

CNF was prepared by the disintegration of unmodified never-dried industrial bleached birch pulp in a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int. Co., Newton, MA) for six passes according to the procedure described in [2]. Prior to fluidization the pulp was washed to sodium form according to the procedure described by Swerin et al. [22], in order to control the ionic

strength and counter ions [18]. The unmodified CNF was weakly anionic due to the carboxylic acid groups introduced during the pulping process; the charge density of the pulp used was 0.065 meq and the zeta-potential of the corresponding CNF gel at pH 8 was  $-3$  mV [23].

### 2.1.2 Water-soluble polysaccharides

Commercial guar gum galactomannan (GG, guar gum galactomannan,  $M_w > 1000$  kDa, [21]) from Sigma Aldrich (Lot#041M0058V, Pcode 10011170894) was used as received, and after enzymatic modification. Spruce galactoglucomannan (GGM, *Picea abies*,  $M_w$  20-60 kDa, Table 1) was obtained from the process water of a Finnish pulp mill in an industrial-scale isolation trial after ethanol precipitation [24]. Prior to use GGM was dissolved in water at  $80^\circ\text{C}$ , cooled to room temperature, stirred overnight and filtered using Glass microfiber filters (Whatman, Scheicher & Schnell Cat No.1820 125). Tamarind seed galactoxyloglucan (XG, *Tamarindus indica*,  $M_w$  1300 kDa [25]) was obtained from Dainippon Sumitomo Pharma. The sodium salt of carboxymethylated cellulose (CMC,  $M_w$  250 kDa, degree of substitution = 0.7, Batch # MKBD4716) was dissolved in water to 5 g/L. The solution was further dialyzed with continuously running ionized water for four days. The solution was frozen to  $-70^\circ\text{C}$  and freeze dried. The water used in the experiments was deionized and further purified with an UV unit (Synergy® Millipore, Molsheim, France) except during CMC dialysis, where only deionized water was used.

### 2.1.3 Enzymes

Endo-1,4- $\beta$ -mannanase (Lot 00803, from *Aspergillus niger*, 42 U/mg) from Megazyme (Wicklow, Ireland) was used for GG hydrolysis, Galactose oxidase (GO, G7400, 3685 U/g, EC 1.1.3.9), catalase (from bovine liver, C30, 22000 U/mg), and horseradish peroxidase (HRP, P8250, type II, 181 U/mg) from Sigma-Aldrich (St. Louis, MO, U.S.A.) were used for GG oxidation.

## 2.2 Methods

### 2.2.1 Hydrolysis of guar gum with mannanase

Commercial endo-1,4- $\beta$ -mannanase and enzyme extracted from *A. niger* (EC number 3.2.1.78 and specific activity of 42U/mg), was used to partially hydrolyze GG. When GG was dissolved to obtain 1.0% (w/v) solution, the enzyme was added and the solution was incubated in a  $40^\circ\text{C}$  water bath for 4 h, whereupon the enzyme was inactivated by heating at  $100^\circ\text{C}$  for ca. 10 min. The samples were centrifuged at 5000 rpm and the supernatant was collected and freeze dried.

### 2.2.2 Oxidation of guar gum with galactose oxidase

GG and partially hydrolyzed GG were enzymatically oxidized either prior to or after GG suspension was combined with the CNF suspension. The dosage of the enzymes was based on the approximate amount of galactose present in the GG sample, as in a previous study [26]: 0.78 U of GO, 150 U of catalase, and 0.9 U of HRP/mg of galactose. The 0.1-0.7% (w/v) solutions of GG and the CNF-GG dispersions containing 1, 2 or 10 w-% of GG with respect to CNF were stirred in the presence of the enzymes at +4°C for 4 hours or 48 hours, depending on the degree of oxidation (DO) desired. The enzymes were inactivated by heating the sample up to 90°C while mixing.

### 2.2.3 Determination of the degree of oxidation, DO

The DO was determined by gas chromatography mass spectrometry (GC-MS) as described earlier [26]. First the samples (1-5 mg of polysaccharide) were deuterium labelled with NaBD<sub>4</sub>, precipitated, and further acid methanolysed. The galactosyl units of GG were selectively oxidized with GO (Scheme 1). The degree of oxidation (DO) was calculated by comparison of the ratio of m/z 361 and m/z 362 ions of silylated galactosyls, where 361 corresponded to the unoxidized galactosyls and 362 to the oxidized galactosyls containing the deuterium label [26].

### 2.2.4 Determination of molecular weight

Size exclusion chromatography (SEC) was used to determine the degree of polymerization and  $M_w$  of GG hydrolysed with mannanase. All the  $M_w$  values were calculated using a dn/dc value of 0.15 mL/g. The mannanase-hydrolysed GG was dissolved in 0.1M NaNO<sub>3</sub> by stirring for 7 days and filtered with 0.45 µm filter according to the procedure in [26].

### 2.2.5 Film preparation

CNF was diluted to 0.80% suspension of 150 ml (dry mass of 0.84 g), and mixed overnight with a magnetic mixer. The amount of CNF was the same in all the composite films. Low CNF concentrations were used to avoid aggregation. An additional amount of water soluble polysaccharides (1-10 wt-%) was added to this dispersion and the dispersions were further stirred for at least 24 h to ensure good mixing. After that the solutions were stirred for at least 1.5 hours with a Heidolph stirrer using a rotation speed of 400 rpm; then the samples were homogenized with the Polytron for 3 min. The composite films were then prepared with sequential filtering and pressing according to [2]. The film thickness was about 70 µm.

### 2.2.6 Tensile testing

Tensile mechanical properties were measured using a MTS 400/M vertical tester (MTS® System Corporation, Eden Prairie, USA), load cell 200N (Adamel Lhomargy serial num.115341, MTS).

The adjustable speed accuracy is 0.1%, the resolution for crosshead displacement is 0.01 mm. Strips with dimensions of (50×15) mm<sup>2</sup> were cut from the uniform composite film with a lab paper cutter. The thickness was separately measured from each sample piece before measurements from three different places with a Lorentz wetter paper thickness meter. The average thickness of these three different measurements was used to normalize the measured force when calculating the tensile stress. The grip distance was 40 mm and the testing velocity 0.5 mm/min. The samples were conditioned for at least 3 days at 23 °C and 50% RH before testing. For the wet measurements the samples were immersed in water for 24 h and measured immediately after removal. The thickness was measured prior to the wetting. For both dry and wet strength, at least 5 parallel samples were tested, and average results for Tensile strength, Young's modulus and Toughness are shown in the graphs as well as example curves. Toughness is calculated as the numerical integration over the stress-strain curve from zero strain to breakage. The error bars in the figures are calculated from the standard error of the mean values.

#### 2.2.7 Water uptake of composites films

The water absorption of the films was measured by immersing the samples in water, removing them periodically and weighting them. The samples were stored in a control room of 50% RH and 24 °C for at least 3 days before starting the experiments. The dimensions of the samples prior to wetting were 40 mm × 15 mm × 70 μm. For 5 min or longer times, at least three parallel measurements were performed, from which the average results were calculated. For the CNF/CMC film, test results are formed from the average values of three tested films. Prior to weighing, the excess water was removed with a tissue to reduce the effect of solvent on film surface. The increased weight (%) for the films was calculated by

$$\text{Increased weight (\%)} = (m_t - m_{\text{origin weight}}) \times 100 / (m_{\text{origin weight}}) \%$$

### 3 Results and Discussion

#### 3.1 Structure, molecular weight and degree of oxidation of the polysaccharides

The polysaccharides studied included the mannans GG and GGM, which contain ca. 40% and 10% terminal α-D-galactosyl residues, respectively, directly attached to C-6 of the mannosyl units of the backbone [21]. The galactoxyloglucan from tamarind seeds, XG, has terminal β-D-galactosyl residues (16% of the sugar units) attached to xylose side chains [27]. GG with a reduced molecular weight (M<sub>w</sub>) was prepared by partial hydrolysis with β-mannanase. According to size exclusion chromatography (SEC), the M<sub>w</sub> of the hydrolysed GG was approximately 30 kDa and the

hydrodynamic radius of the sample ( $R_h$ ) was 4.7 nm. The viscosity of the hydrolysed GG solutions was low at all degrees of oxidation and therefore mixing of the solutions with CNF suspension was easy.

In Table 1 the amount of oxidized galactosyls, the relative amount of oxidized galactosyls in the GG sample and the total relative amount of oxidized galactosyls in the final CNF composite are shown. Due to the selective oxidation of galactosyls only the backbone of the GG chain remains unmodified facilitating adsorption to cellulose. The effect of performing the oxidation reaction after mixing with CNF was evaluated. In Table 1 the degree of oxidation (DO) of galactosyls, the DO of total carbohydrates of GG, and the DO of total carbohydrates of the final CNF composite film are shown. The presence of CNF hindered the oxidations but did not prevent it, resulting in a lower degree of oxidation. The lower degree of oxidation was achieved with shorter oxidation times as well.

### **3.2 Effect of the added amount of water-soluble polysaccharides on dry strength**

Previous results have already shown that the addition of 1 wt-% soft lubricating polymer enhances the mechanical properties of CNF films when using carboxymethylated cellulose with grafted polyethylene glycol chains [18]. This is a lower concentration than would be expected for full coverage of individual fibrils. Since the charge of the added polymers affects adsorption behavior, the optimum ratio between CNF and the soft polymer was evaluated both for uncharged guar gum and anionic CMC (Figure 1).

(Figure 1)

The trends are similar for both uncharged GG and anionic CMC. 1-2 wt-% addition of water-soluble polysaccharide improves the tensile strength of the CNF films by about 40 %, while the Young's modulus decreases slightly, about 10 %. There is no major difference in tensile strength between samples containing 1-5 wt-% of water soluble polysaccharide, but when the ratio of GG or CMC with respect to CNC was 10 wt-%, the strength properties clearly decreased. Due to the decreasing trend in mechanical properties, an amount higher than 10% was not tested and the rest of the experiments were performed at concentrations of either 2 wt-% or 10 wt-% of added polysaccharide.

### **3.3 Effect of oxidized guar gum on dry and wet strength**

Guar gum is commercially available in large quantities and can be easily modified through enzymatic oxidation [26]. It adsorbs to cellulose in similar quantities as xyloglucan and

galactoglucomannan [28] but has previously not been used together with CNF. Hartman et al. [29] reported a 27% increase in the dry strength of paper sheets after mixing kraft pulp with oxidized guar gum. They also found a temporary increase in the wet strength, but the wetting times were short. Due to these promising properties we decided to evaluate if oxidized GG could also be beneficial for the mechanical properties of CNF-based nanocomposite films. In Figure 2 the effect of the degree of oxidation and the molecular weight of the added GG on mechanical properties of dry CNF+GG composites films is shown. There is a clear positive effect on tensile strength and toughness upon the addition of GG, while Young's modulus remained unchanged or slightly decreased. The unmodified, high molecular weight GG was ~~ver~~ viscous and thus it was challenging to form an even dispersion of CNF and GG. This is probably the reason for the lower strength values for CNF+GG at 10% addition of GG. Hydrolysis decreased the molecular weight of GG and facilitated better mixing between components and formation of even composite films. Nevertheless, the degree of oxidation did not significantly affect the dry strength. Similar to the trend shown in Figure 1, 2 wt-% addition of GG was, in general, better than 10% addition.

(Figure 2)

In Figure 3 the corresponding mechanical properties of wet samples soaked in water for 24 hours are shown. The unmodified GG did not enhance the wet strength of the composite film. The oxidation of GG clearly enhanced the strength, modulus and toughness of the CNF-based composites. The highest degree of oxidation resulted in the toughest and strongest film. The average tensile stress was 43 MPa, toughness 2.4 MJ/m<sup>3</sup> and Young's modulus 0.4 GPa for composite films containing 10% GG<sub>hydHox</sub>. These values correspond to more than double the strength and toughness compared to pure CNF films, while the modulus increased by a factor of 1.3. Although comparison of the mechanical properties with literature values should be made with caution, we note that these values are considerably higher than results recently obtained for hydrophobic nanopaper [14] and in the same range as results obtained for oriented and cross-linked CNF/CMC composite films [20]. Interestingly, 10 wt-% addition of oxidized GG was as good as or better than the results for 2 wt-% addition with respect to wet strength. An explanation to this is, for the best sample, CNF+GG<sub>Hox</sub> with 10 wt-% addition of the GG, the total amount of oxidized galactosyls in the composite film is 2.45%, while it was around one or lower for the other samples (Table 1). Probably the amount of oxidized galactosyls has to be high enough for improvement in wet strength. Comparing the wet strength (Figure 3) to dry strength (Figure 2) it can be observed that the CNF+ GG<sub>Hox</sub> retained more than 30 % of its dry strength as compared to 20 % for pure CNF.

(Figure 3)

The oxidation of galactosyl side units of GG induces the formation of hemiacetal bond crosslinks between hydroxyl and aldehyde groups. Strong, elastic gels from oxidized GG have been made [30]. While oxidation did not improve the strength of cross-linked xylan/CNF hydrogels [31], cross-linking has been shown to be advantageous for the wet strength of CNF composite films [20]. We speculate that the intramolecular crosslinks, which may form between GG and CNF, prevent part of the hydroxyl groups of CNF from binding water by hydrogen bonds, thus making the films stronger.

### **3.4 Effect of polysaccharide type on the dry and the wet strength**

In section 3.3 it was shown that a small added amount of oxidized guar gum was able to improve the strength and toughness of CNF films considerably. Still, other studies have focused on xyloglucan for example [32] or CMC [33], and thus it would be interesting to systematically compare other natural polysaccharides with the oxidized guar gum as possible strength additives in CNF-based composite films. Pahimanolis et al. [20] showed that CNF/CMC composites are very weak in the wet state, which is expected as the charge further enhances swelling and the water sensitivity of the cellulose material. Thus neutral polysaccharides may be beneficial if wet strength is desired. Despite our previous promising results using polyethylene glycol-grafted CMC [18], emphasis was put on the use of neutral polysaccharides with an affinity for cellulose. The affinity of the neutral polysaccharides GG, GGM and XG for cellulose has been previously established [28,34], they can also be easily modified [26,35], but there are no previous systematic comparison of their effect on the mechanical properties of CNF/polysaccharide composite films. In Figure 4 the tensile strength, toughness and Young's modulus for dry CNF/polysaccharide composite films containing 2 wt-% water-soluble polysaccharides are shown. The neutral unmodified polysaccharides are compared with anionic CMC and oxidized GG.

*Figure 4*

It should be noted that all the added water-soluble polysaccharides increase tensile strength and toughness of the samples but slightly lower the Young's modulus. This is as expected for composite films, the highly crystalline CNF is the stiff part and the water-soluble polysaccharides act as plasticizer, enhancing the ductility of the composite. The plasticizing effect of the added polysaccharides can be seen from the stress-elongation curves for dry samples in Fig 5. Based on previous quartz crystal microbalance results showing that these polymers form a very water-swollen dissipative layer on the CNF surface [35], it can be speculated that the polymers enhance good

dispersability of the CNF during film formation, which is crucial to avoid aggregates and defects in the final composite. To obtain synergy and the exceptional strength properties expected for biomimetic composites, the polysaccharides would need to be modified, as previously suggested [18]. Based on the properties of the dry composite films, there is no significant difference between the tested polysaccharides and all of them could be useful candidates for further modification.

The sample dimensions and testing parameters affect the measured mechanical properties [18], thus it is always challenging to compare results from different studies. It must be noted that in the present study, relatively large samples were used (5.0 cm×1.5 cm×70 μm) which puts higher requirements on composite film evenness, since one single defect or floc introduces cracking of the sample. The justification of this approach is practical; it leads to better understanding of the strength properties of the material when used in applications, where larger films are needed. In general the toughness values varied more than the other properties. This variation arises mostly from the variation of the elongation at break in the plastic region of the tested composite films.

In Figure 6 the corresponding wet strengths of 24 h soaked samples are shown. In accordance with previous results [2], the pure CNF film can retain about 10-20% of its original dry strength in wet state. The addition of CMC, however, destroyed the wet strength of the samples. The CNF+CMC samples were so weak that they broke when handled, and it was very difficult to test them well, in line with previous findings [20]. For comparison we note that nanopaper prepared from TEMPO oxidized CNF retained only 1 % of its original strength after soaking in water, further confirming that an increase in charge is detrimental for wet strength [17].

#### *Figure 6*

Xyloglucan, galactoglucomannan and GG oxidized with GO all had a positive effect on the wet strength of the CNF films. It must be noted that, in contrast to the case of dry films, also Young's modulus of the composite films increased substantially with the addition of soft polymer. The addition of only 2% of GGM or GGhydHox increased Young's modulus by a factor of 1.3. The effect of the added water-soluble polysaccharides on the ductility of the composite films in wet state can be seen from the representative stress-elongation curves in Figure 7.

#### *Figure 7*

### 3.5 Effect of added polysaccharides on the water uptake of composite films

CNF+GGM and CNF+GGHydHox films showed the best and CNF+CMC films the worst wet strength properties. To understand the reason for this result the water binding of these samples were compared to the water binding of pure CNF (Figure 8). All samples absorbed more than 150 wt-% of water in less than five minutes in accordance to previous results on pure CNF films [2]. The CNF+CMC composite film adsorbed water faster than the other two samples, which is as expected due to their higher charge.

The CNF+CMC films also became so weak when immersed in water that it broke upon removal and hence, the experiment had to be stopped after 5 min. Composite films containing 2 wt-% of added GGM or GGHydHox absorbed slightly less water than pure CNF film. Thus the good mechanical properties of these composite films in the wet state could be due to slightly lower water content. However, the water absorption was still substantial, suggesting that the hydrophilicity of the composite film is retained and the amount of water in the composite film may not be the only reason for the superior properties of CNF+ GGM films. The results also suggest that the wet resistivity of the composite films could be further improved.

*Figure 8.*

All the tested uncharged polysaccharides, except native high Mw GG that was too viscous for even distribution, were able to enhance the tensile strength of dry CNF-based composite films. However, only GGM and GGHydHox were able significantly to enhance both the dry and the wet strength of CNF-based all-polysaccharide composites. This is interesting, since previously the focus has been on improving the dry strength of composites [11,15]. But for many applications, both dry and the wet strength is required. Sehaqui et al. [14] showed that hydrophobation may enhance wet strength of cellulose nanopaper but deteriorates the dry strength. All the tested polysaccharides were renewable and thus sustainable, but upon comparison of the availability and price, the GG is the cheapest and is also commercially available. Thus GG is an attractive candidate for further modification. Nevertheless, GGM is available in wood and up-scalable extraction processes are under development [35], thus the promising properties of GGM are also very interesting. The interactions between cellulose and GGM and oxidized GG should be further studied in order to fully understand the mechanism behind the good wet strength. Chemical modification of these polysaccharides and a focus on ordered structures, such as lamellar ordering, would be needed to achieve biomimetic composite films with mechanical properties close to natural materials.

## 4. Conclusions

All-polysaccharide composite films were prepared from CNF in combination with xyloglucan, spruce galactoglucomannan, carboxymethylated cellulose and guar galactomannan. By systematically comparing the mechanical properties in the dry and the wet state, similarities and differences in how the water-soluble polysaccharides affect the properties of the composite films were revealed. No major differences in the effect on dry strength were found between the polysaccharides. All the polysaccharides enhanced the plasticity and tensile strength of the material, while no improvement in stiffness was observed. However, for applications in the wet state, there were clear differences between the polysaccharides. GGM and enzymatically oxidized GG significantly improved both the stiffness and the toughness of wet CNF composite films, while addition of anionic polysaccharides, like CMC, was detrimental for wet strength. The slightly lower water uptake of composite films containing GGM could be one reason for the superior wet strength properties. Nevertheless, the composite films still absorbed a substantial amount of water, suggesting that they could be useful in applications where a hydrated and strong material is needed.

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## Figure captions

*Scheme 1. GO-catalyzed oxidation of guar gum (GG) and structures of GGM, XG and CMC. GO = galactose oxidase, HRP = horseradish peroxidase.*

*Figure 1. a) Tensile strength and b) Young's modulus as a function of added amount of water-soluble polysaccharide for dry composite films conditioned and measured at 50 % RH. Pure CNF film is marked with a cross for reference. CMC and GG containing samples are marked with spheres and triangles, respectively.*

*Figure 2. Effect of the DO of added guar gum on tensile strength (a), Young's modulus (b) and toughness (c) of dry composite films measured at 50% RH. All samples contain the same dry amount of CNF. Histograms in dark gray color represent samples with 2% added GG and lighter grey histograms represents 10% added GG. Pure CNF film (white bar) is shown as a reference.*

*Figure 3. Effect of the DO of added guar gum on tensile strength, Young's modulus and toughness of wet composite films. All samples contain the same dry amount of CNF. Histograms in dark gray color represent samples with 2% added GG and lighter grey histograms represents 10% added GG. Pure CNF film (white bar) is shown as a reference.*

*Figure 4. Tensile strength (a), Young's modulus (b) and toughness (c) for dry samples with 2% addition of water-soluble polysaccharides measured at 50% RH.*

*Figure 5. Representative stress-elongation curves for dry composite films with addition of 2% water-soluble polysaccharides.*

*Figure 6. Tensile strength (a), Young's modulus (b) and toughness (c) for wet samples with 2% addition of water-soluble polysaccharides measured after 24h soaking in MilliQ water.*

*Figure 7. Representative stress-elongation curves for wet composite films with 2% added water-soluble polysaccharides.*

*Figure 8. Water uptake of pure CNF films (crosses) and CNF films containing 2% added GGM (squares), GGhydHox (triangles) or CMC (spheres). In the insert the first 300s of the water uptake is shown. The uncertainty of the values is about  $\pm 7\%$ .*