Galactoglucomannan Derivatives and Their Application in Papermaking

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Native galactoglucomannans (GGMs), which were isolated from thermomechanical pulping waters of Norway spruce, were modified through cationization, carboxymethylation, and imination at the reducing end with a primary long-chain hydrocarbon amine. The derivatives were tested for their papermaking properties. The native GGMs increased the wet tensile strength as a result of the dispersion of fibrils in the wet fibre web. In wood-containing paper, GGMs increased the retention of fines and extractives without a decrease in paper strength. The GGMs also flocculated fillers effectively. The cationic GGMs were able to interact between fibrous fine material and fibres, as well as with fillers. Therefore, an electrostatic mechanism of action is suggested. Carboxymethylated GGMs are believed to bind to fibres and fines through divalent metal ions present in wood. For the amphiphilic amine-modified GGMs, the alkane chain attached to the reducing end appeared to play a key role. The tail was orientated towards the hydrophobic particles; the resulting paper was the most hydrophilic, since the hydrophobic particles were covered with the polysaccharide. Based on the present results, it can be concluded that galactoglucomannans can be modified to yield new and interesting functionalities to wet-end additives for papermaking and other purposes.

Keywords: Galactoglucomannans; Modification; Cationization; Carboxymethylation; Imination; Reducing end; Amphiphilic; Papermaking; Dewatering

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INTRODUCTION

During pulping and papermaking, hemicelluloses, extractives, and pectins are released into the process waters. Approximately 10% of the total amount of spruce galactoglucomannans (GGMs) can dissolve from thermomechanical pulp (TMP) (Thornton *et al.* 1994). GGMs can be isolated from TMP process waters by ultrafiltration or directly from spruce wood through pressurised hot water extraction (Thornton *et al.* 1994; Willför *et al.* 2003a; Xu *et al.* 2007; Song *et al.* 2008).

GGMs consist of a backbone of (1→4)-linked *β*-D-mannopyranose and (1→4)-linked *β*-D-glucopyranose units; *a*-D-galactopyranose is present as single unit side chains linked *via* (1→6) bonds (Willför *et al.* 2003b). GGMs partly contain acetyl groups, which gives water solubility to the polysaccharide. GGMs have a strong affinity to cellulosic fibres and are able to sterically stabilize colloidal wood pitch droplets (Sihvonen *et al.* 1998; Hannuksela and Holmbom 2004). During alkaline pulp treatments, such as peroxide bleaching, GGMs are deacetylated and adsorb onto fibres (Thornton *et al.* 1991) resulting in decreased amount of dissolved GGMs available for stabilization of wood pitch droplets.

Spruce mannans are able to decrease the detrimental effects of wood resin on paper strength properties (Sundberg *et al.* 2000). Mannans from other sources, such as guar gum, have also shown positive effects on paper sheet properties (Hannuksela *et al.* 2004). Cationised guar gum has proven to be a more efficient flocculant than native guar gum (Levy *et al.* 1995). Cationized guar gum has also been used as a retention and dry strength aid (Barua *et al.* 1996).

Mannans have been modified in different ways. Modifications like etherification (Pal *et al.* 2006), esterification (Savitha Prashanth *et al.* 2006), oxidation followed by alkylation (Sierakowski *et al.* 2000), carboxymethylation (Kobayashi *et al.* 2002; Xu *et al.* 2011), and crosslinking (Motozato 1989) have been reported. These modified mannans have been suggested for use in various applications, such as thickeners in food industry, as flocculating agents, or as packing materials in columns for gel chromatography.

The tension and relaxation properties of a wet paper web are critical for the runnability of paper machines (Kurki *et al.* 2004; Kouko *et al.* 2007). Not only poor strength but also a low tension of the wet web may cause web breaks in papermaking. Good stability and web tension is especially important in the beginning of the dryer section. Web tension is created by a speed difference in the web transfer between the press and dryer section. As the running speeds of paper machines are increasing, higher web tension is required. Recently it has been shown that, in addition to dry paper properties, also wet web properties are affected by the wet-end chemistry (Lindqvist *et al.* 2009; Retulainen and Salminen 2009; Lindqvist *et al.* 2012). Factors that influence the wet web are *e.g.* pH, surface tension, electrolytes, and chemical additives. Most of the runnability problems occur at a dry solids content in the range of 30 to 70% at the press and dryer section (Kouko *et al.* 2007).

The production costs of galactoglucomannans are higher today than the costs for production of starch. Another limiting factor for commercial use is the varying and complex structure such as branching and degree of polymerization and monosaccharide composition. However, GGMs have a great advantage in being more water soluble than starch, enabling modification reactions performed in water. GGMs are also a great resource for further modifications and can easily be tailored according to desired end use. In this study, the aim is to modify GGMs for papermaking purposes and to understand the behaviour of the derivatives in the papermaking environment. By using GGMs/ bifunctional GGMs, the goal is to increase the retention of unwanted compounds, such as anionic trash and pitch particles, in the paper sheet. The work includes the derivatization of GGM and the testing of the compounds in a combined dynamic drainage analyser/sheet former for retention and drainage properties, as well as the testing of mechanical properties of the resulting paper sheet.

MATERIALS AND METHODS

Galactoglucomannans

GGMs were isolated from TMP process waters. Process water was obtained from a Finnish mill producing TMP from spruce, from which GGMs were concentrated through a series of filtration and ultrafiltration techniques (Xu *et al.* 2007). The obtained GGM (Fig. 1A) was spray-dried and consisted of 53 mole-% mannose, 23 mole-% glucose, and 13 mole-% galactose. The purity of the GGMs was 73% and the rest consisted mainly of other sugars.

Pulp

Peroxide-bleached thermomechanical (PB TMP) pulp was used in the dewatering tests. The pulp was obtained from a Finnish pulp mill. The pulp was packed into airtight polyethylene bags and kept at -18°C until used for testing. The dry content of the pulp was about 27.7%.

Elemental chlorine free (ECF) bleached kraft pine pulp was used in the determinations of the mechanical properties of the wet web. The pulp was obtained from a Finnish pulp mill. The pulp was refined and dewatered at the mill. The pulp was packed as never-dried into airtight polyethylene bags, and kept at -18°C until used for testing. The Schopper-Riegler value (°SR, ISO 5267-1) of the pulp after dewatering and freezing was around 20°SR.

Chemicals

Cationic starch (degree of substitution (DS) of 0.2) was obtained from Raisio Chemicals (now Ciba Specialty Chemical, Raisio, Finland). Acicular precipitated calcium carbonate (PCC) was obtained from Specialty Minerals, Inc. (Kaarina, Finland). 1-docosanamide was obtained from Fluka.

The amide was reduced to amine using the following procedure: 50 mL of anhydrous tetrahydrofuran (THF) was added to a dried three-necked round-bottomed flask equipped with a dropping funnel, a magnetic stirrer, and a condenser after flushing with N_2-gas. $LiAlH_4$ (molar ratio $LiAlH_4$: amide of 1:1.5) was added and allowed to mix for 20 min. at room temperature until a homogeneous slurry appeared. The solid docosanamide was added in small portions during 30 min. After the addition, the temperature was raised to 45°C, and the reaction was allowed to continue for 22 h. The progress was monitored using gas chromatography. The reaction mixture was cooled to room temperature, and distilled H_2O was added drop wise through the dropping funnel to quench the reaction. A white precipitation was formed. Na_2SO_4 was added to the reaction mixture and the mixture was filtered. The formed 1-docosanamine was purified and obtained as a liquid in 31% yield by column chromatography (SiO_2, column 30 cm × 3 cm). The eluent used for separation was 3:7 petroleum ether (PEE) to diethyl ether (DEE). The purity of the fractions collected was monitored by thin layer chromatography (3:7 PEE:DEE). The solvent was evaporated and the product analysed with ^1H NMR.

Preparation of Galactoglucomannan Derivatives

Cationic GGMs (C-GGM, Fig. 1B) were prepared by dissolving GGMs into water (10 wt%) heated to 50°C, and by adding 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) to the solution to achieve a targeted DS of 0.05. Aqueous NaOH (4 wt% of dry GGMs) was added after 20 min. as a 30% solution. The reaction was continued for 18 h, after which the pH was adjusted to 6 using 0.1 M HCl. The final product was used as such for retention and drainage tests.

GGMs were carboxymethylated (CM-GGM, Fig. 1C) according to traditional methods described for preparation of carboxymethyl cellulose. GGMs were dispersed into isopropanol (4 wt%). Sodium hydroxide (30 wt% in distilled water, molar ratio

GGMs:NaOH 1:5.5) was added dropwise during 20 min. to the dispersion and allowed to react for 30 min. at room temperature. Monochloroacetic acid (molar ratio GGMs:MCA 1:2) was then added during 30 min., after which the temperature was raised to 55°C. The reaction continued for 90 min. before cooling to room temperature. The reaction mixture was filtered through a Büchner funnel and the solid material suspended in 70 wt% methanol. The mixture was neutralised with 90 wt% acetic acid and filtered. The solid material was re-suspended in 70 wt% ethanol, and the washing cycle without neutralisation was repeated 3 times. After the last washing with 100% methanol, the material was dried overnight in a vacuum desiccator at 30°C.

Reducing end-modified amphiphilic GGMs (A-GGM, Fig. 1D) were prepared by dissolving GGMs into water (10 wt%). Sodium bisulfite was added to the solution (molar ratio 1:1 $NaHSO_3$:amine). The amine (1-docosanamine, molar ratio GGMs:amine 157:1) was dissolved in diethyl ether and added to the reaction mixture. The reaction was left to stir at room temperature for 7 days. The reaction mixture was extracted three times using diethyl ether in order to remove residual amine which did not react.

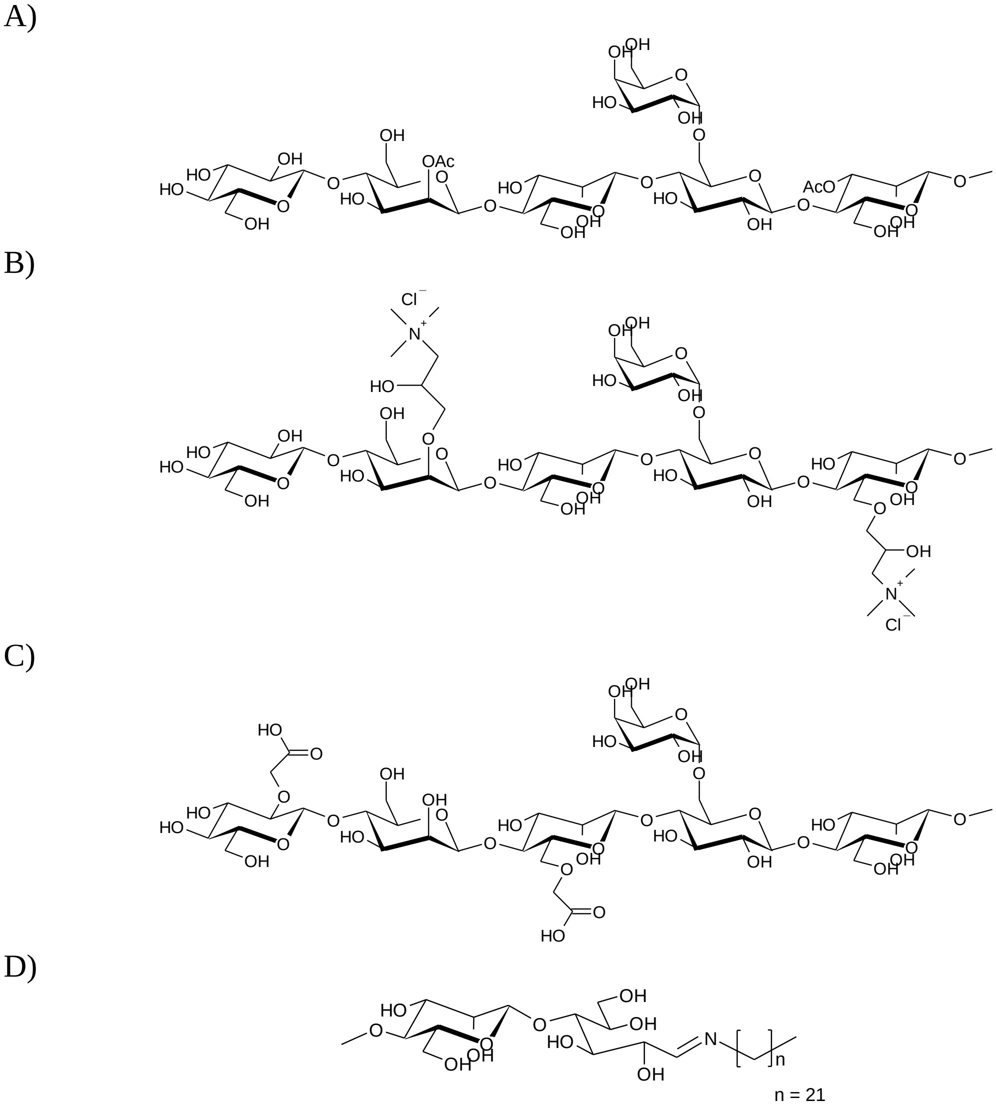

Fig. 1. Galactoglucomannans (A) and derivatives thereof: B) cationized GGMs (C-GGM), C) carboxymethylated GGMs (CM-GGM) and D) GGMs iminated at the reducing end (A-GGM)

^{1}H and ^{13}C NMR Spectroscopy

Approximately 100 mg of native GGMs or CM-GGM were dissolved in D_2O. The spectra were recorded with a Bruker AV 600 instrument at 50°C. For the C-GGM (cationized) or A-GGM (iminated), about 2 mL of the product was further purified through dialysis (Medicell International Ltd, UK, cut-off 12-14 kDa) for 24 h, followed by partial removal of water through evaporation. D_2O was added and the sample was analysed with a Bruker AV 600 instrument at 50°C.

HPSEC-MALLS

Weight-average and number-average molar mass (M_w and M_n) and molar weight distribution (MWD) were determined by high pressure size exclusion chromatography (HPSEC) in conjunction with an on-line multi-angle laser light scattering (MALLS) instrument (miniDAWN, Wyatt Technology, Santa Barbara, USA) and a refractive index (RI) detector (Shimadzu Corporation, Japan). A two-column system, 2 × UltrahydrogelTM linear 7.8 × 300 mm column (Waters, Milford, USA), in series was used. A 0.1 M $NaNO_3$ solution was used as the elution solvent. The flow rate was 0.5 mL min^{-1}. A dn/dc value of 0.150 mL g^{-1} was used (Michielsen 1999). The C-GGM (cationized) and A-GGM (iminated) were further purified through dialysis (Medicell International Ltd, UK, cut-off 12-14 kDa) for 24 h. The samples were filtered through a 0.22 μm nylon syringe filter before injection. The injection volume was 100 μL. Astra software (Wyatt Technology, Santa Barbara, USA) was used to analyze data.

Measurements of Wet Web Mechanical Properties

The conductivity of distilled water was adjusted to 1 mS/cm by addition of $CaCl_2$. The pH was adjusted to pH 8-8.5 using a 1 M $NaHCO_3$ solution. This water was used for disintegration of the pulp and for dilution of the suspension to a final consistency of about 0.3%. The disintegration of the pulp was done according to ISO 5263 at 50°C using 10,000 revolutions. The furnish was left to stand at room temperature overnight. Conductivity and pH were measured and adjusted, if necessary, the next day before the GGMs were added. For wet web tensile strength testing, the GGMs were dissolved in distilled water at 40°C for 2 h. An ultrasonic bath was used to ensure a homogeneous solution. The GGMs were added and the suspension was mixed for 1 h before sheet preparation. Sheets (60 g/m^2) were prepared using white water circulation on a sheet former (SCAN-CM 64:00). The sheets were packed in airtight plastic bags and sent within 24 h for wet web measurements. The sheets were pressed using three different pressures (20, 50, and 350 kPa for 5 + 2 min) in order to reach different levels of dry content of the wet handsheets. Wet handsheets were stored in airtight polyethylene bags at a temperature of 7°C in order to maintain the level of dry content.

Dynamic tensile strength and relaxation properties of samples from the sheet former were measured with the IMPACT (Kurki *et al.* 2004; Kouko *et al.* 2007), a fast tensile strength testing rig using a strain rate of 1 m/s (1000%/s). The width of the test samples was 20 mm and the span length was 100 mm. Before measurements, the samples were attached between two jaws. The lower jaw moved to the desired position creating strain. The upper jaw was equipped with a load sensor. The amount of strain was controlled simply by determining the gap between the lower jaw and target surface. The amount of strain was measured with a laser sensor. In the IMPACT tests, 10 to 14 samples were measured at each dryness level. The validity of each result was tested using

Dixon-Massey criteria (SCAN-G 2:63). For each dry content level, dryness was determined for 4-6 samples using a Mettler Toledo HR73 infrared dryer.

Measurements of Dewatering and Dry Sheet Properties

Dewatering time was determined using a dynamic drainage analyzer (Dynamic Drainage Analyzer of Åbo Akademi, DDÅA, Fig. 2). The device is custom built, is computer controlled, and is a combined drainage analyzer and sheet former. The pressure was adjusted to 1000 mbar in the experiments. A dewatering time of at least 4.8 s was obtained by addition of filtrate from a Dynamic Drainage Jar (DDJ) to the pulp and using a sheet grammage of 100 g/m^2.

A 0.5% PB TMP suspension was prepared and stirred at 150 rpm (1 h, 60°C) using a mechanical stirrer. The suspension was then mixed for 2 min. using a hand blender in order to disintegrate the fibres. The pulp was filtered as 1 L batches through the DDJ equipped with a 100 mesh wire. The DDJ filtration was done with a warm suspension (45 to 50°C) to ensure good recovery of fines as well as dissolved and colloidal substances. The consistency of the DDJ-filtrate was about 0.1%.

A fresh batch of PB TMP was mixed with a mechanical stirrer at 150 rpm (1 h, 60°C). The pulp was then disintegrated with a hand blender for 2 min. After disintegration, the pulp was diluted with the DDJ-filtrate to the right volume and left to mix for 10 min. (150 rpm).

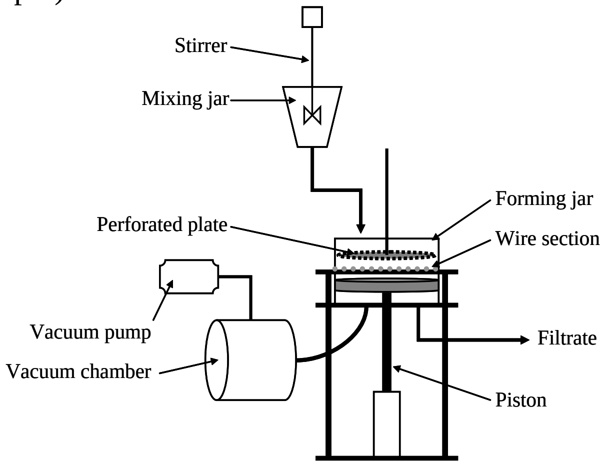

Fig. 2. The Dynamic Drainage Analyzer of Åbo Akademi, DDÅA

The pulp suspension was diluted to a consistency of about 4.9 g/L, and the pH was adjusted to 5 using SO$_2$-water when the pulp suspension was used as such, after which the suspension was stirred for an additional 30 min. The pH was only measured when the filler (PCC) was added to the suspension and stirred for an additional 30 min. The pH was about 8.3 after filler addition. The pulp suspension followed by the GGM derivative was poured into a mixing jar in the DDÅA (Fig. 2). During the first 30 s, the stirrer speed was set to 500 rpm and then the speed was increased to 1000 rpm. After 50 s, a valve between the mixing jar and the forming jar opened and the suspension was sprayed onto the wire. The suspension was mixed with a perforated plate for 50 s before the valve under the wire was opened. Below the wire was a 0.3 bar vacuum, resulting in removal of water from the suspension and formation of a paper sheet. After the valve under the wire was opened, the pressure was continuously measured during 80 s. For each test, 1.0 L of pulp suspension was used and 0.5 L of water was poured onto the wire before the pulp suspension was added. The consistency of the pulp suspension on the wire was about 2.5 g/L.

The properties measured on the sheets were: weight, thickness, tensile strength, and contact angle. All measurements were performed at 50% relative humidity and 23°C. Contact angle was determined with distilled water using a CAM 200 Optical Contact Angle Meter (KSV Instruments, Finland). The results were normalized for comparison purposes according to θ / θ_0, where θ is the contact angle at a given time and θ_0 is the contact angle at 0 s.

RESULTS AND DISCUSSION

Galactoglucomannan Derivatives

The GGMs and the GGM derivatives were analysed with ^{1}H and ^{13}C NMR spectroscopy. In Fig. 3, the peaks for GGMs can be roughly assigned as follows: 173.7-173.2 ppm carbonyl carbon signals from acetyl groups, 103.9-99.3 ppm C-1 signals from the various sugars, 78.9-68.8 ppm signals from carbons in the sugar ring (C-2 - C-5), 61.40-60.70 ppm C-6 signals from the various sugars and 20.9-20.6 ppm methyl carbon signals from the acetyl groups. More detailed spectral data can be found in the literature (Capek *et al.* 2002; Lundqvist *et al.* 2002; Willför *et al.* 2003; Hannuksela and Hervé du Penhoat 2004). When the spectra are compared, it is obvious that the acetyl groups are no longer present in the C-GGM or the CM-GGM, since the signals at about 173 (carbonyl-carbon) and 20 ppm (methyl-carbon) have disappeared. The reaction conditions in both reactions were alkaline and lead to deacetylation of the GGMs. For C-GGM, a new peak appeared at 54.6 ppm, indicating the presence of methyl groups in the functional group (Ren *et al.* 2006). For the CM-GGM, a new peak appeared around 180 ppm, which can be assigned to the carbonyl carbon in the carboxymethyl group (Xu *et al.* 2011). The signal coming from the methylene carbon ($-CH_2-$) was not visible as it is overlapping with the signals from the ring carbons. For the A-GGM spectrum, new signals in the region 42-14 ppm appeared. The signals originate from the aliphatic alkane chain of the iminated group (Sanz *et al.* 2011).

Approximate DS was calculated from the ^{1}H NMR data. The experimental DS for the C-GGM was about 0.05 and for the CM-GGM was about 0.4. The average molar mass (M_w) was determined with HPSEC-MALLS. The M_w was 25,500 g mol^{-1} for native GGM (polydispersity 1.27), 17,300 g mol^{-1} for the cationic GGM (polydispersity 1.74) and 30,600 g mol^{-1} for the iminated GGM (polydispersity 1.15). The cationization shortened the chain length slightly due to the addition of NaOH. The molar mass of the native GGM was slightly lower than the molar mass of the iminated A-GGM. The native GGM was analysed as such, while the A-GGM was dialysed after the reaction.

Wet Web Properties

The wet web properties were measured on handsheets prepared from bleached kraft pulp in order to see the effects on the network formation originating from the GGM addition clearly. Addition of GGMs increased the wet tensile strength at constant dry content (Fig. 4). Guar gum, which is another galactomannan, has been reported to increase wet tensile strength (Myllytie *et al.* 2009).

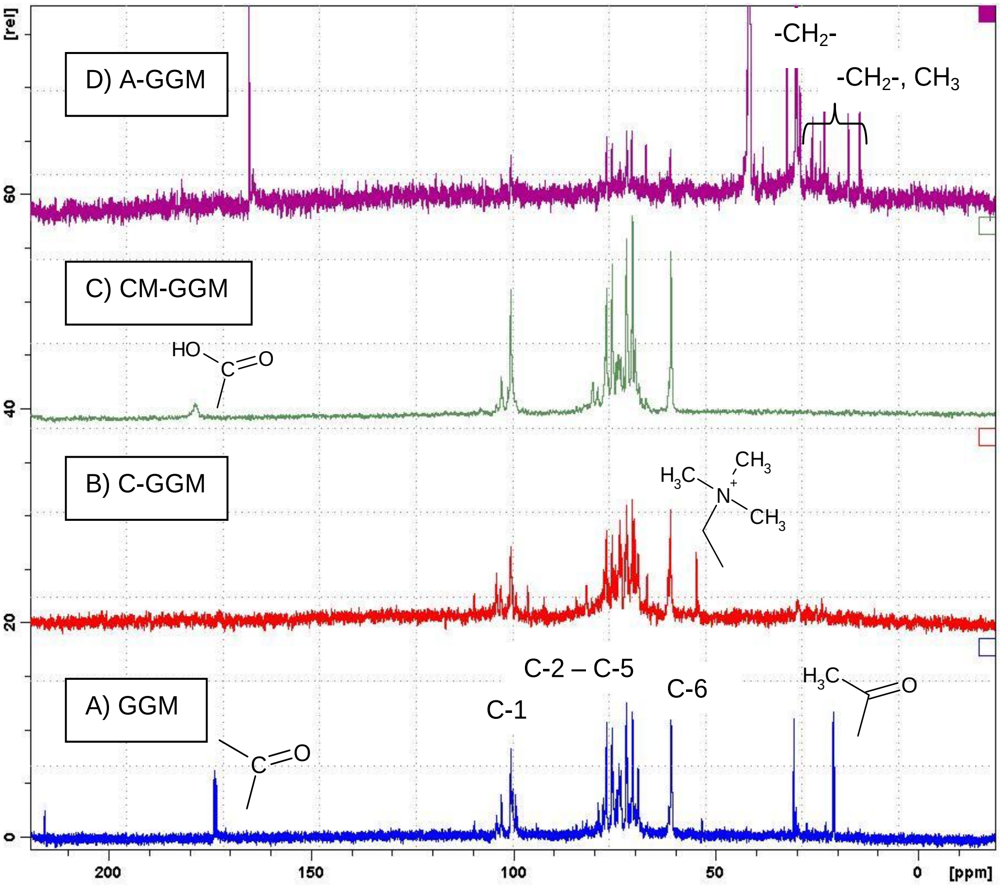

Fig. 3. ^{13}C NMR spectra of GGMs and GGM derivatives. A) Native GGMs, B) C-GGM, C) CM-GGM, D) A-GGM

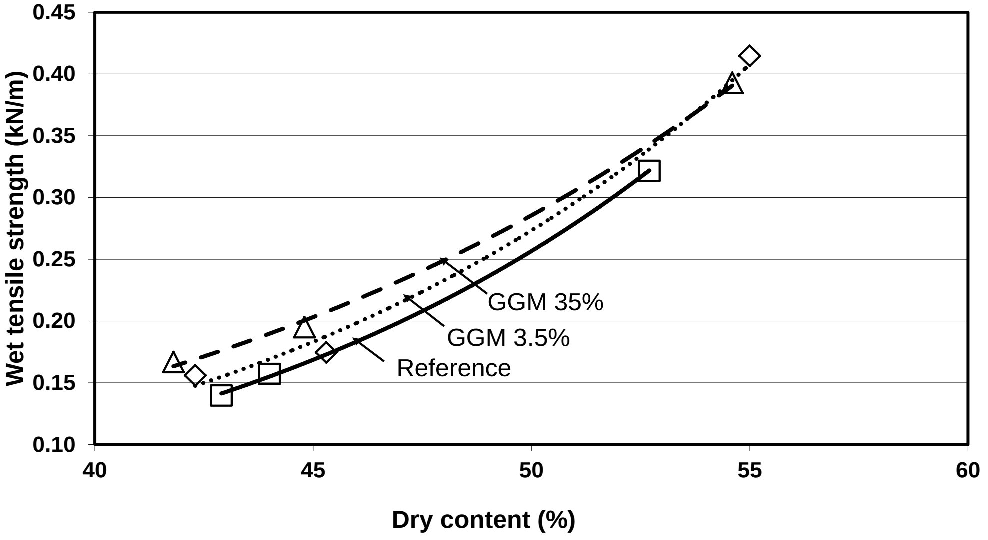

Fig. 4. Wet web tensile strength of wet handsheets prepared from bleached kraft pulp after addition of galactoglucomannans (GGM). The additions are given as % of amount of dry fibre. The sheets were pressed to three different dry contents (using 20, 50, and 350 kPa) and measured with the IMPACT test rig**.**

Recent research looking at the molecular and fibrillar level phenomena, suggest that the wet fibre surface could be considered as a gel-like layer consisting of cellulose and hemicelluloses (Pelton 1993; Kantelinen *et al.* 1997; Hubbe 2006; Pääkkö *et al.* 2007). When polymeric additives are adsorbed onto the fibres, they are mixed with the fibrillar gel-like layer and will change the properties of this layer depending on the interactions between the fibrils and the polymers (Myllytie 2009). Therefore, different polymers can have very different effects on the initial wet web strength. The effects depend mostly on the polymer and its ability to disperse fibrils on the fibre surface and/or to increase the hydration of the fibre surfaces. Eronen *et al.* (2011) found that galactomannans, like guar gum and locust bean gum, had a dispersing effect on fibrils. GGMs have very similar structures as the tested galactomannans, with a main chain containing mannose monomers and side chains containing single galactose monomer pendants. Therefore, GGMs can be expected to have a similar effect on the fibrils as the galactomannans resulting in an increase in wet tensile strength.

Addition of GGMs also increased the elastic modulus of the wet web (Fig. 5). The difference between the two addition levels of 3.5 and 35% was small. The increase in elastic modulus was higher at lower dry contents. Since addition of GGMs increased the wet tensile strength, due to increased dispersion of fibrils and therefore increased interactions between wet fibre surfaces, an increase in the elastic modulus could also be expected. The use of GGMs have a great potential to increase the runnability of the wet web, since the tension of a running web in practice is controlled by the elastic modulus of the fibre network (Alava and Niskanen 2008). The elastic modulus also controls the performance of the end-product through the bending stiffness.

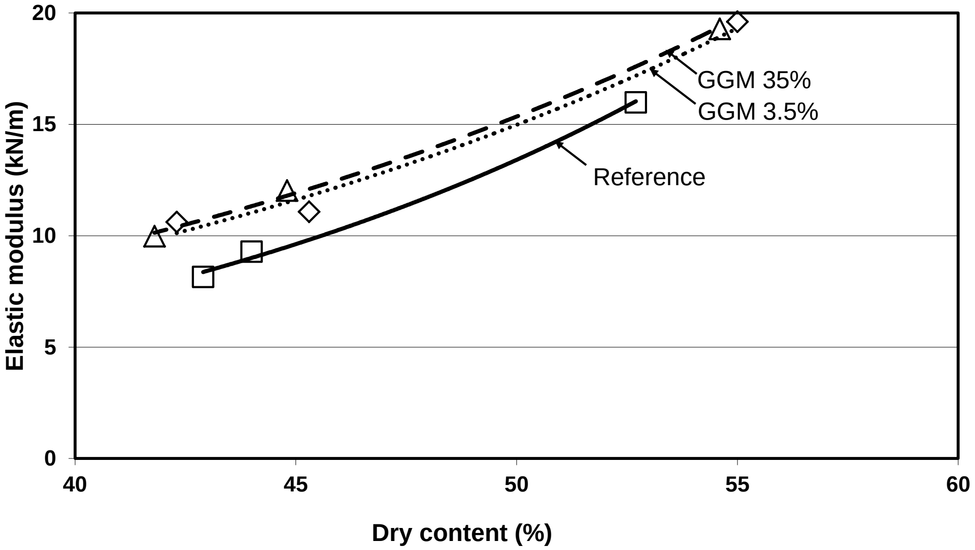

Fig. 5. Elastic modulus of wet handsheets prepared from bleached kraft pulp after addition of galactoglucomannan (GGM). The additions are given as % of amount of dry fibre. The sheets were pressed to three different dry contents (using 20, 50, and 350 kPa) and measured with the IMPACT test rig**.**

Dewatering and Dry Web Properties

Retention, density, dewatering, and dry tensile index were measured for sheets prepared from PB TMP using the DDÅA (Table 1). The retention was calculated based on the weight of the dry sheet and compared to the theoretical sheet weight if all the fibre material would be retained. For the native GGMs, a maximum in retention was observed at a dosage of 0.5 to 1 mg GGMs/g fibre. The maximum strength, however, was reached at higher dosages (10 mg/g). In an earlier study, Rojas and Neuman (1999) found that addition of neutral or cationic guar gum decreased the amount of glucose-containing fines in the supernatant of pulp suspensions. Both types of derivatives showed first a decrease, followed by a minimum amount of fines in the supernatant, after which the amount increased again. This behaviour leads, according to the authors, to improved strength and formation properties due to the adsorption of the guar gum onto different surfaces, followed by formation of aggregates and retention of dissolved and colloidal substances. The native guar gum is subjected to a number of intermolecular interactions like hydrogen and ion bonding, van der Waals and hydrophobic forces, as well as steric interactions (Rojas and Neuman 1999). The long-chained guar gum can bridge over several particles creating large strength increasing flocs. Since the chain of the GGMs is much shorter, a higher amount is required for the same effect. The dewatering time and density also increased when native GGMs were added, which supports the idea of increased bonding between particles. GGMs are known to diminish the negative effects of wood resin on paper strength properties studies (Sundberg *et al.* 2000; Suurnäkki *et al.* 2003); our results are in agreement with these reports.

The retention increased with increased amount of C-GGM, while the tensile strength first decreased and then increased. This could be due to fines and extractives being retained at first, and when these substances have been consumed by the additive, the fibre-to-fibre linkages can be formed. As a result, the fibre network was first weaker and later the network strength was improved. When C-GGM was added to the TMP suspension, the dewatering time increased slightly with increasing dosage. This could be explained by the denser sheet structure being formed. These findings are in line with Rojas and Neuman (1999), who studied the adsorption of cationic guar gum and suggested an electrostatic mechanism, where the cationic polyelectrolyte adsorbs onto oppositely charged surfaces. Steric factors also affect the adsorption (Rojas *et al.* 1998). A similar reasoning seems to be true also for C-GGM. However, with the shorter chain length, the increase in tensile strength is not as evident.

When anionic CM-GGM was used, a slight increase in retention and dewatering time as well as a slight decrease in strength was observed. Rojas and Neuman (1999) suggested that anionic guar gum would together with divalent metal ions bind to negatively charged particles. Wood contains about 0.1 to 1% inorganic elements, *e.g.* calcium and magnesium (Fengel and Wegener 1983), which are partly released during pulping. The anionic CM-GGM may bind to these metals, giving a denser sheet structure with slightly increased retention and dewatering time as a result. The retention was slightly lower when compared to the use of GGMs or C-GGM, thus the ionic binding did not seem to be as effective in retaining fibrous dissolved and colloidal substances to the sheet. Xu *et al.* (2011) studied the sorption of CM-GGM onto softwood kraft fibres and found that the carboxymethylated GGMs might form a mono-electric layer on the fibre surface. About 20% of the added amount of CM-GGM (DS 0.5, 10 mg/g fibre) was adsorbed.

The addition of A-GGM increased retention and dewatering time, while the density and tensile strength were only slightly affected. Since the DS was very low, and the hydrophobic tail is assumed to be only at the reducing end of the GGM chain, it is likely that the A-GGM acted in a similar way as native GGM. The retention was, however, higher than for native GGMs, which could be due to a higher retention of the extractives. The hydrophobic tail was able to orientate towards the hydrophobic particles and increase their retention, maybe through a micelle-like structure.

Addition of conventional cationic starch resulted in increased retention, decreased tensile strength, as well as almost unchanged density and dewatering time. Since much of the extractives and fines were retained in the sheet, a decrease in tensile strength was expected. Cationic starch forms bridges between the anionic particles and the fibres, which is why the retention was increased (Eklund and Lindström 1991).

Table 1. The Total Retention, Density, Dewatering Time, Tensile Index and (Standard Deviation, SD) Measured for Sheets Prepared from Recycled PB TMP Using the DDÅA

*		Retention (%)	Density (kg/m^3)	Dewatering time (s)	Tensile index (N•m/g)
GGM	Ref.	81.0 (11.7)	353	5.6 (1.4)	35.0 (2.1)
	0.5 mg/g	95.2 (3.5)	340	7.2 (0.3)	33.7 (4.0)
	1 mg/g	94.1 (5.7)	352	4.1 (0.9)	34.9 (3.3)
	3 mg/g	94.0 (0.9)	366	8.1 (1.9)	36.7 (6.5)
	5 mg/g	93.7 (1.9)	376	7.2 (0.1)	36.4 (4.0)
	10 mg/g	82.5 (4.9)	325	7.2 (0.7)	39.1 (5.8)
C-GGM	Ref.	75.5 (4.6)	389	9.4 (0.1)	36.3 (2.8)
	0.5 mg/g	90.6 (1.8)	385	8.9 (0.5)	36.9 (6.1)
	1 mg/g	91.1 (1.3)	379	8.8 (0.3)	33.2 (2.6)
	3 mg/g	91.4 (1.9)	376	9.5 (0.7)	35.4 (4.8)
	5 mg/g	92.9 (0.3)	376	9.4 (0.9)	34.2 (5.9)
	10 mg/g	92.3 (2.5)	377	10.5 (0.2)	38.0 (3.5)
CM-GGM	Ref.	83.6 (10.0)	360	6.2 (1.2)	34.2 (1.6)
	0.5 mg/g	89.2 (0.6)	380	8.4 (1.3)	34.2 (3.3)
	1 mg/g	89.0 (0.7)	376	7.0 (0.7)	32.0 (3.0)
	3 mg/g	89.0 (3.6)	383	8.3 (0.6)	34.6 (4.6)
	5 mg/g	90.1 (0.3)	362	7.9 (1.0)	32.6 (2.1)
	10 mg/g	89.5 (5.8)	368	6.9 (0.4)	32.8 (3.4)
A-GGM	Ref.	85.4 (21.6)	370	6.9 (2.4)	31.5 (0.7)
	0.5 mg/g	92.8 (2.5)	383	10.6 (0.1)	34.8 (5.1)
	1 mg/g	99.1 (4.6)	376	9.2 (0.1)	33.0 (6.0)
	3 mg/g	100.5 (2.2)	368	9.2 (0.2)	32.8 (6.3)
	5 mg/g	96.4 (0.1)	377	8.9 (0.2)	32.8 (4.0)
	10 mg/g	101.6 (4.0)	383	10.6 (0.1)	32.0 (2.8)
CS	Ref.	81.0 (11.7)	353	5.6 (1.4)	35.0 (2.1)
	0.5 mg/g	95.4 (0.3)	386	7.7 (2.3)	34.3 (0.4)
	1 mg/g	91.4 (1.3)	352	6.0 (1.5)	33.9 (0.4)
	3 mg/g	93.6 (3.0)	351	5.5 (0.1)	29.9 (3.0)
	5 mg/g	97.1 (0.6)	348	4.8 (0.3)	30.4 (3.7)
	10 mg/g	90.8 (10.5)	355	4.9 (0.7)	30.8 (3.8)

* GGM = Galactoglucomannans, C-GGM = Cationized GGMs, CM-GGM = Carboxymethylated GGMs, A-GGM = Amphiphilic Iminated GGMs, CS = Cationic Starch.

The contact angle of papers containing selected derivatives was measured (Fig. 6). The results showed that all additions decreased the contact angle compared to the reference. The hydrophilicity of the surface increased in the order: Reference < GGMs < CS < A-GGM. The results indicate that hydrophobic particles in the sheet, *e.g.* extractives, were covered with GGMs/derivatives, giving more hydrophilic character to the surface. The hydrophobic tail of the A-GGM was most likely oriented towards the hydrophobic particle surface, leaving the outermost surface covered with the hydrophilic part of the polysaccharide. As a result, addition of A-GGM resulted in the most hydrophilic surface.

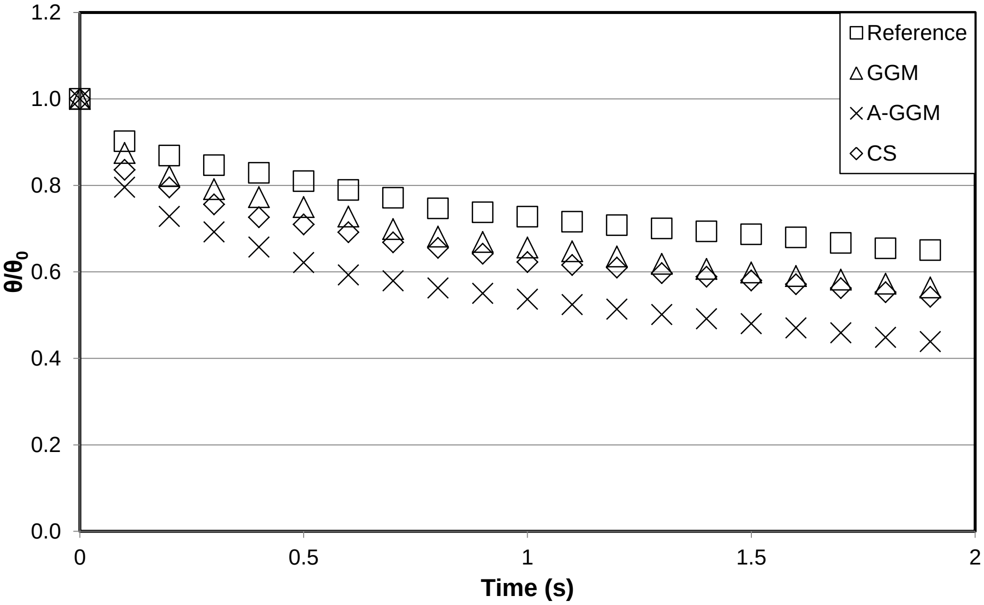

Fig. 6. Contact angle measurements of sheets prepared from PB TMP using the DDÅA. The results have been recalculated for comparison purposes according to θ/θ_0, where θ = contact angle at a given time and θ_0 = contact angle at 0 s. The dosage of the additives was 1 mg/g fibre. GGM = galactoglucomannan, A-GGM = amine end-modified GGM, CS = cationic starch.

Filler

The use of filler in papermaking is increasing primarily due to its low cost; therefore, some experiments were done using PCC. Retention, density, dewatering, and dry tensile index were measured from sheets prepared from PB TMP and 15% PCC using the DDÅA (Table 2). The retention was calculated based on the weight of the dry sheet and compared to the theoretical sheet weight if all the fibrous material and fillers would be retained. The addition of GGMs seemed to create a very dense sheet through flocculation, since the dewatering time significantly increased. The tensile strength simultaneously decreased as a result of the high retention of fillers and fines. When C-GGM was used, the retention increased slightly, while the increase in density indicated that the amount of intermolecular interactions had increased. At the same time, the tensile strength was only slightly affected. In this case, it seems that the shorter chain length of the C-GGM was more beneficial, the longer chain of the cationic starch retained more filler as well as dissolved and colloidal substances, resulting in decreased tensile strength. The surface charge of PCC is slightly positive (Clark and Gill 1998), which results in anionic particles being adsorbed onto the filler surface. The net surface charge becomes anionic as a result. This is why the cationic C-GGM showed a similar retention as native

GGMs, but the decrease in tensile strength was not as large and the dewatering time remained almost unaffected. When adding A-GGM to the furnish, a slight increase in all measured properties was observed. Since it is well known that extractives are adsorbed onto the surface of the filler, resulting in an anionic charge as well as a hydrophobic surface, it can be expected that the tail of the A-GGM was oriented towards the extractive-rich surface of the filler and the GGM towards the fibre surface. The interactions between the A-GGM and fillers did not seem to be that strong in this case since the tensile index and the density were only slightly increased.

Table 2. The Total Retention, Density, Dewatering Time, Tensile Index, and (Standard deviation, SD) Measured for Sheets Prepared from 15% PCC and Recycled PB TMP Using the DDÅA

*		Retention (%)	Density (kg/m^3)	Dewatering time (s)	Tensile index (N•m/g)
GGM	Ref.	81.9 (7.2)	362	8.8 (0.5)	33.7 (2.0)
	1 mg/g	87.8 (0.5)	374	12.6 (3.8)	35.8 (6.8)
	5 mg/g	83.5 (0.5)	376	12.3 (3.0)	33.9 (5.5)
	10 mg/g	88.6 (0.9)	379	22.1 (1.6)	27.5 (5.7)
C-GGM	Ref.	81.9 (7.2)	362	8.8 (0.5)	33.7 (2.0)
	1 mg/g	84.2 (0.9)	375	8.8 (0.7)	30.9 (3.8)
	5 mg/g	86.3 (0.1)	379	11.8 (1.1)	30.3 (5.7)
	10 mg/g	87.6 (1.7)	392	8.8 (0.5)	31.8 (4.4)
A-GGM	Ref.	82.7 (8.5)	380	8.6 (2.8)	30.5 (1.5)
	1 mg/g	87.4 (0.8)	375	8.2 (1.0)	29.6 (9.0)
	5 mg/g	86.6 (1.1)	377	9.2 (1.1)	33.7 (5.3)
	10 mg/g	87.6 (3.3)	383	11.7 (4.6)	31.6 (3.5)
CS	Ref.	81.9 (7.2)	362	8.8 (0.5)	33.7 (2.0)
	1 mg/g	88.7 (0.6)	372	11.1 (3.4)	30.3 (4.1)
	5 mg/g	88.9 (1.9)	374	6.2 (0.4)	27.9 (3.3)
	10 mg/g	90.5 (4.6)	371	4.8 (0.4)	27.5 (3.9)

* GGM = Galactoglucomannans, C-GGM = Cationised GGMs,
A-GGM = Amphiphilic Iminated GGMs, CS = Cationic Starch

CONCLUSIONS

1. Galactoglucomannans (GGMs) were successfully modified and subsequently tested for papermaking purposes. Cationized, carboxymethylated, and iminated GGMs showed very different behaviour in papermaking environment. All of them maintained or improved some of the properties of the paper. Based on these results, it is concluded that galactoglucomannans can be modified to yield new and interesting functional derivatives to wet-end additives for papermaking purposes.
2. Native GGMs were found to slightly increase the wet tensile strength and the elastic modulus of the wet fibre network of kraft pulps. GGMs are proposed to disperse the fibrils on the fibre surface in the wet state. For dry wood-containing papers, GGMs increased the strength of paper and retention of fibrous fine material. The amount of interactions in the paper sheet increased.

3. Cationic GGMs increased the retention of both fibrous fine material and fillers, without deterioration of the mechanical properties. The behaviour indicated that C-GGM functioned through an electrostatic mechanism.
4. Carboxymethylated GGMs increased the retention of fibrous material slightly. CM-GGMs are suggested to act through binding with metal ions present in wood. The formed ionic bond was not as strong, and the dry tensile strength decreased slightly compared to GGMs or C-GGM.
5. Iminated GGMs modified at the reducing end increased the retention of both fibrous material and fillers. The amphiphilic A-GGM is proposed to act through the long alkane chain attached to the reducing end. The hydrophobic tail orientated towards the hydrophobic particles. The resulting paper was the most hydrophilic, indicating that hydrophobic particles were covered with the polysaccharide.

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