

## Use of Quartz Crystal Microbalance (QCM) for Biopolymers Adsorption Studies

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### Abstract

*The importance of biomaterials has been on the increase during the last years, especially in the field of biorefineries. The most abundant biopolymers are plant polysaccharides, which are potential materials for hydrocolloids and novel advanced natural materials. During the thermomechanical pulp (TMP) production, a huge amount of hemicelluloses with a great application potential are disposed with process waters. Hemicelluloses from spruce wood were tested as the material for the production of biodegradable films and as hydrocolloids. Therefore, the adsorption process and stability of adsorbed hemicellulose films are important in the colloid and food chemistry. One of the techniques which can be used for the in situ adsorption studies is quartz crystal microbalance with dissipation unit (QCM-D). In our study, QCM-D was used for monitoring the adsorption of hemicellulose from spruce wood onto model poly(ethyleneterephthalate) (PET) surface. The added salt increased the adsorption of hemicelluloses from softwood due to the shielding of repulsive forces between the negative charges of the PET surface and negative charge groups in hemicelluloses.*

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## Uporaba kremenove mikrotehnice za spremljanje adsorpcije biopolimerov

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### Izvleček

Uporaba polimerov naravnega izvora oziroma biopolimerov se v zadnjih letih povečuje, posebno na področju biorafinerije. Najobetavnejši biopolimeri so rastlinski polisaharidi, ki so potencialni materiali tudi za hidrokoloide in nove napredne naravne materiale. Velika količina potencialno uporabnih hemiceluloz se zavrže med proizvodnjo termomehane pulpe (TMP) z odpadnimi procesnimi vodami. Hemiceluloze iz mehkega lesa, kot je smrekovina, so bile testirane kot material za proizvodnjo biorazgradljivih filmov in hidrokolidov.

Adsorpcija in stabilnost teh adsorbiranih hemiceluloznih filmov sta pomembna dejavnika v koloidni in prehranski kemiji. Ena od tehnik, s katerimi lahko spremljamo adsorpcijo v realnem času, je kremenova mikrotehnica (QCM-D). V našem prispevku smo uporabili kremenovo mikrotehniko za adsorpcijo hemiceluloz iz smrekovine na modelno površino polietilentereftalata (PET). Dodana sol je povečala stopnjo adsorpcije hemiceluloz na površino PET zaradi omiljenja odbojnih sil med negativno nabito površino PET in negativnimi skupinami v hemicelulozah.

Ključne besede: QCM-D, hemiceluloze, PET, termomehane pulpa (TMP), galaktoglukomanan

### 1 Uvod

Uporaba polimerov naravnega izvora oziroma biopolimerov se v zadnjih letih povečuje, posebno na področju biorafinerije. Najobetavnejši biopolimeri so rastlinski polisaharidi, ki so potencialni

**Keywords:** QCM-D, hemicellulose, PET, thermomechanical pulp (TMP), galactoglucomannan

## 1 Introduction

The use of biopolymers has been increasing during the last years, especially in the field of biorefineries. The most abundant biopolymers are plant polysaccharides, which are potential materials for hydrocolloids and novel advanced natural materials. Certain hemicelluloses, e.g. gums from different natural sources, have been applied in the areas such as papermaking, textiles, cosmetics, medicine, foodstuff and health care [1]. However, there is a huge source of water soluble galactoglucomannans (GGMs), which are not efficiently reused and can be isolated during the pulp production from process water (cf. Figure 1). These hemicelluloses are now used in papermaking, improving the paper properties by absorbing on the fibre surface [2]. The amount of hemicelluloses in dry wood is usually from 20–30% and they mostly function as the support material in the cell walls associated to cellulose. The composition and structure of hemicelluloses vary with different plant species, as well as from the part of the plant. O-acetyl galactoglucomannans (cf. Figure 2) from softwoods consist of a backbone of  $\beta$ -(1 $\rightarrow$ 4)-D-mannopyranosyl and  $\beta$ -(1 $\rightarrow$ 4)-D-glucopyranosyl units carrying single  $\alpha$ -D-galactopyranosyl residues that are 1 $\rightarrow$ 6-linked to mannose units, and acetyl substituents are attached to the C-2 or C-3 positions of mannose [3]. The ratio of anhydro mannose : glucose : galactose units of water-soluble spruce galactoglucomannans is approximately 4 : 1 : 0.5, and the degree of acetylation is up to 0.3, and it has been stated that only mannose units bear acetyl groups [4]. The molar masses are about 20–60 kDa. GGMs have a great application potential. At the laboratory scale, GGMs have been tested as the raw material for the production of biodegradable films [5] and in therapeutic reagents [6] as biological response modifiers. GGMs have also been studied as hydrocolloids [4] and as a potential source of novel anticoagulants production [7].

Therefore, the adsorption processes and stability of adsorbed GGM films are important in

materiali tudi za razne hidrokoloide in nove napredne naravne materiale. Nekatere hemiceluloze, kot so razni glukomanani iz različnih naravnih virov, že uporabljajo v industrijski proizvodnji papirja, tekstilni industriji, proizvodnji kozmetike, v medicini, prehranski industriji in na področju varovanja zdravja [1].

Pri proizvodnji termomehanečne pulpe iz smrekovine se s procesnimi vodami odstranijo velike količine galaktoglucomanana (GGM), ki še nimajo širše koristne uporabe in jih lahko izoliramo iz odpadnih procesnih vod (slika 1). Te hemiceluloze se za zdaj uporabljajo v papirni industriji, kjer se med procesom adsorbirajo na površino vlaken papirne pulpe in tako izboljšajo lastnosti papirja [2].

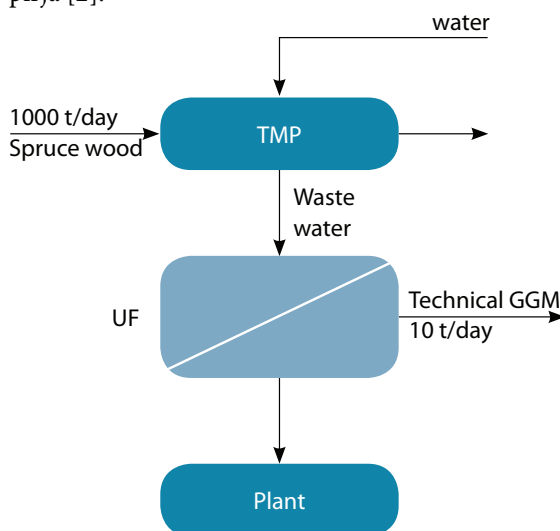


Figure 1: Process scheme of thermomechanical pulp production

V suhem lesu je po navadi od 20 do 30 odstotkov hemiceluloz in so večinoma gradniki celičnih sten v povezavi s celulozo. Sestava in struktura hemiceluloz se razlikujeta glede na vrsto in dele rastlin. O-acetilirani galaktoglucomanan (slika 2) iz smrekovine sestavlja skelet  $\beta$ -(1 $\rightarrow$ 4)-D-manopiranozilnih enot in  $\beta$ -(1 $\rightarrow$ 4)-D-glukopiranozilnih enot s stranskimi  $\alpha$ -D-galaktopiranozilnimi enotami, 1 $\rightarrow$ 6-vezanimi na manozne enote v verigi. Acetilne skupine so vezane na položaje C-2 ali C-3 v manoznih enotah verige [3].

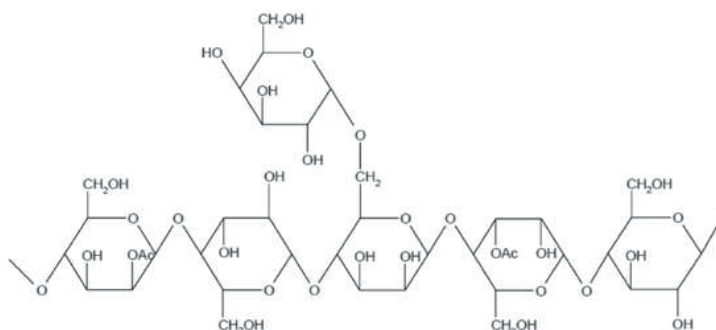


Figure 2: Structural feature of spruce wood galactoglucomannan [1]

the colloid and food chemistry. One of the techniques which can be used for the in situ adsorption studies is quartz crystal microbalance with dissipation unit (QCM-D) [8–11].

In our research, QCM-D was used to monitor the adsorption of unmodified GGM and sulphated GGM on the model PET surface. The adsorption of GGMs was studied and the influence of both, calcium chloride ( $\text{CaCl}_2$ ) and sodium chloride ( $\text{NaCl}$ ), on the GGM adsorption was examined using the QTools software (QSense, Sweden). The charges of both, unmodified and sulphated GGMs, were detected with cationic polyelectrolyte titration according to Tanaka and Sakamoto [12], and the results were compared to the mass adsorbed on the PET film.

## 2 Experimental

### 2.1 Materials

#### Galactoglucomannans (GGMs)

GGM was recovered from the process water of thermomechanical pulping using spruce wood according to Willför et al [1, 13].

GGMSO<sub>4</sub> was prepared according to the procedure described elsewhere [7]. All other chemicals were analytical grades, supplied by Fluka.

#### PET film

The QCM-D analyses were performed on model PET surfaces which were prepared using the spin coating technique. For the substrate, we used AT-cut quartz crystals with gold plate electrodes (supplied by Q Sense AB, Sweden) with fundamental frequency ( $f_0$ ) = 5 MHz and sensitivity constant  $C = 0.177 \text{ mg/m}^2 \text{ Hz}$ . Prior to the spin coating, all crystals were cleaned in a 5 : 1 : 1 mixture of MQ water, H<sub>2</sub>O<sub>2</sub> (30%) and NH<sub>4</sub>OH (25%) for 5 min at 70 °C.

The spin coated PET films were prepared by spin coating 1 wt.% PET solution in 1,1,2,2-tetrachloroethane (Fluka, 86960) onto quartz crystals. The PET film thicknesses were estimated by measuring the mass of spin coated film in air with QCM-D and were found to be  $48 \pm 10 \text{ nm}$ . The AFM imaging of model PET films showed that films were smooth and uniform with the average roughness  $S_a = 0.25 \text{ nm}$  [14].

Razmerje enot manozna / glukoza / galaktoza v vodi topnih galaktoglukomananov je približno 4 / 1 / 0,5. Stopnja acetilacije je 0,3, kjer so acetilne skupine vezane večinoma na manozne enote v verigi [4]. Molske mase izoliranih galaktoglukomananov so 20–60 kDa.

Galaktoglukomanani imajo velik potencial uporabe, zato so bili na laboratorijski ravni testirani kot surovina za proizvodnjo biofilmov [5] in kot terapevtski reagenti – modifikatorji biološkega odziva [6]. Prav tako so jih preskušali kot hidrokoloide [4] in kot morebiten vir surovin za proizvodnjo novih antikoagulantov [7].

Prav zato so pomembni adsorpcijski procesi in stabilnost adsorbiranih galaktoglukomananskih filmov v koloidni in prehranski kemiji.

Ena takšnih tehnik za spremljanje adsorpcije v realnem času je kremenova mikrotehnica s spremljanjem dušenja nihanja (Quartz Crystal Microbalance with dissipation unit -QCM-D) [8–11].

V raziskavi smo uporabili kremenovo mikrotehniko za spremljanje adsorpcije nemodificiranih in sulfatiranih galaktoglukomananov na modelno PET-površino. Spremljali smo adsorpcijo in vpliv kalcijevega klorida ( $\text{CaCl}_2$ ) in natrijevega klorida ( $\text{NaCl}$ ) na adsorpcijo galaktoglukomananov. Naboj na preiskovanih hemicelulozah smo določili s polielektrolitsko titracijo po postopku, ki sta ga uvedla Tanaka in Sakamoto [12], in primerjali odvisnost med nabojem in maso adsorbiranih galaktoglukomananov na modelno površino PET.

## 2 Eksperimentalno delo

### 2.1 Materiali

#### Galaktoglukomanani (GGM)

Galaktoglukomanani so bili pridobljeni iz procesnih voda med proizvodnjo termomehane pulpe (TMP) po postopku, ki ga je opisal Willför s soavtorji [1, 13].

Sulfatirani galaktoglukomanan (GGMSO<sub>4</sub>) smo pripravili s sulfatacijo, ki je podrobno opisana v literaturi [7]. Vse kemikalije so bile analitske čistoče proizvajalca Fluka.

#### PET film

Eksperimenti adsorpcije hemiceluloz s pomočjo kremenove mikrotehnice so bili narejeni na modelni površini PET, pripravljeni s pomočjo tehnike „spin coat“. Za substrat smo uporabili kremenov kristal (AT-rez) z elektrodami iz zlata (Q Sense AB, Švedska) in osnovno resonančno frekvenco ( $f_0$ ) = 5 MHz ter masno konstanto kremenovega kristala,  $C = 0,177 \text{ mg/m}^2 \text{ Hz}$ . Pred samo pripravo filma so bili vsi kristali prej očiščeni v raztopini milliQ vode, H<sub>2</sub>O<sub>2</sub> (30 %) in NH<sub>4</sub>OH (25 %) v razmerju 5 : 1 : 1, za 5 min pri 70 °C.

PET-filmi, pripravljeni s pomočjo tehnike „spin coat“, so bili pripravljene iz 1 wt.-% raztopine PET v 1,1,2,2-tetrakloroetanu (Fluka, 86960). Debelina filma PET je bila ocenjena z razliko v reso-

## 2.2 Methods

### Polyelectrolyte titrations

Polyelectrolyte titrations were performed in order to determine the amount of negative charge, deriving from dissociated sulphate and acetate groups, on different modified polysaccharide samples. Polyelectrolyte titrations were made with a cationic polyelectrolyte pDADMAC as titrant ( $c \approx 1$  mM) and with Toluidine blue as a cationic indicator. The Toluidine blue forms a complex with the negatively charged functional groups of the sample, which results in a red coloured solution. The change in colour from red to blue indicates the formation of a complex between the cationic polyelectrolyte and anionic polysaccharide. The bonding stoichiometry of polyelectrolyte to the negatively charged groups is 1 : 1. The amount of negatively charged groups can be determined from the volume of added polyelectrolyte at the point of equivalence [12, 15]. The procedure is described in details elsewhere [7, 16, 17].

### Quartz crystal microbalance with dissipation unit (QCM-D)

Quartz crystal microbalance with dissipation unit (QCM-D) is one of the few techniques that give direct information on the *in situ* adsorption process [8–10]. It is based on the change in the resonance frequency of a thin AT-cut piezoelectric quartz crystal disc that oscillates in the shear mode when the AC voltage is applied across electrodes. The AT-cut crystal has a crystalline orientation which generates shear waves. The advantage of the AT-cut quartz crystal is also that it has nearly a zero frequency drift in the temperature range 5–50 °C.

The QCM-D device measures the mass of a thin film deposition onto the quartz crystal sandwiched between two electrodes. The quartz crystal connected to power supply oscillates at its fundamental resonance frequency and several overtones. The frequency of the QCM decreases with increasing the mass, viscosity and electrodes roughness.

The adsorbed amount ( $\text{ng}/\text{cm}^2$ ) can be calculated from the frequency shift using the Sauerbrey equation (1). However, the Sauerbrey equation is valid only for rigid, evenly distributed thin adsorbed layers (Equa-

nančnih frekvencah kvarčnega kristala pred nanosom raztopine PET na kristal in po njem, merjeno v zraku. Debelina PET-filma na kvarčnih kristalih je znašala  $48 \pm 10$  nm. S pomočjo mikroskopske na atomsko silo AFM smo določili povprečno hrapavost,  $S_a = 0,25$  nm [14].

## 2.2 Metode

### Polielektrolitske titracije

S pomočjo polielektrolitskih titracij smo določili količino negativnega naboja v raztopinah galaktoglukomananov, ki je posledica disociiranih sulfatnih in acetatnih skupin. Polielektrolitske titracije so bile izvedene s polielektrolitom pDADMAC kot titrantom ( $c \approx 1$  mM) in barvilom Toluidine modro kot kationskim indikatorjem. Toluidine modro tvori z negativno nabitimi funkcionalnimi skupinami kompleks, ki raztopino obarva rdeče. Sprememba barve iz rdeče v modro je posledica nastanka kompleksa med kationskim polielektrolitom in anionskimi polisaharidi. Stehiometrično razmerje med njimi je 1 : 1. Količina negativno nabitih skupin v raztopljenem polisaharidu se določi iz porabe polielektrolita v ekvivalentni točki [12, 15]. Sam postopek je natančneje opisan v literaturi [7, 16, 17].

### Kremenova mikrotehnica (QCM-D)

Kremenova mikrotehnica, ki meri izgubo energije med adsorpcijo (QCM-D), je ena redkih, ki daje neposredne informacije o procesu adsorpcije *in situ* [9–11]. Osnova metode je merjenje resonančne frekvence tankega kremenovega kristala okrogle oblike, ki strižno (laterarno) vibrira, če je priključen na izmenično električno napetost. Sprememba mase resonatorja (kristala) povzroči spremembo resonančne frekvence. Da kristal lahko vibrira v strižnem načinu, mora imeti natančno določeno kristalografsko orientacijo, ki jo dobimo tako, da kremenovo ploščico iz kremenovega kristala izrežemo pod kotom  $35^\circ 15'$  glede na Y-os, kar je znano kot AT-rez. Prednost tega reza je, da je sprememba frekvence v odvisnosti od temperature v temperaturnem intervalu od 5 do 50 °C zanemarljiva. Naprava QCM-D meri maso adsorbirane hemice-luloze na modelnem PET-filmu na kremenovem kristalu. QCM-D kristal, priključen v sistemu, oscilira z osnovno resonančno frekvenco in njenimi nadtoni (večkratniki osnovne resonančne frekvence). Frekvenca kristala QCM pada z naraščajočo adsorbirano maso, z naraščajočo viskoznostjo in s hrapavostjo elektrod. Masa adsorbiranega polisaharida ( $\text{ng}/\text{cm}^2$ ) se zlahka izračuna iz spremembe resonančne frekvence s pomočjo Sauerbreyeve enačbe (1). Sauerbreyeva enačba je veljavna samo za trdne enakomerno adsorbirane in tanke adsorbirane plasti.

$$\Delta m = - \frac{C \times \Delta f}{n} \quad (1)$$

kjer je  $C$  masna konstanta ( $17,7 \text{ ng Hz}^{-1}\text{cm}^{-2}$  za 5 MHz kremenov kristal),  $n$  številka nadtona osnovne resonančne frekvence (1, 3, 5,

tion 1); where  $C$  is mass sensitivity constant ( $17.7 \text{ ng/cm}^2 \text{ Hz}$  for a 5 MHz quartz crystal),  $n$  is the overtone number (1, 3, 5, 7, 9, 11, 13),  $\Delta m$  is change in mass and  $\Delta f$  is frequency change.

It is also possible to estimate the layer thickness of the adhering layer if we know the density of the adsorbed layer.

### 3 Results and discussion

Figure 3 shows the QCM-D system (E4, QSense, Sweden) for the adsorption study of GGMs. The solution of GGM was pumped with a peristaltic pump (IPC, Ismatec, Swiss) over the model PET film surface at the flow rate 0.1 ml/min. Prior

7, 9, 11, 13),  $\Delta m$  je sprememba mase kristala in  $\Delta f$  je sprememba resonančne frekvence.

Prav tako je mogoče s pomočjo Sauerbreyeve enačbe izračunati debelino adsorbiranega sloja, če poznamo gostoto adsorbiranega sloja ali pa določimo približek gostote.

### 3 Rezultati in razprava

Na sliki 3 je prikazan sistem QCM-D (E4, QSense, Švedska), uporabljen pri študiju adsorpcije galaktoglukomananov. Raztopina galaktoglukomananov se je prečrpavala čez modelno PET-površino s peristaltično črpalko (IPC, Ismatec, Švica) pri hitrosti pretoka 0,1 ml/min. Pred adsorpcijo hemiceluloz je bila površina PET čiščena 20 min z milliQ vodo (Direct 8, Millipore, Francija) pri pretoku 0,25 ml/min.

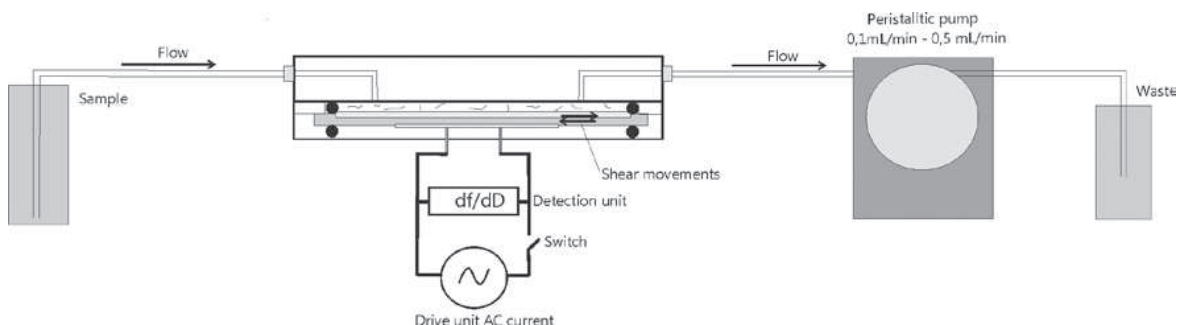


Figure 3: QCM-D system for adsorption studies

to the adsorption step, the surfaces were rinsed with milliQ water (Direct 8, Millipore, France) for 20 minutes at the flow rate 0.25 ml/min.

Figure 4 shows the frequency change in the case when GGM (50 mg/l) was adsorbed on the model PET film with and without the added electrolyte. The change in the frequency represents the mass adsorbed on the surface and it is obvious from the figure that the added salt increased adsorption of GGM on the PET surface. The frequency decreased by around 20 Hz after the water rinsing step, which means that this change represents an irreversible adsorption, since the mass cannot be washed away. When 0.1 M NaCl was in the GGM solution, the frequency decreased by approximately 40 Hz. From the timeline, the adsorption rate can be observed; the latter can be defined as slow, since the adsorption plateau was not reached even after 2 h. In the case of added salt, the adsorption was must faster.

Slika 4 prikazuje spremembo frekvence pri adsorpciji galaktoglukomananov (50 mg/l) na modelni PET-film ob dodani 0,1 M NaCl raztopini in brez dodanih elektrolitov. Sprememba frekvence pomeni adsorbirano maso na modelni PET-površini, na kremenovem kristalu. Resonančna frekvenca se spremeni za približno 20 Hz po spiranju, kar pomeni, da gre za ireverzibilno adsorpcijo, saj nadaljnje spiranje ne vpliva na spremembo frekvence. Pri 0,1 M NaCl, dodanega v raztopini galaktoglukomananov (50 mg/l), frekvenca pade za približno 40 Hz. Iz poteka krivulje spremembe

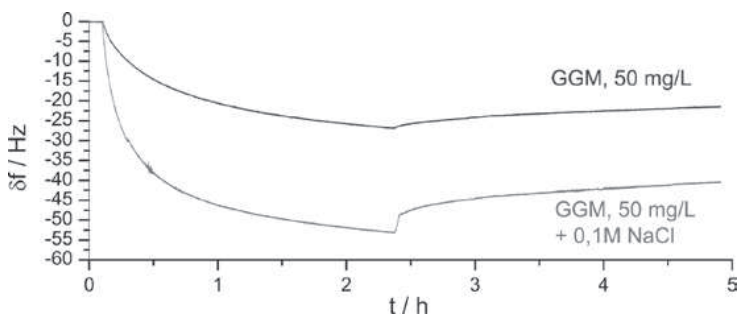


Figure 4: Frequency change during adsorption of GGM onto PET with and without salt



Figure 5 represents the dissipation change for the same experiment. The dissipation changes provide valuable information about the viscoelastic properties of the adsorbed layer. It can be seen that salt, which increases adsorption, also changes the viscoelastic properties of the adsorbed GGM. The layer became softer with more water incorporated in the adsorbed layer; however, after the rinsing step, the dissipation decreased by  $1 \cdot 10^{-6}$  in the case of added salt, which could not be observed when there was no electrolyte in the solution.

The diagram in Figure 6 shows adsorbed mass of GGM (100 mg/l) and GGMSO<sub>4</sub> (100 mg/l) on the PET surface without added salt, and with added NaCl and CaCl<sub>2</sub> (both 0.1 M). The mass was estimated from the frequency changes after adsorbing and after rinsing with milliQ water using software QTools (QSense, Sweden). From the diagram, it can be seen that the sulphated GGM (100 mg/l) does not adsorb on PET, which is a consequence of its negative charge. The uncharged GGM adsorbs quite well and almost 700 ng/cm<sup>2</sup> was adsorbed from 100 mg/l of the GGM solution. The added salt increased adsorption up to 900 ng/cm<sup>2</sup>. In the case of GGMSO<sub>4</sub> adsorption, the salt effect is much more pronounced, as with added NaCl, the adsorption increased to 200 ng/cm<sup>2</sup> and with added CaCl<sub>2</sub>, the adsorption increased to almost 600 ng/cm<sup>2</sup>. Figure 7 shows the connection between the adsorption of GGMs and charge.

GGM which is not charged adsorbs on PET and the negatively charged GGMSO<sub>4</sub> with the charge of almost 5 mmol/l does not adsorb on PET. It can be concluded that the adsorption between the negatively charged PET surface and negatively charged biopolymers increases with added salt due to the shielding of repulsive forces. The QCM-D is a convenient tool for the in situ adsorption studies and is easy to perform on various surfaces; however, the main drawback is that we are limited to model surfaces only.

#### 4 Conclusions

QCM-D is a useful tool for the characterisation of the formation of thin films (proteins,

resonance frequencies in dependence of time is a clear sign of adsorption, which is slower, as the plateau is not reached within two hours of adsorption. When salt is added, adsorption is faster and adsorbs a larger amount of material.

In Figure 5, the damping change is shown for the same experiment. From the change in damping during adsorption (when the system is excluded from the vibration and the damping is measured, i.e. the damping change) from adsorption, we can obtain information about the viscoelastic properties of the adsorbed layer of galactoglucomannan. We can see that the added salt changes the properties of the adsorbed galactoglucomannan. The layer becomes softer and contains more water, so the damping change is approximately  $1 \cdot 10^{-6}$  when galactoglucomannan is dissolved, where the added salt, but not the rinsing, changes the viscoelastic properties of the adsorbed layer.

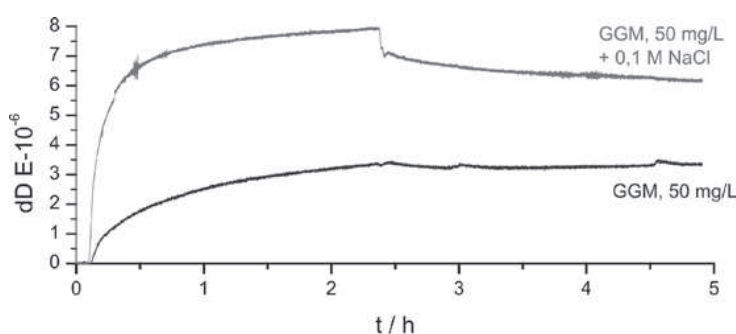


Figure 5: Dissipation change-during adsorption of GGM onto PET with and without salt

Diagram in Figure 6 shows the adsorbed mass of galactoglucomannan and sulphated galactoglucomannan at a concentration of 100 mg/l on the PET surface without added salt and with added 0.1 M NaCl or CaCl<sub>2</sub>. The mass was determined by adsorption and rinsing with milliQ water and using the QTools software (QSense, Sweden).

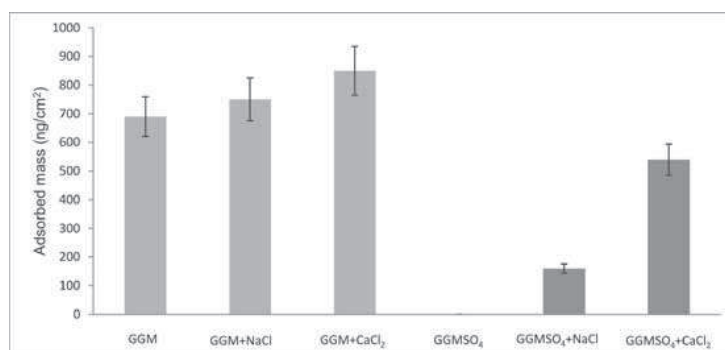


Figure 6: Adsorbed GGMs (ng/cm<sup>2</sup>) estimated with Sauerbrey equation

polymers, cells etc) on different surfaces and as such, it can be applied in the characterisation of the GGM adsorption on PET. The PET surface is more negatively charged; the species with a higher negative charge (GGMSO<sub>4</sub>) thus do not adsorb well on the PET surface, as the repulsion forces are high. On the other hand, GGM which is not charged adsorbs quite well on PET. This study demonstrates that in the presence of electrolytes, the adsorption of GGMs on the PET film increases, the effect being higher for more negatively charged GGMSO<sub>4</sub> in the case of a divalent cation.

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V diagramu vidimo, da se sulfatirani galaktoglukomanan (100 mg/l) ne adsorbira na PET zaradi njegovega negativnega naboja. Nenabiti galaktoglukomanan se kar dobro adsorbira na PET, saj ga je skoraj 700 ng na 1 cm<sup>2</sup> po adsorpciji iz vodne raztopine. Dodana sol dodatno zviša vsebnost galaktoglukomananov na površini PET na 900 ng/cm<sup>2</sup>. Pri adsorpciji sulfatiranih galaktoglukomananov je vpliv dodane soli veliko večji, saj se pri dodanem NaCl adsorpcija zviša na 200 ng/cm<sup>2</sup>, pri dodanem CaCl<sub>2</sub> pa se adsorpcija poviša na skoraj 600 ng/cm<sup>2</sup>. Slika 7 prikazuje povezavo med nabojem in adsorpcijo hemiceluloz.

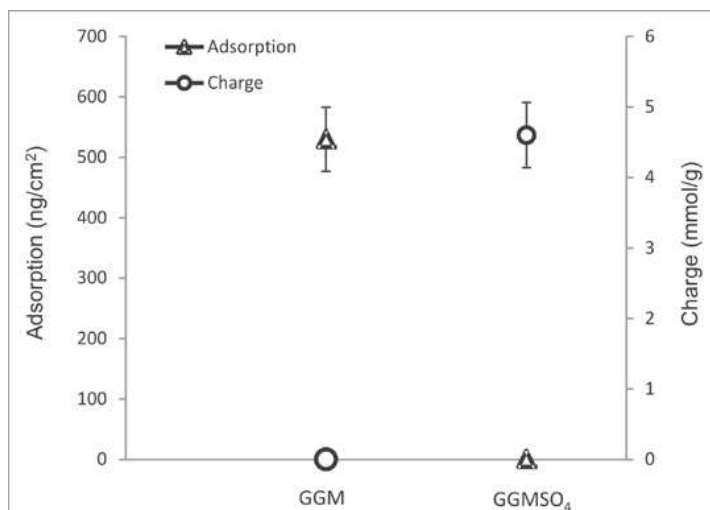


Figure 7: Charge and adsorbed amount of nonmodified and sulphated GGMs

Nenabiti galaktoglukomanan se adsorbira na PET, negativno nabiti sulfatirani galaktoglukomanan z negativnim nabojem skoraj 5 mmol/l pa se ne adsorbira na PET. Torej velja naslednja povezava: velik negativni naboj pomeni zelo majhno ali nično adsorpcijo in nasprotno se adsorpcija poveča z nižanjem negativnega naboja. Iz tega sledi sklep, da z dodatkom soli zvišamo stopnjo adsorpcije negativno nabitih biopolimerov na negativno nabito površino PET. To se zgodi, ker kationi soli omilijo odbojne sile med negativnim nabojem biopolimera v raztopini in med površino PET. QCM-D je uporabno orodje za spremljanje *in situ* adsorpcijskih procesov, zlahka se aplicira na različne površine, glavna pomanjkljivost metode pa je, da smo omejeni samo na uporabo modelnih površin.

## 4 Sklepi

QCM-D je uporabno orodje za karakterizacijo adsorbiranih tankih filmov (proteinov, polimerov, celic ...) na različnih površinah in je tako primerno orodje tudi za spremljanje adsorpcije galaktoglukomananov na modelno površino PET. Za PET-površine ve-

lja, da so negativno nabite, zatorej se negativno nabiti biopolimeri (npr. GGMSO<sub>4</sub>) težje ali pa sploh ne adsorbirajo na površine PET, ker so odbojne sile prevelike. Nenabiti galaktoglukomanan se v nasprotju s sulfatiranim galaktoglukomananom dokaj dobro adsorbira na PET. Ta prispevek dokazuje, da se v prisotnosti dodanih soli raztopinam biopolimerov, pridobljenih iz procesnih vod pri proizvodnji termomehanične pulpe iz smrekovega lesa, adsorpcija na PET zvišuje. To je še bolj izrazito pri uporabi dvovalentnih soli za bolj negativno nabite biopolimere, kot je sulfatirani galaktoglukomanan.

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## 5 Viri

1. XU, C. *Physicochemical properties of spruce water-soluble galactoglucomanan*. Thesis., 2008.
2. SUNDBERG, A., HOLMBOM, B., WILLFÖR, S. and PRANOVICH, A. Weakening of paper strength by wood resin. *Nordic Pulp & Paper Research Journal*, 2000, vol. 15, no. 1, p. 46–53.
3. SJÖSTRÖM, E. *Wood Chemistry Fundamentals and Applications*. Academic Press, Inc., 1993.
4. WILLFÖR, S., SUNDBERG, K., TENKANEN, M. and HOLMBOM, B. Spruce-derived mannans – A potential raw material for hydrocolloids and novel advanced natural materials. *Carbohydrate Polymers*, 2008, vol. 72, no. 2, p. 197–210.
5. MIKKONEN, K. S., HEIKKILA, M. I., HELEN, H., HYVONEN, L. and TENKANEN, M. Spruce galactoglucomanan films show promising barrier properties. *Carbohydrate Polymers*, 2010, vol. 79, no. 4, p. 1107–1112.
6. EBRINGEROVA, A., HROMADKOVA, Z., HRIBRLOVA, V., XU, C. L., HOLMBOM, B., SUNDBERG, A. and WILLFÖR, S. Norway spruce galactoglucomannans exhibiting immunomodulating and radical-scavenging activities. *International Journal of Biological Macromolecules*, 2008, vol. 42, no. 1, p. 1–5.
7. DOLIŠKA, A., WILLFÖR, S., STRNAD, S., RIBITSCH, V., STANA-KLEINSCHEK, K., EKLUND, P. and XU, C. Antithrombotic properties of sulfated wood-derived galactoglucomannans *Holzforchung*, 2011, Article in press, DOI:10.1515/HOLZ.2011.0016.R2
8. INDEST, T., LAINE, J., RIBITSCH, V., JOHANSSON, L. S., STANA-KLEINSCHEK, K. and STRNAD, S. Adsorption of chitosan on PET films monitored by quartz crystal microbalance. *Biomacromolecules*, 2008, vol. 9, no. 8, p. 2207–2214.



9. INDEST, T., LAINE, J., JOHANSSON, L. S., STANA-KLEINSCHEK, K., STRNAD, S., DWORCZAK, R. and RIBITSCH, V. Adsorption of fucoidan and chitosan sulfate on chitosan modified PET films monitored by QCM-D. *Biomacromolecules*, 2009, vol. 10, no. 3, p. 630–637.
10. INDEST, T., LAINE, J., STANA-KLEINSCHEK, K. and ZEMLJIC, L. F. Adsorption of human serum albumin (HSA) on modified PET films monitored by QCM-D, XPS and AFM. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2010, vol. 360, no. 1-3, p. 210–219.
11. GERICKE, M., DOLIŠKA, A., STANA, J., LIEBERT, T., HEINZE, T. and STANA-KLEINSCHEK, K. Semi-Synthetic Polysaccharide Sulfates as Anticoagulant Coatings for PET, 1 – Cellulose Sulfate. *Macromolecular Bioscience*, 2011, vol., no. p. n/a-n/a.
12. TANAKA, H. and SAKAMOTO, Y. Polyelectrolyte titration using fluorescent indicator. I. Direct titration of anionic and cationic polyelectrolytes with 10<sup>-4</sup>N standard solutions. *Journal of Polymer Science Part A: Polymer Chemistry*, 1993, vol. 31, no. 11, p. 2687–2691.
13. WILLFÖR, S., REHN, P., SUNDBERG, A., SUNDBERG, K., HOLMBOM, B. Recovery of water-soluble acetylgalactoglucmannans from mechanical pulp of spruce. *Tappi Journal*, 2003, vol. 2, no. 11.
14. DOLIŠKA, A., VESEL, A., KOLAR, M., STANA-KLEINSCHEK, K. and MOZETIČ, M. Interaction between model poly(ethylene terephthalate) thin films and weakly ionised oxygen plasma. *Surface and Interface Analysis*, 2011, vol., no. p. n/a-n/a.
15. TANAKA, H. and SAKAMOTO, Y. Polyelectrolyte titration using fluorescent indicator. II. Analysis of cationic starches and flocculants. *Journal of Polymer Science Part A: Polymer Chemistry*, 1993, vol. 31, no. 11, p. 2693–2696.
16. FRAS, L., STANA-KLEINSCHEK, K., RIBITSCH, V., SFILIGOJ-SMOLE, M. and KREŽE, T. Quantitative determination of carboxyl groups in cellulose by complexometric titration. *Lenzinger Berichte*, 2002, vol. 81, no. p. 80–88.
17. SFILIGOJ-SMOLE, M., STANA-KLEINSCHEK, K., RIBITSCH, V., POINTNER, B., ZIPPER, P., STAKNE, K. and BELE, M. Electrokinetic properties of surface modified PETP fibres. *Materials Research Innovations*, 2002, vol. 6, no. 1, p. 19–23.