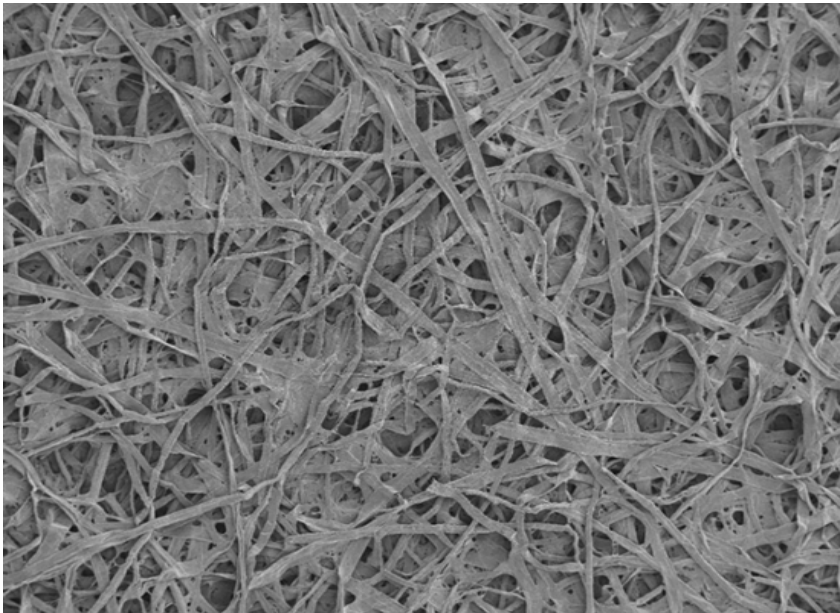


Improvement of wet and dry web properties in papermaking by controlling water and fiber quality

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*”He finns två sätt ti ta sej opp i gräntoppn. Eindera så
klätrar man elder så säter man sej på ein kott o vänt!”
-Åboländskt ordspråk-*

*(There are two ways to reach the top of the spruce;
either to climb or to sit on a cone and wait)*

Preface

Most of the research work was carried out at the Laboratory of Wood and Paper Chemistry during the years 2007-2013. Funding was received from a variety of sources and the main part of the work was carried out in the projects FunPaC (funded by Finnish Funding Agency of Technology and Innovations TEKES, Kemira Oyj, Ciba Specialty Chemicals Oy, UPM-Kymmene Oyj, M-Real Oyj and Metso Paper Oy) and ChemRun (funded by TEKES, Kemira Oyj, UPM-Kymmene Oyj, Stora Enso Oyj and Metso Paper Oy). Financial support was also received from The International Doctoral Programme in Bioproducts Technology PaPSaT, which I had the privilege to be part of during my doctoral studies. Additional funding from the Process Chemistry Centre (PCC) at Åbo Akademi University, Swedish Cultural Foundation in Finland, Paper Engineers' Association, the Walter Ahlström Foundation and the Rector of Åbo Akademi University is gratefully acknowledged.

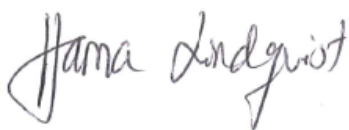
The little girl from Nagu finally made it to the finish line. This work has been a true example of what good collaboration can bring about; without all the help from supervisor, co-workers, collaborators, experts, financiers as well as friends and family I can honestly say that this thesis would not exist. I am grateful to my supervisor, Docent Anna Sundberg. You were the one who brought me into the strange world of wet end chemistry, and the one kicking my butt to get results published. Thank You for your encouragement and patience! Prof. Stefan Willför, thank you for your support and for keeping me on the pay roll and finding other useful tasks for me to take care of, I know now that I am a pretty good organizer too.

I am deeply indebted to Dr. Kristian Salminen, Dr. Elias Retulainen and Mr. Janne Kataja-aho at VTT. Especially you, Kristian, have helped me far beyond the "normal" boundaries between collaborators, and we have had very deep discussions about wet web mechanical properties and paper physics as well as the ins and outs of research, doing a PhD and life in general. In the ChemRun-project, we certainly enjoyed ourselves while trying to carry out all wild ideas, which mostly turned out great. We have two Jasper Mardon Memorial Awards to remind us of how excellent collaboration can be conducted with a smile on our faces.

A big thank you goes to all present and former co-workers at 3PK, especially Affi, Anders, Janne, Jens, Chunlin and Sylwia as well as my officemates Tao and Katja. Having a good laugh can make such a difference if a day turns out good or bad. We have always helped each other when help has been needed, which is so important for keeping up a good working atmosphere. Thank you also Dr. Risto Korpinen, for all the valuable help, nice lunch breaks and for being a dear friend. LOK and TPK, I have invaded your coffee room one morning per week and had the opportunity to sit and chat with former colleagues and present friends. That cup of coffee has always kickstarted my day in a great way, thank you for keeping me company! Dr. Ari Rosling and Dr. Markku Auer, I entered the world of research under your supervision, thank you for getting me started. Ms. Agneta Hermansson, Ms. Anita Forss, Mrs. Päivi Pennanen, Ms. Anna Boedeker, Mr. Johan Isaksson and Mr. Joakim Lind, you have all helped me and contributed to the work in many ways, thank you! All co-authors are also thanked for valuable help. My reviewers Prof. Martin Hubbe and Prof. Tapani Vuorinen, thank you for taking the time to dig deeper into my work. Your valuable comments have certainly improved my thesis.

Lastly, I need to thank the people that are the closest to me. My family; my parents Yngve and Päivi, brother Niklas and niece Camilla, I hope you finally see where all the years have been spent. Äiti ja pappa, kiitos och tack! Peter, thank you for your support and understanding, let us now enjoy it together!

Pargas, September 2013

A handwritten signature in cursive script that reads "Hanna Lindqvist". The ink is dark and the handwriting is fluid and personal.

Hanna Lindqvist

Abstract

Today's need for faster and more efficient processes in papermaking also give rise to greater demands on the mechanical properties of the paper web. Web breaks occur not only due to a low tensile strength of the wet paper web; the reason can also be an insufficient web tension. Most problems with the runnability of the paper machine occur during the wet pressing and/or in the beginning of dryer section when the dry content of the paper is in the range 30-70%. Web tension is created by a speed difference in the web transfer between the press and dryer section. The web tension is not constant after the straining in the open draw, but drops 20-60% due to relaxation. Most of this relaxation occurs during the first 0.5 s after straining.

In this work, the effects of different parameters on dewatering, wet web strength and relaxation, as well as on the mechanical and surface properties of the final product were investigated. A long term aim is to improve the runnability of the paper machine and paper quality by controlling and understanding the properties of the process water, wood fiber, and fiber network.

By using a non-ionic surfactant at concentrations below the critical micelle concentration (cmc), the dewatering was more efficient thereby increasing the dry content after dewatering and wet pressing and thus increasing the tensile strength of wet paper sheets. For dry papers, the density and the tensile strength increased. At concentrations above cmc, the mechanical properties for both the wet and the dry sheets deteriorated, one reason could be that the surfactant hindered the formation of hydrogen bonding. A lower pH during papermaking, resulted in a lower dry content, which might be due to swelling of fibers. By using Na^+ instead of Ca^{2+} , the wet tensile strength decreased, perhaps because the coefficient of friction was decreased allowing the fibers to slide over each other.

The properties of the fibers were changed by using either gentle or harsh refining. The effect of fines was studied by adding fines to the original pulp or by removing the fines from refined pulp. The gently refined pulp generated fines without a decrease in the fiber length. The fibers were more stretched out and flexible after refining, which resulted in increased wet

tensile strength and residual tension. The fines of fibril-type promoted the formation of fiber-fiber bonds and increased the bonded area. The fines were important for the wet tensile strength while the fiber properties, i.e. the internal/external fibrillation, were critical for the residual tension. Harsh refining resulted in shortening of the fiber length. The formed wet web composed of damaged fibers contained more water, which resulted in a decreased dry content after wet pressing. When the non-ionic surfactant was used together with the harshly refined pulp, addition of surfactant gave a shorter dewatering time. When the surfactant was added together with fines to original pulp, the wet tensile strength decreased slightly. The most likely reason was adsorption of the surfactant to the surfaces of the fines and fibers which resulted in the particles and fibers sliding over each other more easily.

Native galactoglucomannans (GGMs) were cationized (C-GGM), carboxymethylated (CM-GGM), and iminated (A-GGM). Native GGMs dispersed the fibrils on the fiber surface when added to the pulp. These more outstretched fibrils were able to interact with fibrils on other fibers, thereby increasing the wet tensile strength and the elastic modulus. C-GGM acted most likely through an electrostatic mechanism, where the cationic chain was adsorbed to negatively charged surfaces. CM-GGM was assumed to form an ionic bond to metal ions, i.e. magnesium and calcium, present in wood. A-GGM acted probably through the hydrophobic hydrocarbon chain attached to the reducing end of the polysaccharide. The tail was oriented towards hydrophobic particles; the paper containing A-GGM had the most hydrophilic surface.

When native GGM, C-GGM and A-GGM were sprayed on freshly formed papers and the surface was analyzed, characteristic signals were found for each of the derivatives using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). C-GGM penetrated through the paper, as signals were also detected on the unsprayed side of the paper. A-GGM formed a film on top of the fibers, and by using Fourier Transform Infrared Spectroscopy (FTIR) it was concluded that the hydrophobic tail was oriented close to the paper surface but not at the outmost surface.

The results obtained in this thesis form a valuable knowledge base, which can be used for controlling runnability of the paper machine and the paper

quality. By using a readily available hemicelluloses and modifying them using simple methods, additives with different properties and effects on papermaking can be obtained.

Keywords: papermaking, initial wet web strength, dewatering, non-ionic surfactant, refining, spruce galactoglucomannans

Svensk sammanfattning

Dagens behov av snabbare och effektivare processer vid papperstillverkning ställer allt större krav på pappersbanans mekaniska egenskaper. Avbrott i produktionen sker inte enbart på grund av låg styrka utan orsaken kan även vara en för låg spänning i pappersbanan. De flesta problemen med körbarheten sker vid våtpressen och/eller i början av torkpartiet då papprets torrhalt är ca 30-70 %. Spänningen i pappersbanan uppkommer genom en hastighetsskillnad då pappersbanan flyttas från presspartiet till torkpartiet. Spänningen hålls inte konstant efter töjningen, utan den sjunker med 20-60 % på grund av papprets relaxering, som till största delen sker inom 0,5 s efter töjningen.

I detta arbete undersöktes hur olika faktorer inverkar på avvattning, initial våtstyrka och relaxering av fibernätverket samt också på slutproduktens mekaniska egenskaper och ytegenskaper. Ett framtida mål var att förbättra körbarheten hos pappersmaskinen och papperskvaliteten genom att förstå och kunna reglera processvattnets, vedfibers och fibernätverkets egenskaper.

I första delen av arbetet varierades processvattnets egenskaper, såsom pH, konduktivitet och ytspänning. Ytspänningen varierades genom tillsatts av ett nonjoniskt ytaktivt ämne, en s.k. surfaktant. Resultaten visade, att den kritiska micellkoncentrationen (cmc) var avgörande för papprets mekaniska egenskaper. Vid doseringar upp till cmc av surfaktanten, ökade torrhalten efter arkformingen samt våtpressningen och därigenom den initiala våtstyrkan samt restspänningen efter 2 % töjning. Avvattningen försnabbades också. För de torra arken erhöles en ökad densitet samt ökad dragstyrka. Surfaktantens primära effekt var effektiviserad avvattning, som ledde till torrare ark och därigenom ökat antal fiber-fiber bindningar och starkare papper. Vid doseringar över cmc försämrades de mekaniska egenskaperna märkbart, både för våta och torra ark. Detta berodde till största delen på surfaktantens benägenhet att förhindra uppkomsten av vätebindningar mellan fibrerna. När pH justerades till 5 istället för 6-6,5, minskade torrhalten vid våtpressning och därigenom också styrkeegenskaperna för våta ark. Densiteten minskade för torra ark; fibrerna svällde mer vid högre pH, vilket ledde till ett större antal fiber-fiber

bindningar. Då natriumjoner användes istället för kalciumjoner, sjönk den initiala våtstyrkan vid konstant torrhalt, troligtvis på grund av lägre friktionskoefficient vilket gjorde att fibrerna lättare gled över varann.

Fiberegenskaperna varierades också. Fibern maldes antingen genom en mild eller genom en hård process. Effekten av finmaterial undersöktes också genom att tillsätta finmaterial till den ursprungliga massan eller genom att avlägsna finmaterialet från den malda massan.

Den milda behandlingen ledde till bildning av finmaterial utan nämnvärd minskning av fiberlängden. Finmaterialet kunde antas bestå mer av fibrillfragment än sönderlitna fibrer. Malningen ledde till ökad initial våtstyrka och restspänning, vilket berodde på att fibrerna blev utträtade och flexiblare av den milda behandlingen. Finmaterialet av fibrilltyp främjade dessutom bildningen av fiber-fiber bindningar, vilket också visade sig genom starkt ökad initial våtstyrka då finmaterial tillsattes till den ursprungliga massan. Finmaterialets benägenhet att öka den bundna arean mellan ytor sågs även genom en ökad densitet och dragstyrka för torra pappersark. En negativ effekt av högre finmaterialshalt var en längre avvattningstid och lägre torrhalt efter våtpressningen. Då finmaterialet avlägsnades ur mälden, sjönk avvattningstiden till en nivå nära den ursprungliga massans. Detta antyder att den interna eller externa fibrilleringen av fibern inte nämnvärt påverkade avvattningen. Restspänningen efter 2 % töjning sjönk inte lika mycket som initiala våtstyrkan då finmaterialet avlägsnades; fiberegenskaperna, dvs. den interna och externa fibrilleringen, visade sig alltså vara viktiga för restspänningen.

Vid den hårda malningen minskade fiberlängden i takt med att malningen framskred. De kortare fibrerna ledde till en något lägre initial våtstyrka än för den mildt behandlade massan. De skadade fibrerna tog även upp mera vatten och torrhalten efter våtpressningen var mycket lägre. Densiteten ökade kraftigt för de torra pappersarken på grund av de korta fibrerna och den höga andelen finmaterial. Då den nonjoniska surfaktanten användes tillsammans med den hårt malda massan, försnabbades avvattningstiden något och torrhalten efter våtpressningen blev aningen högre. Då finmaterial tillsattes tillsammans med surfaktanten till ursprunglig massa, minskade den initiala våtstyrkan något. Orsaken kan vara en adsorption av surfaktanten till fiber- och finmaterialytorna med minskad friktion som

följd. I detta arbete optimerades doseringen av surfaktanten till den malda massan dock inte.

I den sista delen av detta arbete användes en hemicellulosa, som finns i stora mängder i gran, som tillsatsmedel. Förutom nativa galaktoglukomannaner (GGM), tillverkades också en katjoniserad (C-GGM), en karboximetylerad (CM-GGM) samt en iminerad, amfifil GGM (A-GGM). A-GGM hade en kolvätekedja bunden till den reducerande ändan av hemicellulosan. Vid tillsats av nativ GGM till massan, ökade den initiala våtstyrkan och elasticitetsmodulen. GGM dispergerade fibrillerna på fiberytorerna och ökade därigenom växelverkingarna mellan fibrerna. Torrstyrkan ökade också, samt retentionen av lösta och kolloidala substanser samt finmaterial. C-GGM verkade genom en elektrostatisk mekanism; den katjoniska kedjan adsorberades till negativt laddade ytor. CM-GGM antogs verka genom jonbindning till metalljoner, som finns i veden. A-GGM antogs verka genom den hydrofoba kolvätekedjan, som orienterade sig till hydrofoba ytor. Pappret som innehöll A-GGM var mest hydrofilt och kedjeändan antogs vara orienterad mot kärnan av pappret.

GGM och derivaten sprayades på nybildade pappersytor och de torra pappren analyserades med hjälp av olika ytanalysmetoder. Med flygtidsseparerande sekundärjonmasspektrometri (eng. Time-of-Flight Secondary Ion Mass Spectrometry, ToF-SIMS) detekterades karaktäristiska signaler för GGM, C-GGM och A-GGM. C-GGM trängde igenom pappersarket och signaler erhöles då även på den obesprutade sidan av arket. A-GGM däremot bildade en film ovanpå fibrerna, och med hjälp av fouriertransformerad infrarödspektroskopi (eng. Fourier Transform Infrared Spectroscopy, FTIR) fastslogs att de hydrofoba kolvätekedjorna låg nära pappersytan, men inte i det yttersta ytskiktet. GGM-delen av A-GGM bildade filmen ovanpå fibrerna.

Resultaten, som erhöles i denna avhandling, bildar en värdefull kunskapsbas, som kan användas för kontroll och reglering av pappersmaskinens körbarhet och papperskvalitet. Genom att använda en lättillgänglig hemicellulosa och modifiera den med enkla metoder, erhöles tillsatsmedel med mycket olika egenskaper och effekter för papperstillverkning.

Suomenkielinen yhteenveto

Paperikoneiden tuotantotehokkuuden vaatimukset kasvavat jatkuvasti kiristyvän kilpailun takia, jolloin myös paperirainan mekaanisilta ominaisuuksilta vaaditaan enemmän. Rainan katkokset alentavat tuotantotehokkuutta, katkoksten syinä voi olla alhaisen vetolujuuden lisäksi rainan liian alhainen jännitys. Suurimmat ongelmat paperikoneen ajettavuuden kannalta tapahtuvat märkäpuristimen ja/tai kuivatusosan alussa rainan kuiva-ainepitoisuuden ollessa noin 30–70 %. Paperirainan siirtyessä puristimelta kuivatusosaan syntyy nopeuserosta johtuvasta vedosta jännitys. Jännitys ei pysy tasaisena venytyksen jälkeen, vaan se pienenee 20–60 % paperin relaksoitumisen myötä. Relaksaatioissa paperin jännitys pienenee venymän pysyessä vakiona. Tämä tapahtuu noin puolen sekunnin sisällä venytyksen jälkeen.

Tässä työssä tutkittiin, miten erilaiset tekijät vaikuttavat rainan vedenpoistoon, märkälujuuteen ja relaksaatioon. Lisäksi tutkittiin erilaisten tekijöiden vaikutuksia lopputuotteen mekaanisiin ominaisuuksiin ja pintaominaisuuksiin. Yksi työn päätavoitteista oli ymmärtää, miten prosessiveden, käytetyn puukuidun ja kuituverkoston ominaisuudet ja niiden muokkaaminen vaikuttavat paperikoneen ajettavuuden ja paperin laadun parantumiseen.

Työn ensimmäisessä osassa selvitettiin prosessiveden ominaisuuksien, kuten pH:n, johtokyvyn ja pintajännityksen vaikutuksia paperin ominaisuuksiin. Pintajännitystä muutettiin lisäämällä massan joukkoon ionitonta pinta-aktiivista ainetta, ts. surfaktanttia. Tulosten perusteella voitiin todeta, että kriittinen misellikonsentraatio (cmc) vaikutti ratkaisevasti paperin mekaanisiin ominaisuuksiin. Kun surfaktanttia lisättiin korkeintaan cmc:n verran, paperiarkkien kuiva-ainepitoisuus märkäpuristuksen jälkeen nousi ja sen myötä sekä märkälujuus että jäännöskireys 2 % venymässä kasvoivat. Suotautumisen aikana tapahtuva vedenpoisto nopeutui ja vastamuodostuneen arkin kuiva-ainepitoisuus kasvoi. Myös kuivatettujen arkkien tiheys ja vetolujuus kasvoivat. Surfaktantin ensisijainen vaikutus ilmeni tehokkaampana vedenpoistona suotautumisen ja märkäpuristuksen aikana, mikä nosti kuiva-ainepitoisuutta ja sen myötä kuitu-kuitusidosten määrää ja paperin lujuutta.

Kun surfaktantin annostus oli korkeampi kuin cmc, sekä märkien että kuivattujen arkkien lujuusominaisuudet heikentyivät huomattavasti. Syynä oli surfaktantin taipumus estää mahdollisten vetysidosten muodostuminen kuitujen välillä. Kun prosessiveden pH-arvo laskettiin viiteen, märkäpuristuksen jälkeinen kuiva-ainepitoisuus laski ja sen myötä märkien papereiden lujuusominaisuudet pienentyivät. Lisäksi kuivattujen arkkien tiheys pieneni kuitujen ollessa vähemmän turvonneita, mikä johti kuitukuitusidosten määrän laskuun. Myös paperin märkäljuuus vakiokuiva-ainepitoisuudessa laski, kun johtokyvyn säätämiseen käytettiin Na-ioneja Ca-ionien sijaan. Suurin syy oli alentunut kitkakerroin, jolloin kuidut liukuivat enemmän toistensa yli.

Jauhatuksella tutkittiin kuitujen ominaisuuksien muokkaamisen vaikutusta paperin ominaisuuksiin. Kuidut jauhettiin joko matalaa tai korkeaa jauhatusintensiiteettiä käyttäen. Lisäksi tutkittiin, miten hienoaine vaikuttaa paperin ominaisuuksiin joko lisäämällä hienoainetta alkuperäisen massan joukkoon tai poistamalla hienoaine jauhetusta massasta.

Matalaintensiiteettinen jauhatus nosti hienoaineksen osuutta ilman havaittavaa kuidun pituuden lyhentymistä. Hienoaineksen oletettiin koostuvan lähinnä kuidun seinämästä irtoavista fibrilleistä. Jauhatus nosti märkäljuutta ja jäännöskireyttä, mikä johtui kuitujen suoristumisesta ja niiden muuttumisesta joustavammaksi. Kun hienoaines lisättiin alkuperäiseen massaan, fibrillimäinen hienoaines edisti myös kuitukuitusidosten muodostumista, mikä havaittiin korkeampana märkäljuutena. Hienoaineksen taipumus nostaa sidotun pinta-alan määrää, näkyi kuivattujen arkkien korkeampana tiheytenä ja vetoljuutena. Hienoaineksen lisäyksen haittapuolena oli pidempi vedenpoisto-aika suotautumisen aikana ja alhaisempi kuiva-ainepitoisuus märkäpuristuksen jälkeen. Kun hienoaines poistettiin jauhetusta massasta, vedenpoisto-aika lyheni lähes samalle tasolle alkuperäisen massan kanssa. Tämä viittaa siihen, että kuidun fibrillointi ei merkittävästi vaikuttanut vedenpoistoon. Paperin jäännöskireys ei kuitenkaan laskenut yhtä paljon kuin märkäljuuus, kun hienoaines poistettiin. Tämä viittaa taas siihen, että kuitujen fibrilloinnilla on tärkeä merkitys paperin jäännöskireyteen.

Korkeaintensiiteettinen jauhatus johti kuidunpituuden lyhenemiseen jauhatuksen edistyessä. Lisäksi märkäljuuus pieneni enemmän

kuidunpituuden pienentyessä verrattuna matalaintensiteettiseen jauhatusmenetelmään. Kuituihin imeytyi myös enemmän vettä, jolloin kuiva-ainepitoisuus puristuksen jälkeen oli alhaisempi. Paperin tiheys nousi huomattavasti lyhyempien kuitujen ja lisääntyneen hienoaineksen takia. Kun surfaktanttia käytettiin yhdessä jauhetun massan kanssa, vedenpoisto suotautumisen aikana nopeutui ja kuiva-ainepitoisuus nousi hieman, lähinnä sileämmän kuidun pinnan takia. Kun hienoainesta ja surfaktanttia lisättiin alkuperäiseen massaan, sen märkälujuus laski jonkin verran. Syynä voi olla surfaktantin adsorptio kuitujen ja hienoaineksen pinnalle, jolloin surfaktantti vähensi kuitujen ja hienoaineksen välistä kitkaa. Tässä työssä tosin ei optimoitu surfaktantin annostusta jauhettuun massaan.

Työn viimeisessä osassa käytettiin lisäaineena paperinvalmistuksessa kuusesta saatavaa hemiselluloosaa, galaktoglukomannaania (GGM). Natiivin GGM:n lisäksi valmistettiin kationisoitu (C-GGM), karboksimeetyloitu (CM-GGM) sekä iminoitu amfifilinen GGM (A-GGM). A-GGM:ssa hiilivetyketju on sidottuna hemiselluloosan pelkistävään päähän. Kun natiivia GGM:ia lisättiin massaan, siitä valmistetun paperin märkälujuus ja kimmokerroin kasvoivat. GGM dispergoi eli levitti kuidun pinnassa olevia fibrillejä, jolloin kuitujen väliset vuorovaikutukset lisääntyivät. Lisäksi vetolujuus sekä hienoaineksen ja liuenneiden sekä kolloidaalisten aineiden retentio kasvoivat. C-GGM oletettiin vaikuttavan paperin ominaisuuksiin elektrostaattisen vuorovaikutuksen välityksellä, jossa kationinen ketju adsorboitui negatiivisesti varautuneille kuitujen ja hienoaineksen pinnoille. CM-GGM:n oletettiin muodostavan ionisidoksia kuitumateriaalissa olevien metalli-ionien kanssa. A-GGM päätettiin vaikuttavan paperin ominaisuuksiin hydrofobisen funktionaalisen ryhmän kautta, jolloin GGM:iin liitetty hiilivetyketju suuntautui hydrofobisia kuitujen ja hienoaineksen pintoja kohti. A-GGM sisältävä paperi oli kaikkein hydrofiilisin ja hiilivetyketjun oletettiin olevan suuntautunut kohti paperin ydintä.

GGM, C-GGM ja A-GGM suihkutettiin vastamuodostuneille arkeille ja kuivatut arkit analysoitiin eri pintakemiallisia analyysimenetelmiä käyttäen. Lentoaikaerotteisella sekundääri-ioni massaspektrometrilla (eng. Time-of-Flight Secondary Ion Mass Spectrometry, ToF-SIMS) tunnistettiin ominaiset piikit jokaiselle johdannaiselle. C-GGM tunkeutui paperin läpi, koska C-GGM:lle ominaisia piikkejä löydettiin myös paperin

suihkuttamattomalta puolelta. A-GGM muodosti kalvon kuitujen päälle ja Fourier-muunnos infrapunaspektroskopiolla (eng. Fourier Transform Infrared Spectrometry, FTIR) voitiin todeta, että hydrofobiset hiilivetyketjut sijaitsivat paperin pinnan läheisyydessä, mutta ei ihan uloimmassa kerroksessa. Polysakkaridiketju muodosti puolestaan kalvon kuitujen päälle.

Tässä työssä saadut tulokset muodostavat tärkeän tietoperustan, jota voidaan käyttää paperikoneen ajettavuuden ja paperilaadun hallintaan ja säätämiseen. Käyttämällä helposti saatavilla olevaa hemiselluloosaa ja muokkaamalla sitä yksinkertaisia menetelmiä käyttäen, saadaan paperinvalmistukseen lisäaineita, joilla voidaan räätälöidä valmistetun paperin ominaisuuksia.

List of important abbreviations and symbols

A-GGM	Iminated amphiphilic galactoglucomannans
C-GGM	Cationized galactoglucomannans
cmc	Critical micelle concentration
CM-GGM	Carboxymethylated galactoglucomannans
CS	Cationic starch
d.c.	Dry content
DDJ	Dynamic Drainage Jar
DDÅA	Dynamic Drainage Analyzer of Åbo Akademi
DS	Degree of substitution
ECF	Elemental Chlorine Free
FE-SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GGM	Galactoglucomannans
LC	Low consistency
PB TMP	Peroxide-bleached thermomechanical pulp
M_w	Average molar mass
PA	Polyamide
SD	Standard deviation
SR	Shopper-Riegler
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
VRW	Water retention value
θ_0	Contact angle at 0 s
θ	Contact angle at a given time

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1. Introduction

Paper as it is known today, is a material with a long history. Paper made by a similar principle as is used in the modern world dates back to around 70-50 B.C. to China (Lindberg 2008). The first paper machine was patented in 1799 in France and consisted of a moving belt of wire cloth onto which a fiber suspension was poured and allowed to drain. The result was a continuous paper sheet. The process was improved by the Fourdrinier brothers in 1801 and by the 1820's, paper made by machines had overtaken the market. Since those days, the process has become more sophisticated and the production speeds have increased from 1000-1200 m/min in the 1980's to around 2000 m/min in the 2010's (Karlsson and Paltakari 2010). The trim width of the paper machines used today varies between 7.6 and 10.6 m depending on the type of paper produced (Sundholm 2008).

The increased speed of paper machines also leads to problems with the runnability of the wet paper web. The meaning of good runnability is that each subprocess in the papermaking process runs smoothly without breaks in the running paper web (Fig. 1.1) (Kurki 2005). Even a slight disturbance in one subprocess can decrease the overall efficiency of the paper machine.

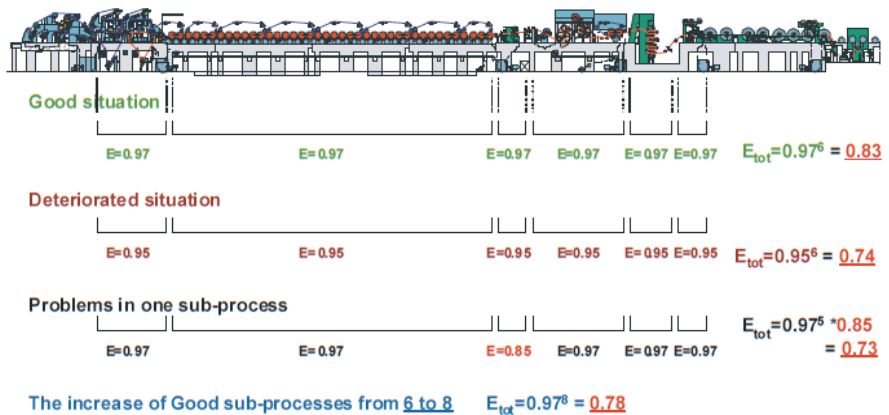


Fig. 1.1. Example of the impact of the efficiency of subprocesses on total efficiency of the process (Kurki 2005).

The paper industry faces many challenges with demands coming from governments, the market and the end-users. Efforts are made continuously

to decrease pollution, increase the productivity, lower the costs, and improve the quality of the product. Energy costs, which include heat and electricity, account for 25% of the manufacturing costs (Karlsson and Paltakari 2010). A major process requiring a large part of the energy is the water removal, which is divided between the wire, press, and drying sections (McGregor and Knight 1996). The costs for removal of one unit of water from the sheet are divided in the ratios 1:5:220 between the wire, press and drying sections. While most of the water is removed in the forming section, the industry has strived to maximize the water removal at the press section. From a research point of view, the equation of smoothly running operations with possible energy savings opens up possibilities of improving existing papermaking processes and process parameters.

1.1 Objective of the work

The aim of this work was determine the effects on dewatering, wet strength and stress relaxation as well as of the properties of the dry paper by altering the process waters and pulp used. The long term goal is to improve the runnability of the paper machine and the quality of the paper. The properties of the water were changed by altering the pH and conductivity, and surface tension by adding a non-ionic surfactant. Fiber properties were changed by using gentle and harsh refining. Readily available hemicelluloses, spruce galactoglucomannans, were modified using simple methods in order to create additives for papermaking with varying effects on both the mechanical properties, as well as the surface properties of the paper. The obtained results form a valuable knowledge-base for improvement of existing papermaking processes and paper properties.

1.2 List of publications and contribution of the author

This thesis is a summary of the following original publications:

- I. Lindqvist, H., Salminen, K., Kataja-aho, J., Sundberg, A., Holmbom, B. and Retulainen, E. (2009). Effects of electrolytes, pH and surface tension on dewatering, dry and wet web properties, *J. Pulp Pap. Sci.* 35(3-4), 148-154. Publisher: PAPTAC.
- II. Lindqvist, H., Salminen, K., Kataja-aho, J., Retulainen, E., Fardim, P. and Sundberg, A. (2012). The effect of fibre properties, fines content and surfactant addition on dewatering, wet and dry web properties, *Nord. Pulp Pap. Res. J.* 27(1), 104-111.
- III. Lindqvist, H., Holmback, J., Rosling, A., Salminen, K., Holmbom, B., Auer, M. and Sundberg, A. (2013). Galactoglucomannan derivatives and their application in papermaking, *BioResources* 8(1), 994-1010.
- IV. Lindqvist, H., Bialczak, S., Willför, S. and Sundberg, A. (2013). Functionalization of paper surfaces by modified galactoglucomannans in paper, submitted August 12, 2013 to *J-FOR*.

The Roman numerals I-IV are used in this thesis when referring to the original papers. The original publications are reproduced with the kind permission of the respective copyright holders.

Contribution of the author:

The author was responsible for the experimental design in papers I-IV. The author did part of the experimental work in paper I, was responsible for the experimental work in papers I-II and did all the experimental work in papers III-IV. The wet strength tests in papers I-III and the dry strength tests in papers I-II were conducted in collaboration with the co-authors at VTT. Most of the surface analyses and analyses of GGMs/derivatives properties (contact angle, ToF-SIMS, FE-SEM, FTIR, NMR, HPSEC-MALLS) were conducted in collaboration with specialists. The author was responsible for evaluating the results and writing the first drafts and finalizing of the manuscripts to papers I-IV.

1.3 Supporting publications

1. Lindqvist, H., Auer, M., Holmbom, B., and Rosling, A. (2006). Modification of galactoglucomannan, in Proceedings of the 6th International Paper and Coating Chemistry Symposium, Stockholm, Sweden, p. 154.
2. Lindqvist, H., Auer, M., Holmbom, B., and Rosling, A. (2007). Modification of galactoglucomannan, in Book of abstracts for the Nordic Polymer Days 2007, Helsinki, Finland, p. 37.
3. Lindqvist, H., Salminen, K., Kataja-aho, J., Sundberg, A., Holmbom, B. and Retulainen, E. (2009). Effect of electrolytes, pH and surface tension on dry and wet web properties, in Proceedings of the 7th International Paper and Coating Chemistry Symposium, Hamilton, Canada, pp. 63-66.
4. Retulainen, E., Salminen, K., Lindqvist, H., Oksanen, A. and Sundberg, A. (2011). Improving the wet web strength and runnability, in Proceedings of the 65th Appita Annual Conference, Rotorua, New Zealand.
5. Salminen, K., Kataja-aho, J., Lindqvist, H., Retulainen, E., Rantanen, T. and Sundberg, A. (2011). The effect of certain polymers on tensile strength and tensile relaxation of wet web, in PaperCon 2011, Cincinnati, USA, pp. 825-832.
6. Lindqvist, H., Salminen, K., Kataja-aho, J., Retulainen, E., Fardim, P. and Sundberg, A. (2011). The effect of fines on dewatering, wet and dry web properties, in PaperCon 2011, Cincinnati, USA, pp. 887-894.
7. Kataja-aho, J., Salminen, K., Rantanen, T., Retulainen, E., Lindqvist, H., and Sundberg, A. (2012). The effect of sequential polymer addition on wet and dry web mechanical characteristics: Laboratory and semi-pilot studies, in PaperCon 2012, New Orleans, USA.
8. Salminen, K. Kataja-aho, J., Lindqvist, H., Retulainen, E., Rantanen, T. and Sundberg, A. (2012). The effects of guar gum on wet web runnability – laboratory and pilot-scale studies, in PaperCon 2012, New Orleans, USA.

9. Lindqvist, H., Leppänen, A-S., Bialczak, S. and Sundberg, A. (2012). The location of modified galactoglucomannans in paper, in Book of abstracts for the 8th International Paper and Coating Chemistry Symposium 2012, Stockholm, Sweden, p. 326.
10. Retulainen, E., Salminen, K., Lindqvist, H., Oksanen, A. and Sundberg, A. (2012). Improving the wet web strength and runnability, *Appita J.* 65(3), 255-261.
11. Lindqvist, H., Bialczak, S. and Sundberg A. (2013). Occurrence of GGM in Paper by ToF-SIMS, in Book of abstracts for the Nordic Polymer Days 2013, Helsinki, Finland, p. 91.
12. Strand, A., Lindqvist, H., Vähäsalo, L., Blomquist, M., and Sundberg, A. (2013). Analysis of interactions between colloidal wood pitch and various mineral particles by flow cytometry, *BioResources* 8(3), 3884-3900.
13. Kisonen, V., Xu, C., Eklund, P., Lindqvist, H., Sundberg, A., Pranovich, A., Sinkkonen, J., Vilaplana, F. and Willför, S. (2014). Cationised O-acetyl galactoglucomannan: synthesis and characterization, *Carbohydr. Polym.* 99(1), 755-764.
<http://dx.doi.org/10.1016/j.carbpol.2013.09.009>

2. Background

2.1 Papermaking

The basic function of a paper machine is to produce a continuous and uniform paper sheet using high speed and efficiency. The design of the paper machines depends on the produced paper grade, but they all consist essentially of the same building blocks (Fig. 2.1). The headbox distributes the furnish evenly onto the wire at a consistency of about 0.2-1.0% (Karlsson and Paltakari 2010). On the wire section, drainage of water takes place using gravitation, pulsation, or vacuum and the consistency of the newly formed paper web increases to 15-25%. In the press section, the dry solids content increases to 33-55% by mechanical compression. The drying section consists usually of more than 50 drying cylinders, and here the water is removed by evaporation. After the drying section, the dry solids content is about 95-99%. In terms of water removed, about 97.4% of the water is removed in the wire section, 2.1% in the press section, and 0.5% in the drying section. The maximum speeds of paper machines vary from 2200 m/min for tissue to 2000 m/min for newsprint lines, 1800 m/min for fine paper and 900 m/min for multiply board (Sundholm 2008).

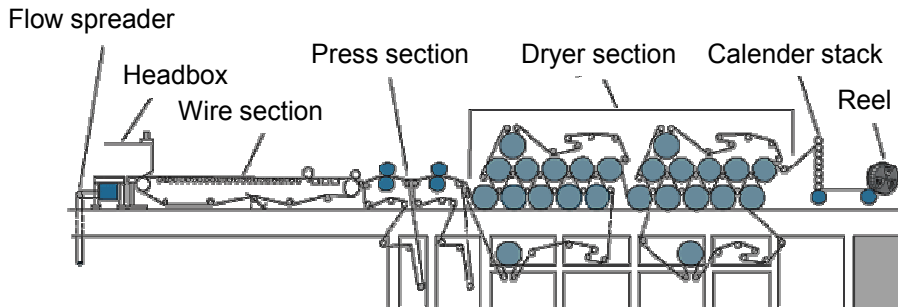


Fig. 2.1. The Fourdrinier paper machine (Smook 2002).

2.2 Runnability

The wet web strength, tension at certain strain and the rate of relaxation of the wet web are critical factors affecting 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 of the wet web and sufficient 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 speeds of paper machines are increasing, higher web tensions are required. The web tension is not constant after the straining in the open draw, but drops 20-60% due to relaxation (Fig. 2.2). Most of this relaxation occurs during the first 0.5 s after straining.

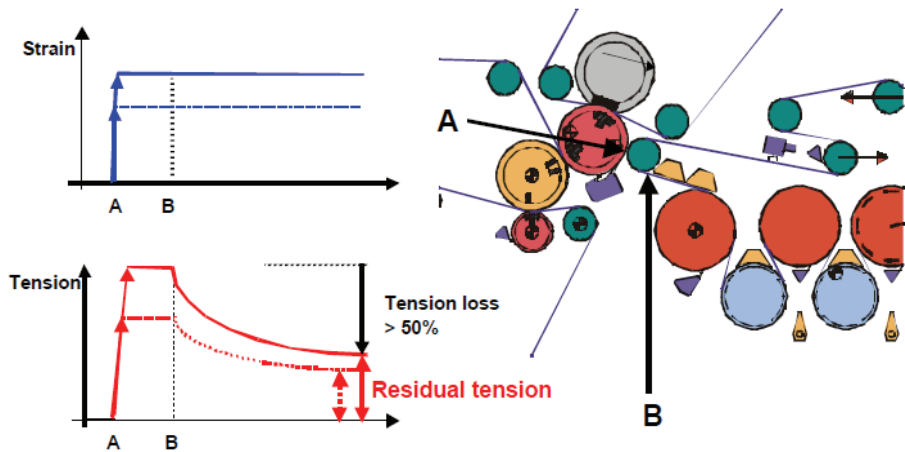


Fig. 2.2. Drop in the web tension during the press-to-dryer transfer (Kurki et al. 2004).

With increasing machine speeds, greater forces, i.e. centrifugal forces and air flows, affect the stability of the moving web before and after the draw. Higher web tensions are required to avoid for instance fluttering of the paper (Fig. 2.3) (Kuhasalo et al. 2000). Most of the runnability problems occur at dry solids contents of 30-70% at the press and dryer section (Kouko et al. 2007).

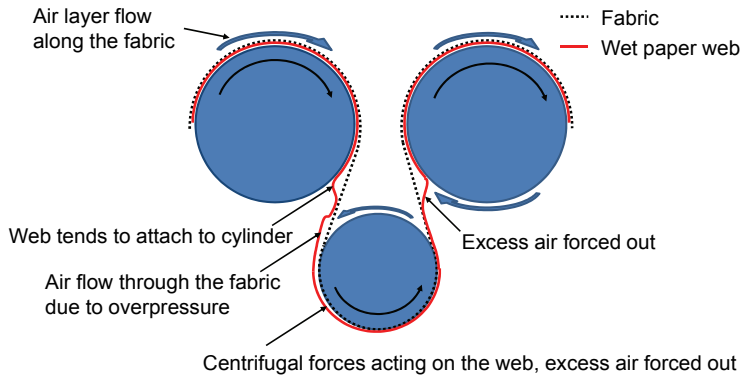


Fig. 2.3. Instabilities caused by centrifugal forces and air flows in a single-felted dryer group (modified from Kuhasalo et al. 2008).

2.3 Wood – fiber morphology

Wood consists of cells, which are mostly oriented in the longitudinal direction of the stem. The cells are connected through pits. The shapes of the cells vary according to the function of the cell and tree species. The most important cell type in softwood is the tracheid or fiber, which stands for 90% of the total amount and is responsible for the mechanical support (Alén 2000).

The wood fiber is built up from several different layers, namely the middle lamella (ML), primary wall (P) and the secondary wall (S) (Fig. 2.4). The middle lamella binds the cells together and consists mainly of lignin (Sjöström 1993). The P layer is relatively thin, 0.05-0.1 μm . The microfibrils form an irregular network on the outer surface of the P layer, but on the inner surface they are almost perpendicular to the cell axis (Alén 2000). The P layer consists of cellulose, hemicellulose, pectins and lignin. The S wall is thick and is divided into three sublayers: secondary wall S1, secondary wall S2, and secondary or tertiary wall S3. The S1 is 0.1-0.3 μm thick and the fibrils are oriented either to the left (S helix) or to the right (Z helix). The average microfibrillar angle is 50°-70°. The S2 layer is the thickest, 1-8 μm , and controls to a large extent the physical properties of the fiber. The microfibrillar angle varies between 5° (latewood) and 30° (earlywood). The thickness of the S3 layer is < 0.1 μm , and the microfibrils are oriented in a very strict manner with an angle of 60°-90°.

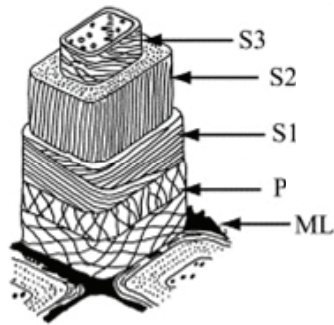


Fig. 2.4. Model of the cell wall structure (Fengel and Wegener 1989). ML – middle lamella, P – primary wall, S1 – outer secondary wall, S2 – middle secondary wall, S3 – inner secondary wall or tertiary wall.

The wet fiber surface could be treated as a gel-like layer consisting of hydrated cellulose and hemicelluloses (Pelton 1993, Kantelinen et al. 1997, Hubbe 2006, Pääkkö et al. 2007). The molecular segments are mixed in a wet state, and when the water is removed, it has been proposed that they become entangled and interpenetrated (Fig. 2.5) (Hubbe 2006). The mechanical properties of the paper can be varied by changing the properties of the contact area, like surface charge and molecular adhesion, between fibers (Torgnysdotter et al. 2007). When polymeric additives are adsorbed onto the fibers, 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). The effects depend mostly on the polymer and its ability to disperse fibrils on the fiber surface and/or to increase the hydration of the fiber surfaces.

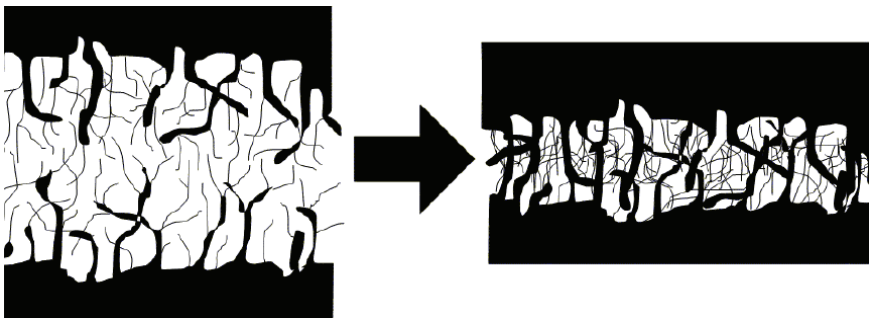


Fig. 2.5. A schematic approach to the mixing of the molecular segments extending from the wet fiber surfaces. When the water is drained, the 3D structure forms rigid fiber-fiber bonds (Hubbe 2006).

2.4 Formation of the fiber network

The role of fiber bonding in the strength of dry paper has been well established and the concepts of fiber bonding and paper strength have been extensively reviewed (Lindström et al. 2005, Hubbe 2006). However, the cohesion of wet paper is not due to inter-fiber bonding, the reason is mainly the combined effects of inter-fiber friction and capillary forces. Two kinds of water are present in the buildup of the fiber network at low solids content (Alinec et al. 2006). Part of the water is associated with the hemicelluloses and amorphous cellulose in the swollen fibers, while the rest of the water is mobile. It is believed that the free water is partly responsible for keeping the fibers together through capillary forces (Fig. 2.6) (Lyne and Gallay 1954a, Campbell 1959, Brecht and Erfurt 1959). The capillary forces are suggested to be caused by liquid bridges in fiber crossings (Van de Ven 2008). At low solids content, the strength of the fiber network is also dependent on inter-fiber friction (Lyne and Gallay 1954a, Brecht and Erfurt 1959, Van de Ven 2008). When air starts to penetrate the fiber network, capillary attraction forces and surface tension dominate. According to van de Ven (2008), capillary forces appear to reach a maximum at 40% solids. Surface tension forces have been assumed to be active in a wide dry content range, 20-60% (Shallhorn 2002). So-called entanglement friction has also been claimed to be an important factor in the development of the wet web strength and to determine the strength of wet webs at 30-50% solids (Van de Ven 2008, De Oliveira 2008). As the amount of solids increases, air-water interfaces are broken up and inter-fiber bonding starts to dominate. Hydrogen bonding starts to dominate at solids contents above 50% (van de Ven 2008). However, inter-fiber friction still plays an important role at these dry contents.

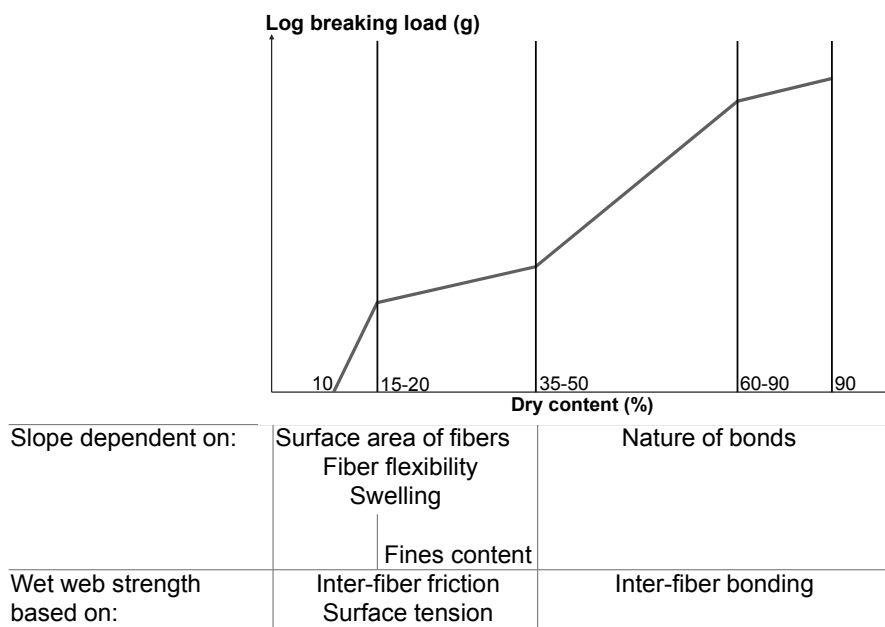


Fig. 2.6. Factors influencing the tensile strength at different dry contents (redrawn from Brecht and Erfurt 1959).

In addition to dry paper properties, also wet web properties are affected by the wet-end chemistry (Retulainen and Salminen 2009). The chemical environment, like pH and concentration of metal ions, plays an important role for dewatering and formation of the wet web, as well as in the final paper properties (Lindström 1992, Hammar et al. 2000, Fält and Wågberg 2003). The type of electrolyte can have a big impact on the dewatering properties (Thomas 1960, Lindström and Kolman 1982) and sheet forming (Lindström and Kolman 1982). It has been observed that replacing existing cations in the pulp by a single cation, favors paper strength in the order $Al^{3+} < H^+ < Mg^{2+} < Ca^{2+} < Li^+ < Na^+$ (Scallan and Grignon 1979). The effect is related to the valence of the cation used. This increase was accompanied by an increase in the fiber saturation point and a decrease in the freeness. It has also been found that increasing pH increases the water retention value (WRV) up to a maximum, but if pH is further increased, the WRV starts to decrease (Lindström and Carlsson 1982). The pH, where maximum WRV was obtained, varied between different pulps and was dependent on the number of acidic groups. Increasing the pH increased the degree of dissociation of the acidic groups in the cell wall, leading to a swollen fiber

due to increased electrostatic repulsion. When an electrolyte was added, the swelling of the fibers decreased, since addition of electrolyte decreased the repulsive forces as the charged groups became shielded. At a high pH, the NaOH acted as an electrolyte by shielding the charged groups, which resulted in decreased swelling. The degree of swelling also influences the water removal during wet pressing, where the high osmotic swelling pressure of the fibers significantly decreases the removal of water in the cell wall (Carlsson et al. 1977, Lindström 1992). Furthermore, increased fiber swelling leads to increased density of the paper sheet.

2.4 Refining

Refining is an important step in improving the mechanical properties of the pulp and paper. Refining of chemical pulp is employed to improve the bonding ability of fibers and to form a strong and smooth paper sheet (Lumiainen 2000). The effects include, among others, cutting and shortening of fibers, straightening of fibers, generation of fines, as well as internal and external fibrillation of the fibers (Page 1989). The initial action of refining is the partial removal of the primary wall (Smook 2002). The secondary wall is thus exposed, and water is absorbed into the molecular structure. The internal structure is loosened, with increased fiber swelling and flexibility, also known as internal fibrillation, as a result. The external fibrillation comprises of loosening and stretching out of the fibrils extending from the fiber surface by which the surface area of fibers increases dramatically. The cell walls collapse, resulting in increased flexibility and surface area of the fibers.

Low-consistency (LC) refining aims at improving the paper strength, the smoothness of the paper surface, and/or the paper formation by changing the fiber structure (Koskenhely 2008). In LC refining, the pulp consistency is usually 2-6% (Lumiainen 2000). The design of the refining system, e.g. the number of refining stages, is determined by the end product and takes into account e.g. types of pulp used, types of paper produced, production capacity, and future outlook. Modern refiners are usually of conical, cylindrical, or disc type (Koskenhely 2008). The most common laboratory refiners and beaters are the Valley beater, the Lampén mill, the Jokro mill and the PFI mill. The laboratory refiners are batch type and operate using a

repeated action of shearing and compression. The refining mechanisms of these refiners are very different from each other, giving varying degrees of internal/external fibrillation and content of fines (Wang and Paulapuro 2005, Wang et al. 2007).

Fines are generally highly swollen particles (Laivins and Scallan 1996) with a large surface area, and they significantly affect the wet-end chemistry (Peterson et al. 2001). They fill the spaces between fibers and slow down dewatering (Seth 2003). Fines also affect the sheet properties by increasing the density and the bonded area of the sheet, thereby increasing the tensile strength (Retulainen et al. 2002). The secondary fines, generated during refining of chemical pulp, are usually of fibrillar nature (Sirviö 2008), which bring fibers into closer contact and enhance fiber-fiber bonding during drying (Sirviö 2003). Additions of kraft fines to long kraft fibers improve the wet tensile strength while the dry content after wet pressing decreases (Salminen and Retulainen 2006). Fines also increase the shrinkage forces during drying (Seth 2003).

2.5 Surface tension in papermaking

Surface-active agents are amphiphilic compounds having both a hydrophilic and a hydrophobic part and they lower the surface energy of liquids or solids (Zhao et al. 2004). Surfactants are widely used in the paper industry, e.g. in deinking, as defoamers, lubricants, and dispersants. Addition of surfactants has been shown to increase water removal (Touchette and Jenness 1960), affect paper strength properties (Touchette and Jenness 1960, Christensen 1969, Bruun et al. 1975), and decrease wet web strength (van de Ven 2008). The effects depend on the type of surfactant used.

In papermaking, air in the form of bubbles and foam can cause problems. Surfactants can act as foam stabilizers through a number of different mechanisms (Eklund and Lindström 1991). One of the most important mechanisms is the Marangoni effect. If a bubble lamella is elastic, it can be deformed by external forces without breaking the lamella – when the forces are withdrawn the lamella returns to its original shape. In the Marangoni effect, the surface tension increases because the number of surface-active molecules decreases in the stretched region as the lamella of a surfactant-

stabilized bubble is stretched. The lamella has thus gained elasticity. Surfactants can also lower the gas permeability, which results in increased interfacial resistance to mass transfer (Hanwright et al. 2005).

In dewatering, the surface tension affects the water removal in the wet web (Asmatulu 2001). By decreasing the surface tension, the water can be pulled out from small channels and pores to a higher degree. The effects are dependent on the type of surfactant used.

Surface tension plays an important role in the formation of the fiber network through capillary forces (Lyne and Gallay 1954a, Campbell 1959, Brecht and Erfurt 1959, Alince et al. 2006, van de Ven 2008). The effect of varying the surface tension on both wet and dry tensile strength has raised conflicting discussions. Laleg et al. (1991) found, that additions of cationic starch decreased the surface tension. Both the stretch and tensile strength of the wet web decreased. Nordman and Eravuo (1955) found that a decreased surface tension decreased the initial wet web strength dramatically, while the water removal seemed unaffected. On the other hand, it has been stated, that the increased water removal due to changes in the surface tension should bring the fiber surfaces closer together and thus increase the number of contact points between fibers (Lyne and Gallay 1954b).

2.6 Galactoglucomannans

During pulping and papermaking, hemicelluloses, pectins, and extractives 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; α -D-galactopyranose is present as single unit side chains linked via (1→6) bonds (Fig. 2.7) (Willför et al. 2003b). GGMs contain acetyl groups, which give water solubility to the polysaccharide by preventing the GGM chains from associating with each other.

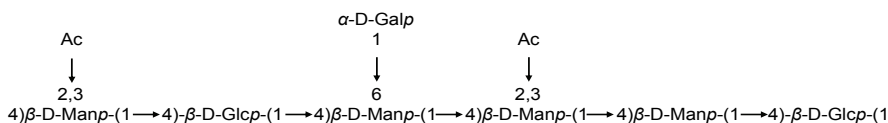


Fig. 2.7. Schematic partial structure of spruce galactoglucomannans (GGM).

GGMs, especially deacetylated GGMs, adsorb onto cellulosic surfaces (Hannuksela 2004). If mixed with cellulose fibers, GGMS are sorbed in a monolayer and deacetylated GGMs in multilayers. GGMs are furthermore able to sterically stabilize colloidal wood dissolved droplets (Sihvonen et al. 1998, Hannuksela and Holmbom 2004). During alkaline pulp treatments, such as peroxide bleaching, GGMs are deacetylated and adsorb onto fibers (Thornton et al. 1991), resulting in a decreased amount of dissolved GGMs available for stabilization of wood pitch droplets.

Mannans have been employed in papermaking for a long time, at first being used as a beater adhesive (Swanson 1950, Leech 1954, Dugal and Swanson 1972). The effect was related to the ability of the gums to increase the swelling of the fibers and thus increase the refining efficiency (Cottrall 1950). Locust bean gum, a galactomannan, was found to also increase the uniformity of formation, the number of bonds, and the bond strength in paper (Leech 1954).

Spruce galactoglucomannans 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 can be chemically or enzymatically modified in different ways, thereby increasing the potential use of the polysaccharides. The modifications can occur randomly along the chain, like etherification (Pal et al. 2006), esterification (Savitha Prashanth et al. 2006, Kisonen et al. 2012), oxidation followed by alkylation (Sierakowski et al. 2000), carboxymethylation (Kobayashi et al. 2002, Xu et al. 2011) and crosslinking (Motozato 1989). The modifications can also be targeted, e.g. oxidation of the C-6 in the galactose (Parikka et al. 2009). Enzymatic modifications are

easy to target where it is desired, e.g. to remove side groups or hydrolyze the backbone of the polysaccharide (Tenkanen 2004). The modified mannans have been suggested to be used in applications like thickeners in food industry, as flocculating agents, as hydrogels, in films and coatings, or as packing materials in columns for gel chromatography.

3. Materials and methods

3.1 Chemicals (I, II)

The non-ionic poly(ethylene glycol)-based surfactant had a cloud point at approximately 33°C in an aqueous solution containing 1% (w/w) non-ionic surfactant. The critical micelle concentration (cmc) was obtained at 0.25 g/L in distilled water at room temperature (I). $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ and NaCl were used as a 1 M aqueous solution for conductivity adjustments. NaOH, NaHCO_3 , and HCl were used for pH adjustments. NaN_3 was used as a preservative during storage of fines.

3.2 Pulp and furnish preparation

3.2.1 Changes in water properties (I)

The pulp that was modified or treated to tailor its wet web characteristics was an ECF-bleached pine pulp 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 (°SR) value of the pulp after dewatering and freezing was about 20.

The same pulp was used for dewatering after refining using a Valley beater in order to prolong the dewatering time (I). The refined pulp was diluted and the conductivity was adjusted to 1.0 mS/cm by addition of electrolytes (CaCl_2 or NaCl). The level was chosen to correspond to circumstances in a fine paper mill using CaCO_3 as fillers. The pH was adjusted to 8-8.5 or 5. The surfactant was added and the pulp suspension was stirred. The surfactant concentrations used in the dewatering tests were 0.125 g/L, 0.25 g/L, and 1.5 g/L.

The pH of distilled water was adjusted to 5 or 8-8.5 using NaOH, NaHCO_3 , or HCl, and the conductivity to 1 mS/cm by adding CaCl_2 or NaCl (I). This water was used for dilution of the furnishes. After disintegration and dilution, the furnish was left to stand at room temperature overnight. The pH dropped to 6-6.5 during the experiments, even if the pH was adjusted prior to testing. Conductivity and pH were checked and adjusted, if

necessary, the next day before the surfactant was added. The surfactant concentrations and obtained surface tensions were: 0.05 (64.8 mN/m), 0.125 (60.6 mN/m), 0.25 (cmc, 53.2 mN/m), 0.4 (48.8 mN/m), 0.8 (46.7 mN/m), and 1.5 g/L (46.4 mN/m). The surface tension of the reference without added surfactant was 73.4 mN/m. After addition of surfactant, the furnish was mixed for 1 h before sheet preparation.

3.2.2 Changes in fiber properties (II)

The pulp, ECF-bleached pine, used in tests of fiber treatments was refined using two different laboratory refiners; gentle refining with the Valley beater and harsh refining using the ProLab refiner (II). The pulp refined in the Valley beater was refined to the desired SR value according to SCAN-C 25:76. In this context, fines were defined as the particles passing a 100 mesh wire. The amount of fines, determined with a McNett classifier, increased from 2% (SR 20) to 13% in the pulp refined to SR 70 when the Valley beater was used (Fig. 3.1). When the ProLab refiner was used, a calibration curve displaying specific refining energy (SRE, kWh/t) vs. °SR was used in order to reach different SR values. Following the disintegration, the pulp was diluted and the pH was adjusted to 6. During the refining, the rotational speed was 1500 rpm, the pulp flow rate 100 l/min and the specific edge load (SEL) 3.0 J/m. The refiner was equipped with standard long medium (LM) conical fillings, with a crossing edge length of 52 m/rev. The amount of fines increased from 6% (SR 20) to 7% (SR 30), and 13% (SR 70) (Fig. 3.1).

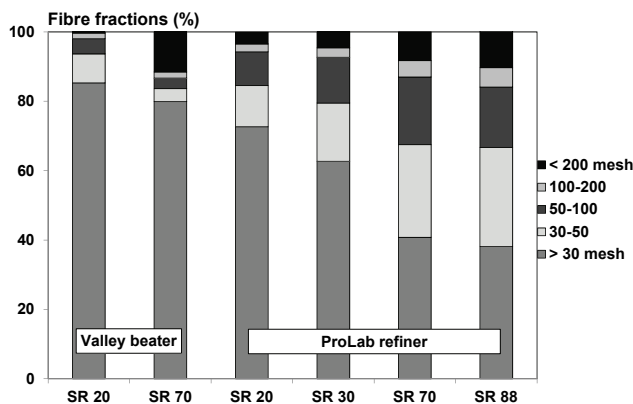


Fig. 3.1. The amount of fibers in different fractions in the original (SR 20) and the refined pulps determined with a McNett classifier (II).

Fines were in this work defined as the particles passing a 100 mesh wire. In order to produce fines to add to the original pulp, the pulp was extensively refined in either the Valley beater or the ProLab refiner. The separation of fines from the fibers was done with a Dynamic Drainage Jar (DDJ) equipped with a 100 mesh wire. The fines were concentrated by sedimentation. The sediments were stored in a refrigerator until used with 0.01% NaN₃ as a preservative.

Fines were removed from the pulp suspension in order to study the effects of refining on the fibers. The refined pulp was filtered through the DDJ equipped with a 100 mesh wire and the pulp residue was collected. The pulp residue was diluted and left to stand overnight before sheetmaking.

For dewatering tests, the conductivity was adjusted to 1.0 mS/cm by addition of CaCl₂. The pH was adjusted to 8-8.5. The pulp suspension was stirred prior to experiments. In the tests with the surfactant, the surfactant was added to the suspension before stirring. Pulp furnishes were prepared from refined pulp, refined pulp from which the fines had been removed, original pulp to which fines had been added, or from original pulp that had been only disintegrated.

For sheetmaking, the conductivity of distilled water was adjusted to 1 mS/cm by addition of CaCl₂. The pH was adjusted to pH 8-8.5. This water was used for dilution of the suspension. The furnish was left to stand at room temperature overnight. Conductivity and pH were checked and adjusted, if necessary, the next day. The suspension was mixed before sheet preparation. If the surfactant was used, it was added before stirring.

3.2.3 Addition of galactoglucomannans (III, IV)

Peroxide-bleached thermomechanical (PB TMP) pulp was used in the tests with galactoglucomannans (III). The pulp was obtained from a Finnish pulp mill and packed into airtight polyethylene bags, and kept at -18°C until used for testing.

A PB TMP suspension was prepared and disintegrated. The pulp was filtered through a DDJ equipped with a 100 mesh wire and the filtrate containing fines as well as dissolved and colloidal substances was collected. A fresh batch of PB TMP was mixed and disintegrated and then diluted

with the DDJ-filtrate to the right volume and left to mix. The pH was adjusted to 5.

ECF-bleached pine kraft pulp was used for preparation of handsheets for surface analysis (IV). The furnish was done by mixing and disintegration of the pulp. The suspension was then diluted and finally mixed for 1 h before use.

3.3 Galactoglucomannans (III, IV)

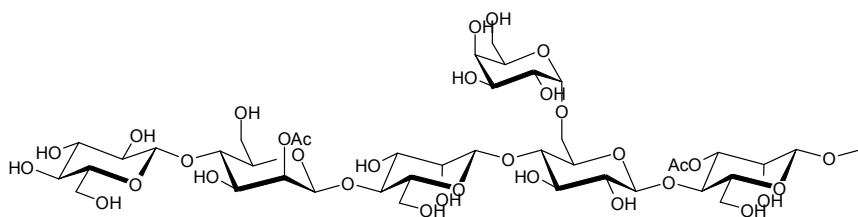
GGMs were isolated from TMP process waters. Process water was obtained from a Finnish mill producing TMP from spruce, from which GGMs were concentrated through a series of filtration and ultrafiltration steps (Xu et al. 2007). The obtained GGMs (Fig. 3.2 A) were spray-dried and consisted of 53 mole-% mannose, 23 mole-% glucose and 13 mole-% galactose. The remaining 11% consisted mainly of other sugar units, e.g. arabinose, xylose and galacturonic acid originating from arabinogalactans, methylglucuronoxylans and pectins. The average molar mass (M_w) was 25 500 g/mol and the polydispersity 1.27 (III).

Cationic GGMs (C-GGM, Fig. 3.2 B) with a degree of substitution (DS) of 0.05 were prepared (III). The M_w was 17 300 g/mol and the polydispersity 1.74. The obtained degree of substitution (DS) was 0.05.

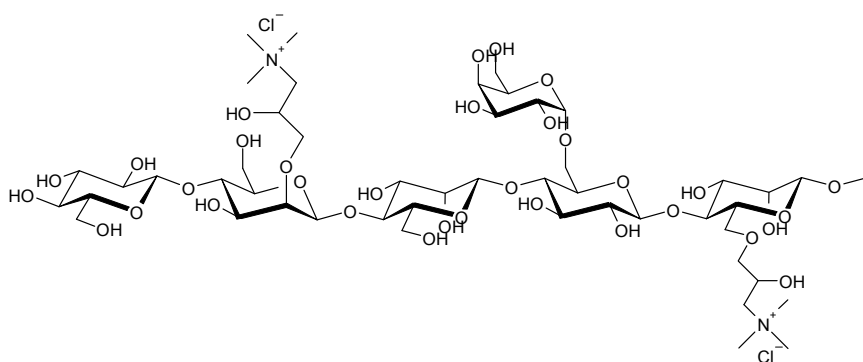
GGMs were carboxymethylated (CM-GGM, Fig. 3.2 C) according to traditional methods described for preparation of carboxymethyl cellulose (III). The obtained DS was 0.4.

Iminated amphiphilic GGMs (A-GGM, Fig. 3.2 D) were obtained by a reaction between the aldehyde at the reducing end of the GGM chain and the primary amine 1-docosanamine (III). The obtained M_w was 30 600 g/mol and the polydispersity 1.15.

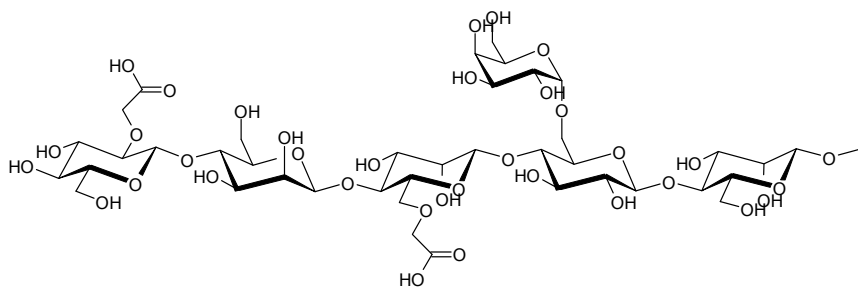
A)



B)



C)



D)

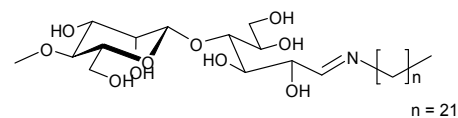


Fig. 3.2. Galactoglucomannans (A) and derivatives thereof; B) cationized GGMs (C-GGM), C) carboxymethylated GGMs (CM-GGM), and D) GGMs iminated at the reducing end (A-GGM).

3.4 Dewatering tests (I-III)

Dewatering time and air permeability were determined using a custom built dynamic drainage analyzer (Dynamic Drainage Analyzer of Åbo Akademi, Åbo/Turku, Finland, DDÅA) (Fig. 3.3). The DDÅA is a combined drainage analyzer and sheet former, which is computer controlled and has a high repeatability.

The general operating procedure: The pulp suspension was poured into the mixing jar in the DDÅA (Fig. 3.3). During the first 30 s, the stirrer speed was set to 500 rpm and then the speed was increased to 1000 rpm. After a predetermined time (water tests: 70 s, refining tests: 60 s) the suspension was sprayed onto the wire. The suspension was mixed with a perforated plate (for 30 s during water tests, 35 s for refining tests) before the valve below the wire was opened. The container under the wire had a 30 kPa vacuum, resulting in removal of water from the suspension and formation of a paper sheet on top of the wire. After the valve under the wire had been opened, the pressure was continuously measured during 60 s. From the obtained graph, it was possible to determine the dewatering time (a shift in the slope) and air permeability (the pressure difference between the opening of valve and stabilizing pressure) (Fig. 3.3). For each test, 1.5 L of pulp suspension was used and 0.5 L of water was poured onto the wire before the pulp suspension was added. The outside pressure was adjusted to 100 kPa in the experiments.

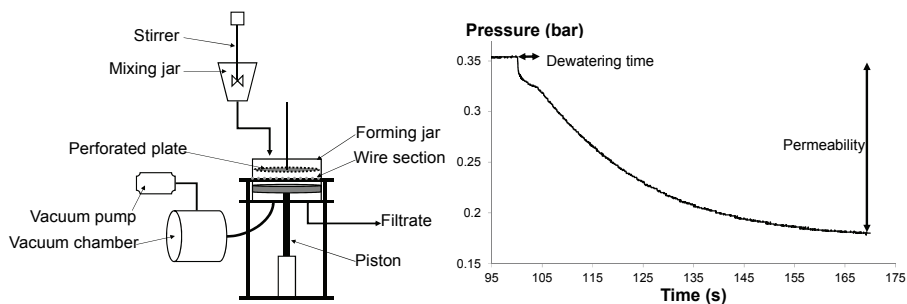


Fig. 3.3. Left: The Dynamic Drainage Analyzer of Åbo Akademi, DDÅA, a custom built dynamic drainage analyzer. Right: The data from the DDÅA is plotted as the pressure versus the time. From this graph, the dewatering time, and air permeability was determined.

A grammage of 175 g/m² was used in the determination of effects of water and fiber treatments (I, II). The consistency of the pulp suspension on the wire was about 4.3 g/L.

In the tests with added galactoglucomannans, a grammage of 100 g/m² was used (III). The consistency of the pulp suspension on the wire was about 2.5 g/L.

3.5 Preparation of laboratory handsheets (I, II, IV)

For determination of effects of water properties, as well as fiber properties, sheets (60 g/m²) were prepared using white water circulation on a sheet former (SCAN-CM 64:00) (I, II). The sheets were packed in airtight plastic bags and sent within 24 h for wet and dry web measurements. The sheets were pressed in order to reach different levels of dry content on 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.

For surface analysis, paper sheets (60 g/m²) were prepared using a modified procedure of SCAN-CM 26:99 (IV). A 50 µm polyamide (PA) filter was placed on top of the 125 mesh metal wire. After addition of pulp and mixing, the water was drained until the water level was just below the wire. The upper container was opened and then the water level was brought back up until the sheet was rewetted. GGMs/derivatives were sprayed on top of the sheet. The water was then drained until all the water had been removed from the lower container. A 36.5 µm PA filter was placed on top of the sheet, followed by two blotting papers. A 3 kg weight was placed on top for 20 s. The sheet was lifted from the wire between the PA filters and placed between four dry blotting papers on a table under the 3 kg weight for an additional 20 s. The sheet was then transferred from the PA filters avoiding touching the surface to a drying plate covered in aluminum foil and a second drying plate with aluminum foil was placed on top. Aluminum foil was used to avoid contaminants that could interfere with surface analysis. The sheets were dried in drying frames and stored in a conditioned room (23°C, RH 50%).

3.6 Wet web strength and stress relaxation (I-III)

Dynamic tensile strength and relaxation properties of samples from the sheet former were measured with the IMPACT (Fig 3.4) (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 velocity is approximately 3000 times higher than that used in standard tensile testing methods (Kurki et al. 2004, Kouko et al. 2007). 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.

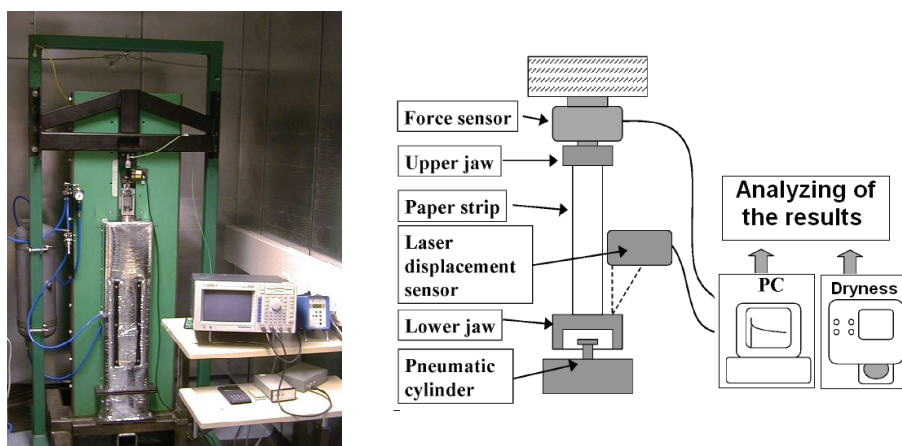


Fig. 3.4. Left: The IMPACT test rig (Salminen et al. 2005) and right: the working principle (Kurki et al. 2004).

The relaxation properties of the wet paper samples were determined at 2% strains and the relaxation time was 0.475 s. The tension measured after this relaxation time is referred to as residual tension. The highest tension after straining is called maximum tension, which also refers to the initial tension. Fig. 3.5 (left) shows an example of a curve from a relaxation test of wet paper.

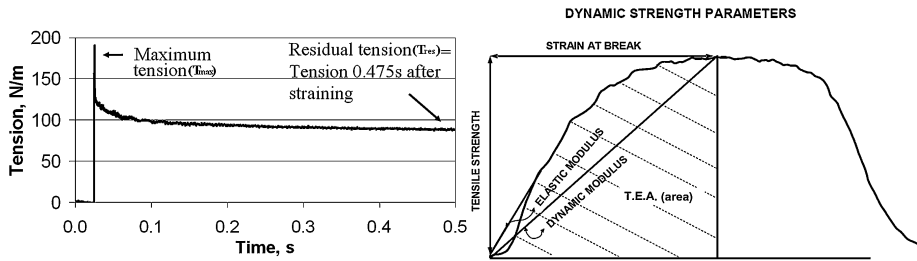


Fig. 3.5. Left: Tension-time-figure of relaxation (Kurki et al 2004). The sample was strained to 1% strain with the Impact test rig. Right: Tension-strain-figure of a dynamic tensile strength test measured with the Impact test rig. T.E.A. = tensile energy absorption (Kurki et al. 2004).

Tensile strength, residual tension, and elastic modulus (the maximum slope at the beginning of the stress-strain curve) were the main parameters established from the tests when straining samples to the breakpoint (Fig. 3.5 right). The results of the wet web measurements are mainly presented as a function of dry content. The mechanical properties (tensile strength, residual tension, and elastic modulus) of a wet fiber web are known to be highly dependent on the dry content in the range of 30-90% (Brecht and Erfurt 1959, Kurki et al. 2004).

3.7 Surface analysis (III, IV)

Contact angle was determined with distilled water using a CAM 200 Optical Contact Angle Meter (III). 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.

The paper surfaces were analyzed by Time-of-Flight Secondary ion Mass Spectrometer (ToF-SIMS) (IV). The instrument used was a PHI TRIFT II equipped with a Ga^+ ion gun in positive mode with charge compensation. The spectra were recorded using a voltage of 15 keV and the images using a voltage of 25 keV. The surface-excited area was $200 \mu\text{m} \times 200 \mu\text{m}$ and a 3 min acquisition time was used. Three replicate runs were recorded for each sample. Samples of GGM and its derivatives were prepared by pressing the powder between two clean plates.

The surface morphology of the sprayed papers was studied using a JEOL JSM-6335F Field Emission Scanning Electron Microscope (FE-SEM) (IV). The samples were coated twice with platinum before analysis. An accelerating voltage of 5.0 kV was used for the SEM imaging.

The sprayed papers were analyzed with Fourier Transform Infrared (FTIR) spectroscopy (IV). The instrument used was a Bruker Alpha with a platinum ATR module. 24 scans were obtained at 400–4000 cm^{-1} . The analysis was performed directly on the papers.

4. Results and discussion

4.1 Dewatering and wet web properties

An efficient way of improving a process is to modify the existing process parameters. In this work, the first step was to control the properties of the water used for papermaking and to understand how these properties affect the properties of the wet fiber web and runnability. The fibers were also modified in order to achieve the best combination of good dewatering and improved wet tensile strength properties. Lastly, a wood-derived hemicellulose was added to the furnish, and the effects were determined. More details can be found in Papers I-III.

4.1.1 *Change in water properties (I)*

By adding a non-ionic surfactant to the pulp suspension, the dewatering time decreased (Fig. 4.1). Surfactants lower the surface tension, which in turn affects the water removal through the laws of capillary flow (Touchette and Jenness 1960). The concentration of the surfactant was shown to be a determining factor, as concentrations above cmc (0.25 g/L) did not further affect the rate of water removal. There was no significant difference in dewatering time comparing pH 6-6.5 and 5. When the conductivity was adjusted with Na⁺ instead of Ca²⁺, the dewatering time increased. Ions with lower valence give a higher degree of swelling of fibers (Nelson and Kalkipsakis 1964, Fält and Wågberg 2003), which should increase the dewatering time. The degree of swelling of fibers is not as high in bleached kraft pulp as in unbleached due to lower amount of acidic groups (Lindström and Carlsson 1982). Based on our results, some swelling probably occurred even if the dry content of the DDÅA sheets was even higher when Na⁺ was used. The addition of the surfactant resulted in a more rapid water removal and the water was pulled out from the fibers more efficiently.

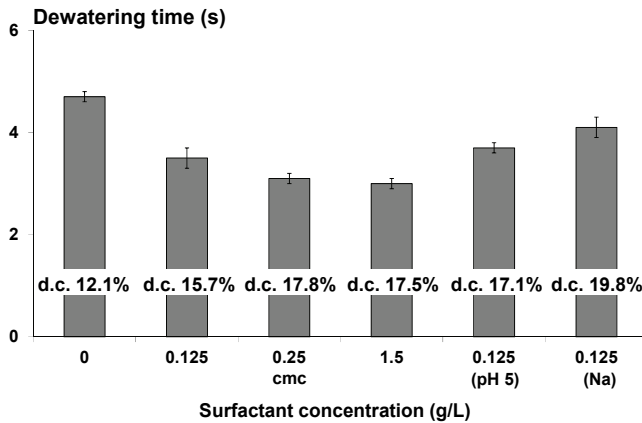


Fig. 4.1. Dewatering time and the dry content (d.c.) of the formed sheets measured with the DDÅA. The pulp was refined to SR 74, the pH was 6-6.5 or 5, and the conductivity was adjusted to 1 mS/cm with CaCl_2 or NaCl (I).

At higher concentrations of the surfactant, the air permeability increased (Fig. 4.2). Surfactants have been shown to be adsorbed onto fiber surfaces (Bruun et al. 1975, Friberg et al. 1975). The consequence of the adsorption is a repelling effect between the fibers. At the same time, the fiber surface might become more even. Increased air permeability is usually not desired from printing point of view, as the paper adsorbs more ink. In the production of sack paper, the situation is the opposite; high air permeability is desired in order to remove air when sacks are filled. The effects of possibly more even fiber surface was also seen as shorter dewatering times and increased dry content of the formed sheets. There were only minor differences in air permeability comparing pH 6-6.5 and pH 5, as well as when the conductivity was adjusted with Na^+ compared to Ca^{2+} .

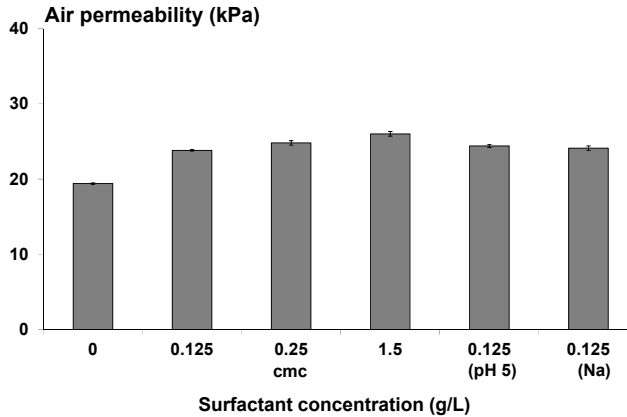


Fig. 4.2. Air permeability measured with the DDÅA. The pulp was refined to SR 74, the pH was 5 or 6-6.5, and the conductivity was adjusted to 1 mS/cm with CaCl_2 or NaCl (I).

Addition of a non-ionic surfactant up to concentrations of 0.25 g/L (cmc) increased the dry content after constant wet pressing and, as a result, also the wet tensile strength was higher (Fig. 4.3). The dry content after wet pressing reached the highest level at a surfactant concentration of 0.25 g/L. The hydrogen bonding is believed to dominate at dry contents above 50% (Van de Ven 2008). Since the wet pressing resulted in dry contents above this at surfactant concentrations of cmc or higher, it can be assumed that the number of contact points between fibers increased. However, an addition of surfactant at concentrations above cmc resulted in lower dry content and tensile strength. A surfactant concentration higher than the cmc can interfere with the inter-fiber bonding by hindering the formation of hydrogen bonds (Brandal and Lindheim 1966, Christensen 1969, Bruun et al. 1975). The surfactant can either be adsorbed to the fiber surface or allow the fibrils to collapse on the fiber surface.

With fibers involved, some of the surfactant was also probably adsorbed within the cell wall of the fibers. In these experiments, the surface tension was measured on the recirculation water after sheetmaking (Table 4.1). The cmc level was determined from pure water solutions. Although some adsorption of the surfactant probably took place, there was still enough surfactant present in the water to significantly decrease the surface tension of the water.

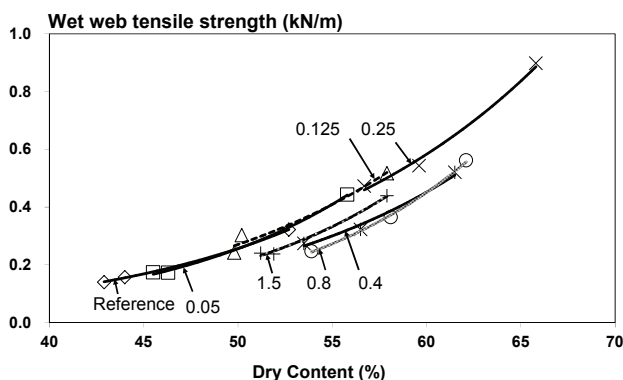


Fig. 4.3. Wet web tensile strength after addition of a non-ionic surfactant. The amounts of surfactant are given as g/L in the figure. The pH was 6-6.5 and the conductivity was adjusted to 1 mS/cm with CaCl₂. The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (I).

Table 4.1. Surface tension (mN/m) measured from distilled water and from recirculation water after sheetmaking (I). The surface tension of distilled water was about 72 mN/m.

Surfactant concentration (g/L)	Distilled water	After sheetmaking
0.125	53	61
0.25	48	53
0.4	46	49
0.8	44	46

The residual tension describes the ability of the wet web to remain tense after straining. Good runnability and web handling is achieved when the web tension is lower than the wet tensile strength (Kurki et al. 2004). Since paper is a viscoelastic-plastic material and the elastic properties are time-dependent, the web tension does not remain constant after straining in the open draw but drops with 20-60% at the beginning of the dryer section. Most of the relaxation occurs during a 0.5 s relaxation time. In order to

study this kind of behavior, the residual tension at 2% strain was measured. The residual tension at 2% strain (Fig. 4.4) showed similar trends as the results from tensile strength measurements (Fig. 4.3). The residual tension increased when the surfactant concentration was about cmc, mostly because of more efficient dewatering and wet pressing.

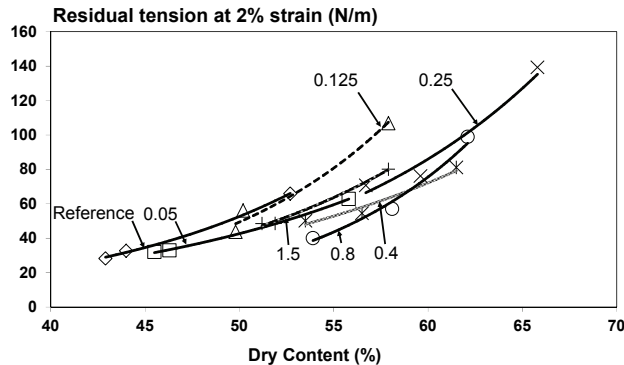


Fig. 4.4. Residual tension at 2% strain after addition of a non-ionic surfactant. The amounts of surfactant are given as g/L in the figure. The pH was 6-6.5 and the conductivity was adjusted to 1 mS/cm with CaCl_2 . The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (I).

When sheets were prepared at pH 5 instead of pH 6, the wet tensile strength decreased slightly primarily due to lower dry content after wet pressing (Fig. 4.5). Use of Na^+ instead of Ca^{2+} decreased the wet web tensile strength at constant dry content. Na^+ ions decrease the coefficient of friction and increase the wet adhesive forces between fibers (Andersson et al. 2000). A decreased coefficient of friction allows the fibers to slide over each other more easily. The sheets made at pH 5, as well as the adjustment of the conductivity with Na^+ both resulted in a slight decrease in residual tension (Fig. 4.6).

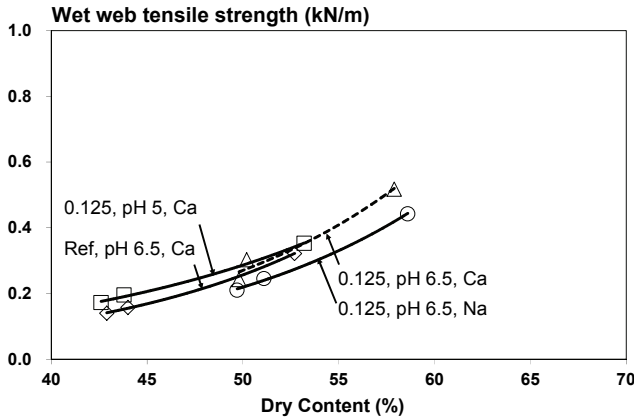


Fig. 4.5. Wet web tensile strength after addition of a non-ionic surfactant. The amount of surfactant was 0 (Ref) or 0.125 g/L. The pH was 6-6.5 or 5 and the conductivity was adjusted to 1 mS/cm with CaCl₂ or NaCl. The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (I).

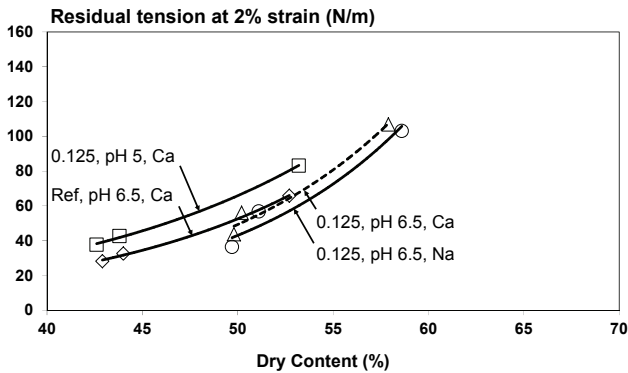


Fig. 4.6. Residual tension at 2% strain after addition of a non-ionic surfactant. The amount of surfactant was 0 (Ref) or 0.125 g/L. The pH was 6-6.5 or 5 and the conductivity was adjusted to 1 mS/cm with CaCl₂ or NaCl. The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (I).

4.1.2 Change in fiber properties and fines content (II)

Refining of pulp using two refining intensities, gentle and harsh, increased the dewatering time and decreased the air permeability (Figs. 4.7 and 4.8).

When the pulps were refined to SR 70, the dewatering time was much longer and the air permeability lower for the harshly refined pulp than for the gently refined pulp. Harsh refining generally results in a higher proportion of fines relative to internal delamination and fibrillation. During sheet forming, the cut fibers, fiber fragments and fines were able to form a more densely packed sheet than the gently refined pulp. Gentle refining to SR 70 produced a lot of fines without cutting fibers too much (Fig 3.1). Gentle refining resulted also in prolonged dewatering time and increased air permeability (Figs. 4.7 and 4.8), but the changes were not as extensive as for the pulp submitted to harsh refining.

Removal of fines from the gently or harshly refined pulp resulted in dewatering time and air permeability being similar to that of the original pulp (Figs. 4.7 and 4.8). This implies that the internal/external fibrillation of the fibers did not significantly affect dewatering and air permeability.

Addition of 15% fines from ProLab refined pulp to original pulp prolonged the dewatering time, but not as much as refining to SR 70 (Figs. 4.7 and 4.8). The changed fiber properties seemed to have a combined effect with the fines in the pulp refined to SR 70. Refining creates more flexible fibers, which respond to the increased drainage pressure caused by fines, resulting in a more dense fiber mat being formed during the dewatering stage.

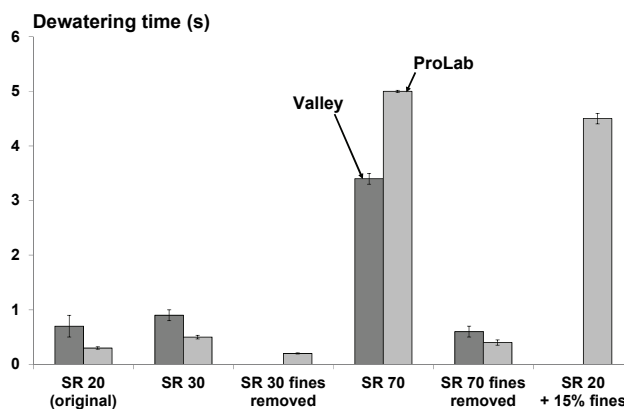


Fig. 4.7. Dewatering time measured with the DDÅA. The pulp was refined using the Valley (gentle) or ProLab (harsh) refiner (II).

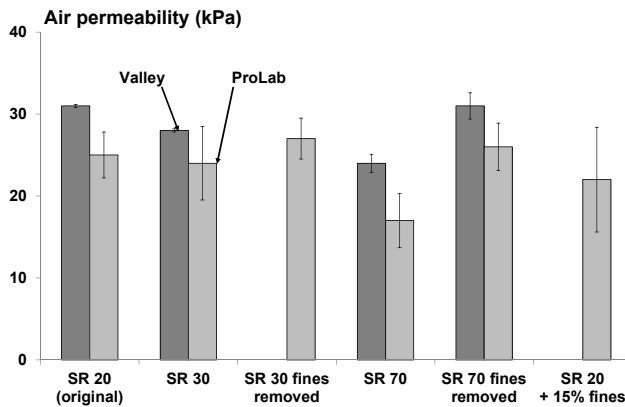


Fig. 4.8. Air permeability measured with the DDÅA. The pulp was refined using the Valley (gentle) or ProLab (harsh) refiner (II).

During the gentle refining, the wet web tensile strength increased and the dry content after wet pressing decreased with increased degree of refining (Fig. 4.9). At a dry content of about 43%, the wet tensile strength of the pulp refined to SR 70 was about 0.25 kN/m higher than the original pulp. At a dry content of 50%, the difference was even higher, 0.40 kN/m. This indicates that the highly refined pulp had a higher wet web tensile strength at lower solids content, and was additionally able to form more hydrogen bonds during drying. Hydrogen bonding starts to dominate at dry contents above 50% and the observed difference is explained by more bonds that were formed. Refining increases the relative bonded area as the fibers become more conformable and flexible, which might also increase the bond strength per unit of bonded area (Pikulik 1997).

Removal of fines caused a decrease in the wet web tensile strength compared to sheets containing fines (Fig. 4.9). In the case of SR 70 were fines were removed, the tensile strength was still higher than the tensile strength for sheets made from the original pulp (SR 20), indicating that the changes in the fibers, e.g. internal and external fibrillation, increased fiber-fiber bonding, but not as much as the addition of fines. The dry content after wet pressing was similar to the dry content of the original pulp, which is due to the removal of the swollen and water-containing fines. When 30% fines were added to the original pulp, the wet web tensile strength increased the most. Fines also contribute to the increase in bonded area, as more available surfaces are created by refining (Ingmanson and Andrews 1959).

During the harsh refining (Fig. 4.10), the results were similar to the results obtained after gentle refining. The wet web tensile strength was slightly lower for the SR 70 compared to when the Valley beater was used, which could be due to the fiber cutting during the harsh refining. The harsher treatment of the fibers resulted in the fibers being more damaged (Figure 3.1). The consequence was higher water retention of the fibers (Stone et al. 1968), which was seen as a slightly lower dry content after wet pressing. The ProLab refined pulp did not show an increase in wet web tensile strength with increasing dry content as the gently refined pulp (comparing SR 70 with the original pulp), implying that the amount of fibril-like fines, which could promote hydrogen bonding, was smaller.

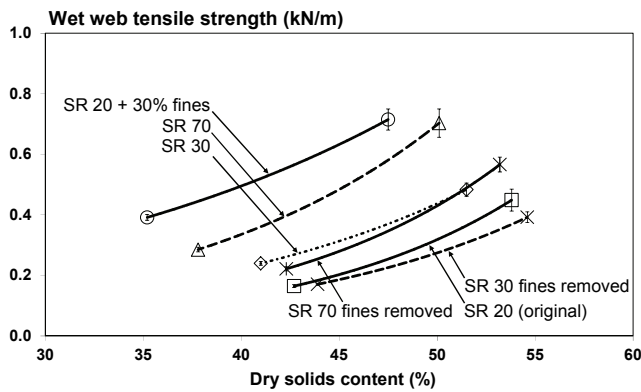


Fig. 4.9. Wet web tensile strength after gentle refining (Valley). The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

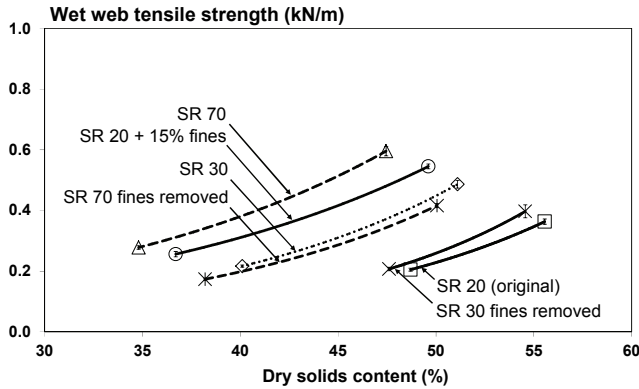


Fig. 4.10. Wet web tensile strength after harsh refining (ProLab). The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

The residual tension increased when the pulp was refined (Figs. 4.11 and 4.12). When the fines were removed from the gently refined pulp, the residual tension was slightly higher than for the fines-free harshly refined pulp. The fibers refined in the Valley beater were straightened out and more flexible than the fibers refined in the ProLab refiner, which was seen as a slightly higher residual tension. When fines were added to original pulp (SR 20), the residual tension at 2% strain did not increase as much as the wet web tensile strength did, indicating that the fiber properties are more important for the residual tension than the fines content.

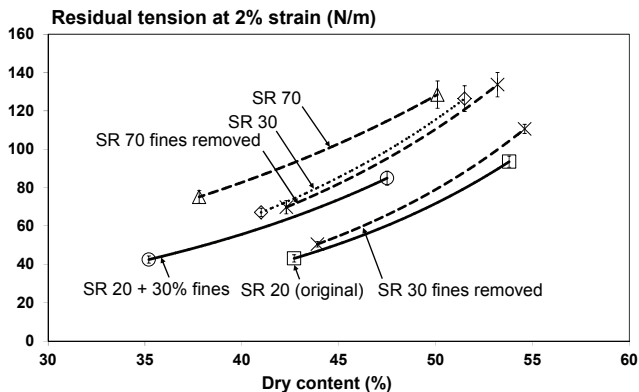


Fig. 4.11. Residual tension after 0.475 s at 2% strain after gentle refining (Valley). The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

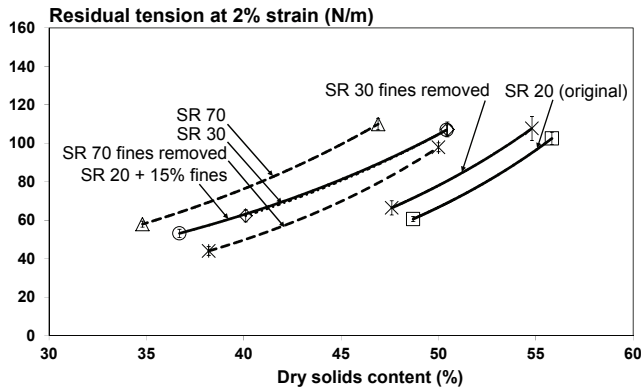


Fig. 4.12. Residual tension after 0.475 s at 2% strain after harsh refining (ProLab). The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

Refining of pulp increased the dewatering time (Fig. 4.7) and therefore an attempt to avoid this negative effect was made by adding the same non-ionic surfactant, which was able to decrease the dewatering time for the original pulp (Fig. 4.1). Using a concentration of 0.125 g/L of the surfactant decreased the dewatering time, both for original pulp with added fines and for refined pulp (Fig. 4.13). The air permeability increased somewhat when the surfactant was added to refined pulp (Fig. 4.14), indicating that the fiber network was more porous.

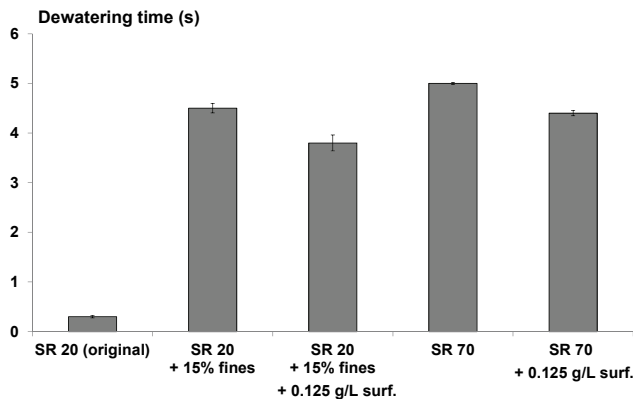


Fig. 4.13. Dewatering time measured with the DDÅA after harsh refining (ProLab), addition of 15% fines and/or addition of 0.125 g/L non-ionic surfactant (II).

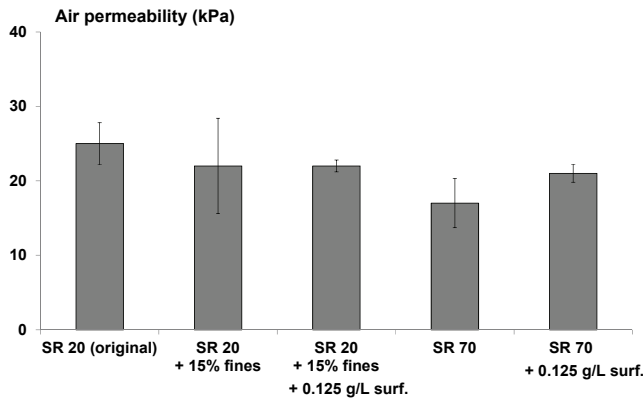


Fig. 4.14. Air permeability measured with the DDÅA after harsh refining (ProLab), addition of 15% fines and/or addition of 0.125 g/L non-ionic surfactant (II).

Addition of fines and a non-ionic surfactant to original pulp increased the dry content after wet pressing but slightly decreased the wet web tensile strength, as well as the residual tension at constant dry content (Figs. 4.15 and 4.16). Since fines have a large surface area, the surfactant might have been adsorbed to the surface adding to the gel-like layer (Bruun et al. 1975, Karademir and Imamoglu 2007), which allows the particles to slide over each other more easily. The adsorption can also take place within the cell wall. Different polymers can adsorb to cellulosic surfaces and give a kind of lubricating effect (Alince et al. 2006, Laleg and Pikulik 1993). At the same time the surfactant could also interfere with the interaction between the fiber surfaces. The concentration of the used surfactant was not optimized for the refined furnishes, and thus a concentration from the tests with the original pulp was chosen.

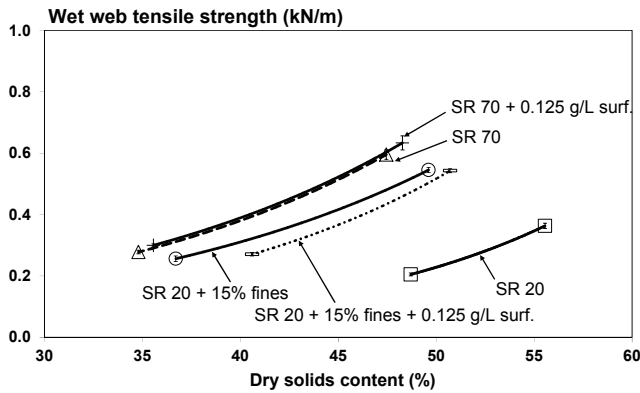


Fig. 4.15. Wet web tensile strength after harsh refining (ProLab), addition of 15% fines and/or addition of 0.125 g/L non-ionic surfactant. The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

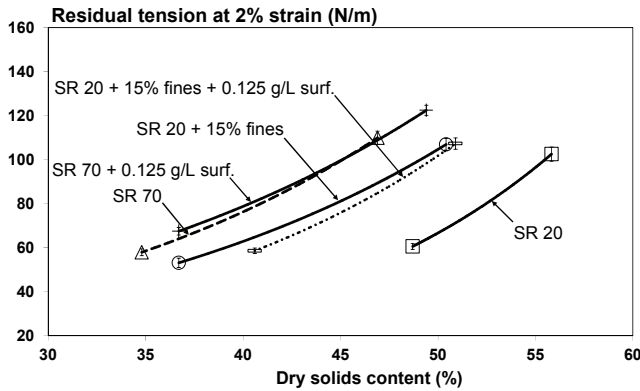


Fig. 4.16. Residual tension after 0.475 s at 2% strain after harsh refining (ProLab), addition of 15% fines and/or addition of 0.125 g/L non-ionic surfactant. The sheets were pressed to two different dry contents using 50 and 350 kPa and measured with the IMPACT test rig (II).

4.1.3 Addition of galactoglucomannans (III)

Addition of GGMs increased the wet web tensile strength at constant dry content (Fig. 4.17). Recent research looking at the molecular and fibrillar level phenomena, suggest that the wet fiber surface could be considered to be a gel-like layer consisting of cellulose and hemicelluloses (Pelton 1993, Kantelinen et al. 1997, Hubbe 2006, Pääkkö et al. 2007). Pelton (1993)

suggested that the fiber surface is covered with a hydrated polymer layer, which determines the interactions between fibers and other particles. When polymeric additives are adsorbed onto fibers, they are mixed with the 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 fiber surface and/or to increase the hydration of the fiber surfaces. Eronen et al. (2011) found that galactomannans, like guar gum and locust bean gum, had a dispersing effect on fibrils making them more stretched out with greater possibility of interaction with fibrils on other fiber surfaces. GGMs have structures very similar to 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, and the fiber surfaces, as the galactomannans resulting in an increase in wet web tensile strength.

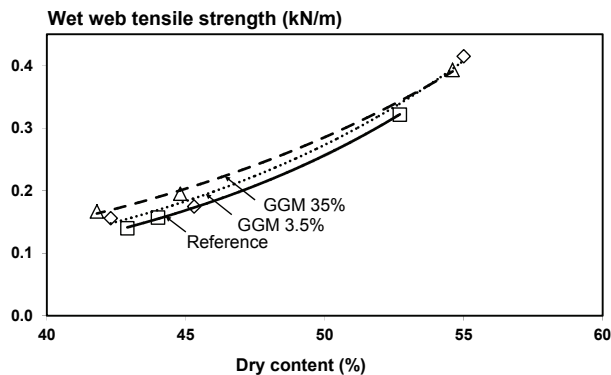


Fig. 4.17. Wet web tensile of wet handsheets prepared from bleached kraft pulp after addition of galactoglucomannans (GGM). The additions are given as % of amount of dry fiber. The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (III).

Addition of GGMs also increased the elastic modulus of the wet web (Fig. 4.18). The difference between the two addition levels was small. The increase in elastic modulus was higher at lower dry contents implying that

the positive effects of GGMs are found already at low solids content. The use of GGMs in papermaking have a great potential to increase the runnability of the wet web, since the tension of a running web in practise is controlled by the elastic modulus of the fiber network (Alava and Niskanen 2008). The elastic modulus also controls the performance of the end-product through the bending stiffness.

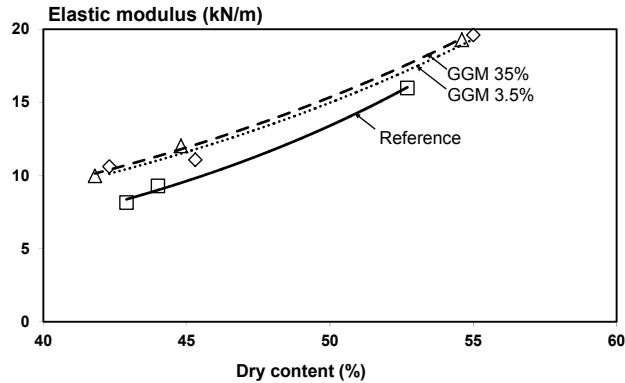


Fig. 4.18. Elastic modulus of wet handsheets prepared from bleached kraft pulp after addition of galactoglucomannans (GGM). The additions are given as % of amount of dry fiber. The sheets were pressed to three different dry contents using 20, 50, and 350 kPa and measured with the IMPACT test rig (III).

4.2 Dry paper properties

When a papermaking process is modified and made more efficient at the wet end stage, the follow-up of the changes in the final dry product become important as well. Here the effects of changes in water and fiber properties, as well as addition of modified galactoglucomannans on dry paper properties have been determined. More details are found in papers I-III.

4.2.1 Change in water properties (I)

The tensile strength of dry samples (Fig. 4.19) made from the original pulp showed similar results as the wet tensile strength (Figs. 4.3 and 4.5). The tensile strength and density increased when a non-ionic surfactant was used at concentrations below the cmc. The strength as a function of sheet density is related to the level of bonding in a paper sheet, increased bonding

contributes to higher strength. Addition of surfactant at concentrations below the cmc seemed to promote hydrogen bonding by increasing the bonded area, since the density increased. When the concentrations of surfactant were above cmc, the dry tensile strength and density were on the same level as the reference, or even lower. High surfactant concentrations maybe disturbed the hydrogen bonding by hindering the formation of interfiber bonds. When the sheets were made at pH 5 instead of pH 6.5, the density was lower, but the tensile strength was not affected. The difference was due to the increased fiber swelling occurring at higher pH (Lindström and Kolman 1982). Replacing Ca^{2+} ions with Na^+ ions did not affect the density, but decreased the tensile strength slightly. In unbleached kraft pulp Na^+ increases the dry tensile strength compared to Ca^{2+} because of swelling effects and increased bonded area (Scallan and Grignon 1979). Less swelling occurs in bleached kraft pulp due to lower amount of acidic groups (Lindström 1992).

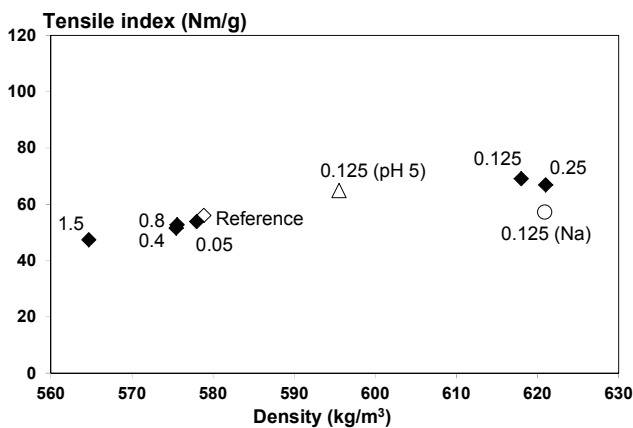


Fig. 4.19. Tensile index versus density of dry sheets after addition of non-ionic surfactant. The amounts of surfactant are given as g/L in the figure. The pH was 6-6.5 or 5 and the conductivity was adjusted to 1 mS/cm with CaCl_2 or NaCl . The sheets were tested with the IMPACT test rig (I).

4.2.2 Change in fiber properties and fines content (II)

Both gentle and harsh refining increased the density and the dry tensile strength (Figs. 4.20 and 4.21). Fines are known to increase the density and the bonded area of the sheet (Retulainen et al. 2002). The density was

slightly higher after the harsh refining than after gentle refining, which could be explained by the shorter fibers formed during the harsh refining giving a more densely packed sheet. The increase in tensile strength for the Valley refined sheets was higher than the increase for ProLab refined sheets. Refining in Valley beater results in fibers being straightened out under compression and shear forces (Kang and Paulapuro 2006), which increases the tensile strength (Page 1989). The larger increase in tensile strength when using the Valley beater can also be partly explained by generation of fibrillar fines that enhance the fiber-fiber bonding (Sirviö 2003).

Removal of fines decreased both the tensile strength and density; the decrease in density was much higher for sheets prepared from ProLab-refined pulp (Figs. 4.20 and 4.21). The density was still higher in the sheets where the fines were removed (ProLab refined pulp) than the density of the original pulp, which was due to the fiber shortening during refining. Addition of fines to both types of pulps (Valley and ProLab) increased both the tensile strength and the density by increasing the amount of bonded areas in the sheets giving an improved bonding ability of the pulp (Peterson et al. 2001) as a result. The harsher refining seemed to produce fines that were closer to the dimensions and properties of the cut fibers. This was seen as a linear relationship between the tensile index and density in pulps with or without fines.

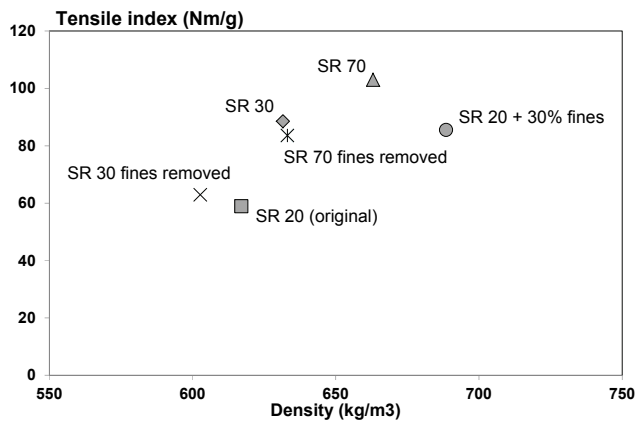


Fig. 4.20. Tensile index vs. density of dry sheets after gentle refining (Valley). The sheets were tested with the IMPACT test rig (II).

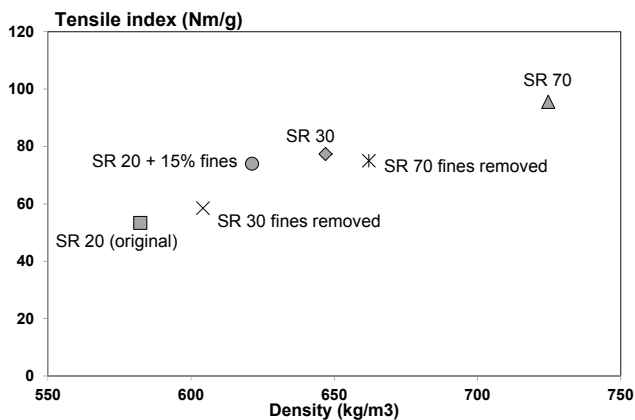


Fig. 4.21. Tensile index vs. density of dry sheets after harsh refining (ProLab). The sheets were tested with the IMPACT test rig (II).

Addition of surfactant decreased the density and had only minor effects on the dry tensile strength (Fig 4.22). The decreased density can be interpreted as a decrease in the level of bonding, which could be due to more even fiber surfaces and hindering of bond formation by the surfactant. From papermaking point of view, the decrease in density means an increase in bulk and therefore an improved bending stiffness (Kajanto 2008).

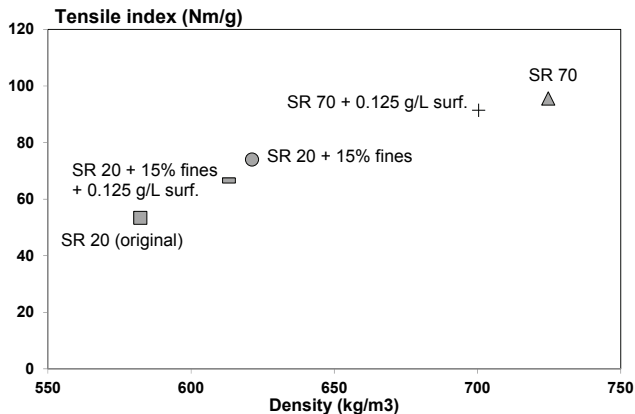


Fig. 4.22. Tensile index vs. density of dry sheets after harsh refining (ProLab), addition of 15% fines and/or addition of 0.125 g/L non-ionic surfactant. The sheets were tested with the IMPACT test rig (II).

4.2.3 Addition of galactoglucomannans (III)

Retention, density, dewatering and dry tensile index were measured for sheets prepared from PB TMP using the DDÅA (Table 4.2). The retention was calculated based on the weight of the dry sheet and compared to the theoretical sheet weight if all the fiber 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 fiber (Table 4.2). The maximum strength, however, was reached at higher dosages, 10 mg/g. Rojas and Neuman (1999) found that the addition of neutral or cationic guar gum increased the retention of glucose-containing fines. Both types of derivatives showed first an increase in the fines retention, followed by a maximum amount of fines retained, after which the retention decreased again. This behaviour was, according to the authors, 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. 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 larger amount is possibly 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.

The retention increased with increased amount of C-GGM, while the tensile strength first decreased and then increased (Table 4.2). The observed behaviour could be due to fines, as well as pitch-type dissolved and colloidal substances being retained at first, and when these substances have been consumed by the additive, the fiber-to-fiber linkages started to form. The dewatering time increased slightly with increasing dosage of C-GGM, which was due to 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 was 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 (Table 4.2). 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. Xu et al. (2011) suggested that the carboxymethylated GGMs can form a mono-electric layer on the fiber surface and by binding to metals and negatively charged particles, the sheet structure would be denser. The retention was slightly lower when compared to the use of GGMs or C-GGM, the ionic binding did not seem to be as effective in retaining fines and dissolved and colloidal substances to the sheet.

The addition of A-GGM increased retention and dewatering time, while the density and tensile strength were only slightly affected (Table 4.2). Since the DS was very low, and the hydrophobic tail is assumed to be found 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 dissolved and colloidal substances. The hydrophobic tail was able to orientate towards the hydrophobic particles and increase their retention, possibly through a micelle-like structure.

Table 4.2. The total retention, density, dewatering time, tensile index and, in brackets, 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)

4.3 Surface properties of final products (III, IV)

The last part in this thesis is related to the surface modification of paper. The possibility of using GGMs/GGM derivatives was examined. The surface properties of paper are equally important as the mechanical properties of the dry paper, as they influence printing for instance. More details are found in papers III-IV.

The contact angle of TMP papers containing selected derivatives was measured (Fig. 4.23). 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 < cationic starch (CS) < A-GGM. The results indicate that hydrophobic particles in the sheet, e.g. extractives, were covered with GGMs/derivatives, giving a more hydrophilic character to the paper 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.

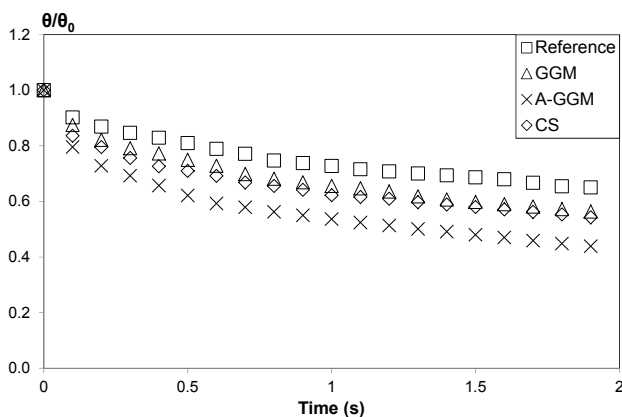


Fig. 4.23. Contact angle measurements of sheets prepared from recycled PB TMP using the DDÅA. The results have been recalculated for comparison purposes according to θ/θ_0 , where θ = contact angle at a given time and θ_0 = contact angle at 0 s. The dosage of the additives was 1 mg/g fiber. GGM = galactoglucomannan, A= iminated GGM, CS = cationic starch (III).

ToF-SIMS was used as a tool to map the presence of GGMs/derivatives on the paper surface. GGMs and modified GGMs were at first analyzed separately in order to determine distinguishing peaks for each of the

samples (Table 4.3). The fiber sample displayed peaks at 19 (H_3O^+), 31 (CH_3O^+), 60 ($\text{C}_2\text{H}_4\text{O}_2^+$), and 61 Da ($\text{C}_2\text{H}_5\text{O}_2^+$) (Goacher et al. 2011). In general, the GGMs and C-GGM displayed stronger patterns for carbohydrate fragmentation than the fiber sample (IV). The C-GGM also showed peaks at 58, 102, 132, and 134 Da, which originate from N-containing fragments (Staudigel et al. 2007, Juhanaja et al. 2007). The A-GGM displayed peaks at 64 and 68 Da, which could originate from $\text{C}_4\text{H}_2\text{N}^+$ and $\text{C}_3\text{H}_2\text{NO}^+$ fragments.

Table 4.3. Suggested positive secondary ions found in the ToF-SIMS spectra.

Source	Positive secondary ion and mass (Da)
Hydrocarbon fragments	$\text{C}_n\text{H}_{2n+1}^+$ 15, 29, 43..., $\text{C}_n\text{H}_{2n-1}^+$ 13, 27, 41..., $\text{C}_n\text{H}_{2n-3}^+$ 39, 53, 67...
Carbohydrates	$\text{C}_6\text{H}_7\text{O}_3^+$ 127, $\text{C}_6\text{H}_9\text{O}_4^+$ 145
Fiber	H_3O^+ 19, CH_3O^+ 31, $\text{C}_2\text{H}_4\text{O}_2^+$ 60, $\text{C}_2\text{H}_5\text{O}_2^+$ 61
C-GGM	$\text{C}_3\text{H}_8\text{N}^+$ 58, $\text{C}_5\text{H}_{12}\text{NO}^+$ 102, $\text{C}_5\text{H}_8\text{O}_4^+$ 132, $\text{C}_5\text{H}_{10}\text{O}_4^+$ 134
A-GGM	$\text{C}_4\text{H}_2\text{N}^+$ 64, $\text{C}_3\text{H}_2\text{NO}^+$ 68

The GGMs/derivatives were sprayed on freshly formed paper sheets made from kraft pulp and these sheets were analyzed on both sides by ToF-SIMS (IV). For C-GGM, the peaks at 58, 102, 132, and 134 Da were easy to detect. The GGMs/GGM derivatives showed stronger signals for the carbohydrate fragments of the $\text{C}_x\text{H}_y\text{O}_z^+$ type compared to the fiber sample (Goacher et al. 2011). A-GGM seemed to cover more of the fibers, since the peaks at 19, 31, 60, and 61 Da were much weaker or not visible at all compared to GGM or C-GGM. The characteristic peaks of the A-GGM at 64 and 68 Da were almost non-existent in the paper samples. The reason could lie in the low proportion of the functional group to the polysaccharide; only one hydrocarbon chain per GGM chain. Another possibility is the orientation of the hydrocarbon chain at the reducing end of the A-GGM. The A-GGM was sprayed as a water solution onto wet paper; therefore the orientation of the A-GGM could be driven by the air-water interface. As the amount of

water decreased through the paper, the A-GGM was deposited on top of the fiber and the tail oriented towards the spaces between the fibers. With ToF-SIMS only the outermost 1-2 atomic layers are analyzed (Vickerman 2001), and if the hydrocarbon tail was oriented towards the center of the paper, it would not show in the spectra. The images of the papers (Fig. 4.24) revealed that the A-GGM covered most of the surface of the paper.

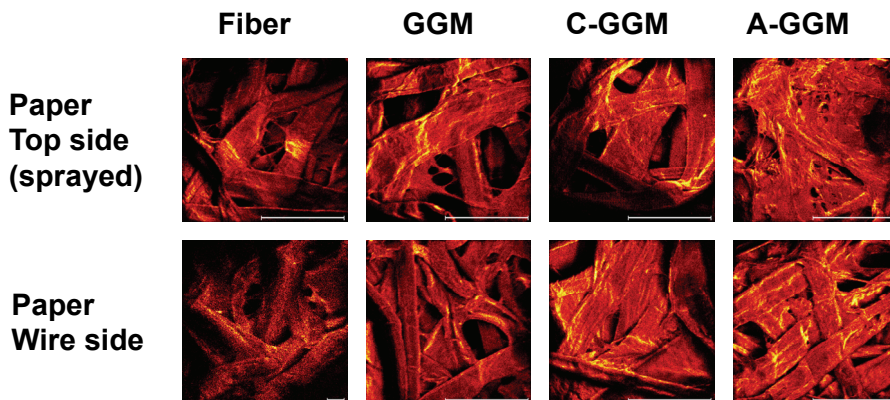


Fig. 4.24. ToF-SIMS total ion images of the two sprayed top side and the wire side of the paper (bar: 100 μm , except in the wire side of the paper containing fibers 10 μm) (IV).

When comparing the two sides of the paper, it was seen that e.g. C-GGM penetrated through the paper to the wire side when sprayed on the top-side, since the wire side also displayed the characteristic peaks for C-GGM (IV). The wire side of the A-GGM did not show any of the characteristic peaks, the underlying reason could be the low content of the functional group, the orientation as described above or that no penetration had taken place. The reason could also lie in the molecular structure of the A-GGM resulting in rheological effects that keep the compound on the surface.

The paper sheets sprayed with A-GGM were further analyzed by FTIR spectroscopy (Fig. 4.25). The papers showed the stretching of O-H at 3400-3200 cm^{-1} and the C-O-C stretching at 1300-1000 cm^{-1} . Also a peak at $\sim 1735 \text{ cm}^{-1}$ originating from the C=O in the acetyl groups appeared (Yu et al. 2007). The A-GGM sprayed paper further displayed peaks at 2915 and 2848 cm^{-1} , originating from $-\text{CH}_2-$. The results indicate that the hydrocarbon chain was detected by the FTIR spectroscopy, which has an analysis depth

of a few μm , while it was not detected with ToF-SIMS, which analyzes only 1-2 atomic layers. This points towards the hydrocarbon chain being close to the surface, but not at the outermost layer, and supports the assumption that the tails were oriented away from the surface of the paper.

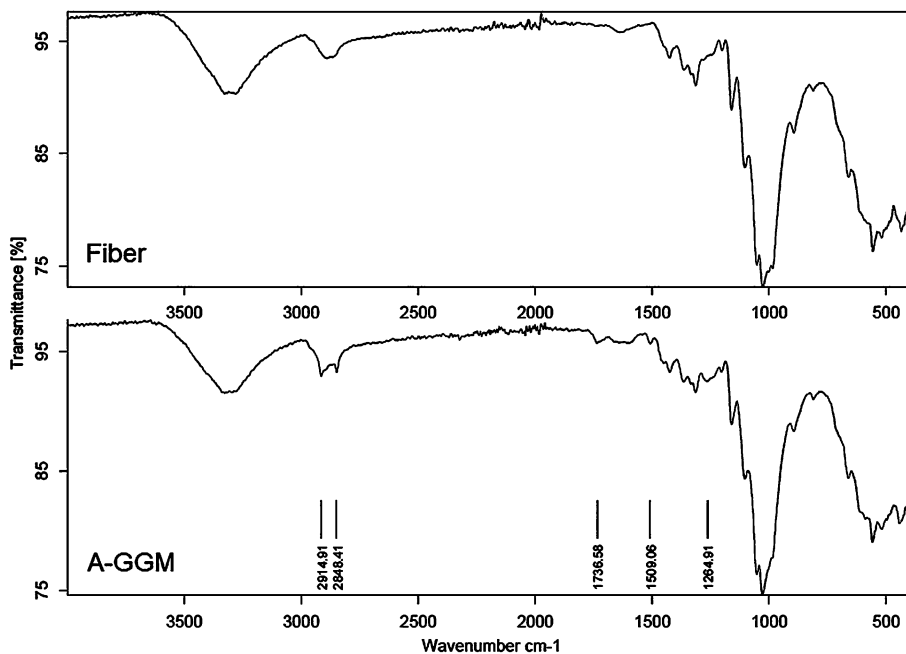


Fig. 4.25. FTIR spectra of papers containing only fibers (top) and with A-GGM added by spraying (bottom) (IV).

FE-SEM was used as a tool to confirm and visualize the observed changes in the surface morphology due to spray addition of GGM derivatives (Fig. 4.26). When GGM or C-GGM was sprayed, they seemed to increase the bonding between fibers slightly by penetrating into the fiber network. When A-GGM was added, it created a film on top of the fibers.

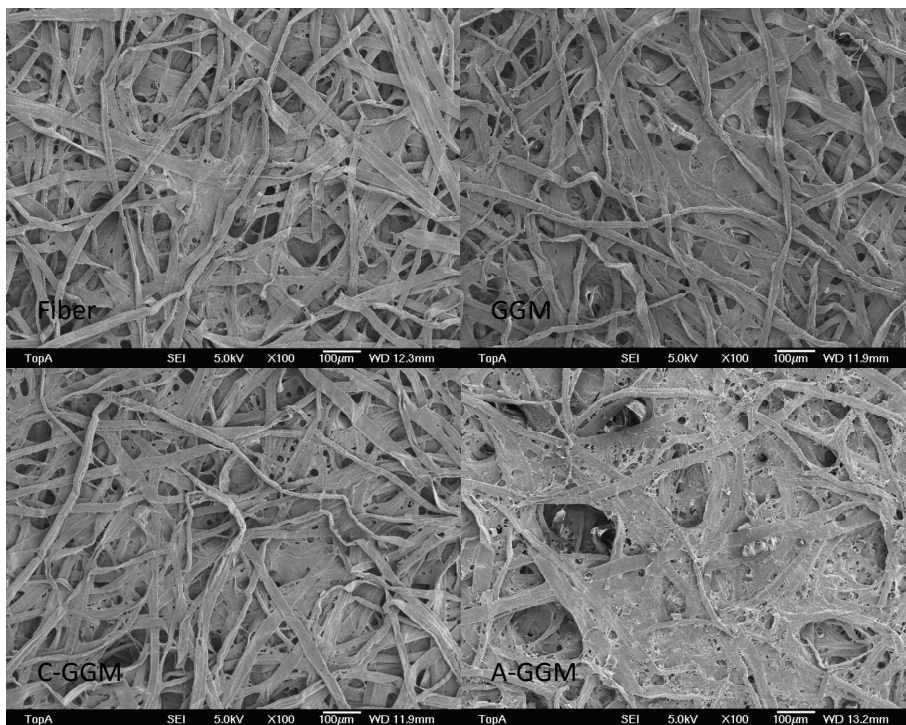


Fig. 4.26. FE-SEM images of papers made of bleached kraft pulp after spraying of GGM derivatives. Top left: Fiber, top right: GGM, bottom left: C-GGM, bottom right: A-GGM (magnification $\times 100$, bar $100\ \mu\text{m}$) (IV).

5. Conclusions and future outlook

By altering the surface tension, the pH and the conductivity of the water used for papermaking, it is possible to change the dewatering behavior, as well as the mechanical properties of the wet and dry web. When using a non-ionic surfactant, the cmc is crucial for the mechanical properties. At concentrations up to cmc, the dry content after wet pressing increases thereby increasing the initial wet tensile strength and residual tension at 2% strain. The dewatering is faster, and the density and the tensile strength increase for the dry sheets. The more efficient dewatering is the primary effect of the surfactant, which results in dryer paper sheets and an increased amount of fiber-fiber bonds in the paper after wet pressing. At concentrations above cmc, both the wet and dry mechanical properties deteriorate perhaps due to the hindered formation of hydrogen bonds sites by the surfactant.

Using a slightly acidic pH results in decreased dry content after wet pressing and deteriorated wet mechanical properties. The density for dry sheets decreases, as the fibers are less swollen at the lower pH. When Na^+ ions are used instead of Ca^{2+} ions for conductivity adjustment, the initial wet tensile strength at constant dry content decreases, most probably due to a decreased coefficient of friction.

Gentle refining of fibers results in increased initial wet tensile strength and residual tension as the fibers are stretched out and more flexible after the treatment. The formed fibril-like fines promote hydrogen bonding, which is also seen as an increased initial wet tensile strength when the fines are added to original pulp. A prolonged dewatering time and lower dry content after wet pressing are seen as negative effects of the refining. When the fines are removed, the dewatering time is close to the dewatering time of the original pulp, which indicates that the internal or external fibrillation does not significantly affect the dewatering. Instead, the amount and the quality of the fines are critical for the dewatering process. The residual tension at 2% strain does not decrease as much as the initial wet tensile strength when the fines are removed, implying that the fiber properties, i.e. the internal/external fibrillation, are important for the residual tension. Also

the straightening out of the fibers significantly increases the load distribution in the wet fiber network.

After harsh refining, the fibers are much shorter and the fines consist of fiber fragments. The dry content after wet pressing and the wet tensile strength are lower than for gently refined pulp. The density for dry sheets increases due to the damaged fibers and fiber fragments. When the non-ionic surfactant is added to the harshly refined pulp, the dewatering time is somewhat shorter and the dry content after wet pressing increases. This could be due to collapsed fibrils on the fiber surface. The initial wet web strength decreases slightly when the surfactant is added together with fines to original pulp, maybe due to adsorption of the surfactant to the surfaces of the fibers and fines, which results in particles sliding over each other more easily.

GGMs can be modified by cationization (C-GGM), carboxymethylation (CM-GGM), and imination (A-GGM). When native GGMs are added to the pulp, the initial wet web strength and elastic modulus increase due to the dispersing effect of GGM on the fibrils. Native and modified GGMs also increase the dry tensile strength and the retention of substances released from TMP. C-GGM acts through an electrostatic mechanism by adsorbing to negatively charged surfaces. CM-GGM is suggested to bind to metal ions present in wood which are released upon refining. A-GGM is assumed to act through the hydrophobic hydrocarbon chain at the reducing end of the GGM chain. The tail is oriented towards the hydrophobic particles, the paper containing A-GGM are the most hydrophilic.

Native GGMs, C-GGM and A-GGM can also be sprayed on freshly formed paper sheets and the surface of the papers can be analyzed. GGMs and C-GGM penetrate through the paper, while A-GGM creates a film on top of the fibers. The hydrophobic tail is located close to the surface but not at the outmost layer.

The results obtained in this thesis can be used for improvement and tailoring of paper properties as well as for controlling the runnability of the paper machine. In the next step continuing this work, it could be interesting to take a closer look at the mechanisms of action; how different polymers and chemical modifications of fiber surfaces affect the interdiffusion between the fibers. The importance of the gel-like layer could be studied

and how the interactions over the gel-like layer can be tailored to give desired effects. A step towards tailoring of interactions could be taken, where design of additives and optimization of fiber treatments would be possible in order to obtain bio-based products with desired properties.

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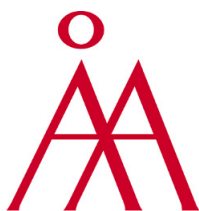
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