Papíripar

Special issue for COST

COST Action E54
Characterisation of the fine structure and properties of
papermaking fibres using new technologies

BUDAPEST
16–17 October 2008

COST is supported by
the EU RTD Framework Programme

![Hamburger Hungaria Containerboard logo]

Hamburger Hungaria
Containerboard

Dunaújváros new PM7
– in the heart of Europe

The New Papermill
is growing!

Just a year ago, on November 9, 2007, we laid the foundation stone - and on a sunny day in October, we could hold the topping ceremony in the huge construction.

A new landmark is born , with its 400 m length and 28 m height. The built-up space corresponds to 600 family houses!

Day by day, the paper machine moves into its home, from where it will serve you from July 2009.

Papíripar

TARTALOM

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Előszó

Prof. Arnis Treimanis

Először is szeretném megköszönni a „Papíripar" szerkesztőbizottságának, hogy megjelenteti az EU E54 COST Akció 2008. október 16-17-én Budapesten **„Papírgyártásban használt rostok finomszerkezetének és tulajdonságainak jellemzése új technológiákkal"** címmel megtartott szakszemináriumának előadásait.

Az E54 COST Akció 2006-ban indult és 2010. decemberig tart. Máig 19 ország csatlakozott az Akcióhoz, és számos, a COST-ban nem résztvevő ország tudósai fejezték ki kívánságukat, hogy bekapcsolódjanak a projekt tevékenységébe.

Az E54 Akció fő célkitűzése az, hogy új ismereteket szerezzünk a papíripari rostok mikro- és nanoszerkezetéről, és a rostok hatékony és fenntartható felhasználásához szükséges tulajdonságokról a hagyományos és az új termékekben.

Örömömre szolgál, hogy arról tájékoztathatom Önöket, hogy az Akció eddigi kétéves periódusa alatt számos nagyon érdekes megközelítést és módszert dolgoztak ki az Akció résztvevői. Ennek egy része tükröződik az újságnak ebben a kiadásában.

Az E54COST Akció három munkacsoportot (MCS) fog át.

MCS1: Különböző kezelések hatása a papíripari rostok szerkezetére és kémiai összetételére

A Munkacsoport tevékenységének célja, hogy
- új jellemzési és értékelési módszereket fejlesszen ki és
- új adatokat gyűjtsön és generáljon a papírgyártásban használt rostok finomszerkezetére vonatkozóan, olyan körülmények között, ahogy ezeket az ipari folyamatokban előállítják.

A Munkacsoport tevékenysége a rostok finom- és nanoszerkezetére koncentrál a leginkább releváns ipari kezelési, elsősorban rostosítási, fehérítési, őrlési és recycling technikákat követően.

MCS2: Egyedi rostok kezelése és jellemzésük mikrotechnológiákkal;

Ez a Munkacsoport új eszközök kidolgozására fókuszál, nevezetesen a mikrotechnológiákra, melyekkel az egyedi rostokat kezelni lehet, és a rostszerkezeteket laboratóriumi körülmények között lehet vizsgálni.

MCS3: Rostok finomszerkezetének hatása papírképző tulajdonságaikra, valamint kémiai és enzimatikus reakcióképességükre

A 3. Munkacsoport kutatói és szakértői tapasztalatot cseréltek a rostok finomszerkezetének és módosításaiknak a belőlük gyártott papírok tulajdonságaira gyakorolt hatásáról. A munka lényege különböző kérdésekre koncentrált:

- milyen hatást gyakorolnak a kémiai mechanizmusok a rostok nano-felületén (azaz például a maradék lignin, hemicellulóz és funkcionális csoportok mennyisége és elhelyezkedése) a fontosabb rosttulajdonságokra, és ezt hogyan lehet értelmezni a papír minőségére vonatkozóan?
- a rostfelületek mechanikai paraméterei, mint pl. a rostfal vastagsága, a rostfal porozítása, valamint keménysége hogyan hat a rost tulajdonságaira és így a végső papírtermékre?

A három munkacsoport között kapcsolat alakult ki és ezt fenn is kell tartani, mivel minden szempont fontos a papírgyártásban használt rostok finomszerkezetének és kémiájának jobb megértéséhez.

Végezetül szeretném megköszönni az E54 COST Akció Budapesten megtartott szakszemináriuma helyi szervezőinek a kiváló munkát, mellyel biztosították a nagyon sikeres és gyümölcsöző tanácskozást. Közülük szeretném megemlíteni Dr. Víg András, Lele István, Szőke András, Pesti Sándor és Dr. Szikla Zoltán urakat.

Az Akció következő ülésére Tamperében, Finnországban kerül sor, 2009. május 4-6 között.

Prof. Arnis Treimanis, Riga, Lettország
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Preface

First of all I would like to thank the Editorial Board of the journal „Papíripar" for its kind consent to publish the proceedings of the EU COST Action E54 **„Characterisation of the fine structure and properties of papermaking fibres using new technologies"** Workshop in Budapest 16-17 October 2008.

COST Action E54 started in 2006 and will last till December 2010. Now 19 countries have joined the Action, and the scientists from several COST non-participating institutions have expressed their wish to enroll in the project activities.

The main objective of the Action E54 is to generate new knowledge on the micro- and nanostructure of papermaking fibres and properties required for efficient and sustainable use of fibres in traditional and new products.

It is my pleasure to note that during two years of the Action's time span several very interesting approaches and methods were developed by the Action's participants. Part of them is reflected in this journal issue.

COST Action E54 comprises three working groups.

WG1: **Structure and chemical composition of papermaking fibres after different types of treatments**

The objective of the activities of this WG is to
- develop new methods for the characterisation and assessment, and
- to accumulate and generate new data on the fine structure of fibres for papermaking as they are produced in industrial processes.

The activities of this WG are focused on the fine and nano-structure of the fibres after the most relevant industrial treatment techniques, in particular pulping, bleaching, beating and recycling.

WG2: **Treatment and characterisation of individual fibres by microsystem technologies**

This WG is focused on the development of new instruments namely microsystem technologies by which individual fibres can be treated and fibre structures can be investigated at laboratory scale.

WG3. The impact of the fine structure of fibres on their papermaking properties and their chemical and enzymatic reactivity

The scientists and experts of WG3 exchange their experience with respect to the impact of the fine structure of fibres and their modification on the quality of the paper produced thereof. The emphasis of the work is focused on different questions:

- what is the impact of the chemical mechanisms at the nano-surface of fibres, i.e. the amount and localisation of, for example, residual lignin, hemicelluloses and functional groups, on major fibre properties and how does this translate into paper quality?
- how will mechanical parameters of fibre surfaces such as fibre wall thickness, fibre wall porosity as well as hardness influence the fibre properties and thus that of the final paper product?

The links between the three working groups are created and have to be maintained since all aspects are important for a better understanding of the fine structure and chemistry of papermaking fibres.

Finally I would like to cordially thank the local organizers of the COST Action E54 Workshop in Budapest for their excellent work to guarantee a very successful and fruitful meeting. Among them I would like to mention Dr. András Víg, Mr. István Lele, Mr. András Szőke, Mr. Sándor Pesti, Mr. Zoltán Szikla.

Next meeting of the Action takes place in Tampere, Finland, 4-6 May, 2009.

Chairman of the COST Action E54
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Különkiadás

Polyánszky Éva

Megtiszteltetés egyesületünk PAPÍR-IPAR c. lapja számára, hogy egy nemzetközi kutatási együttmüködés (COST E54 akció) 2008 október 16–17-iki budapesti üléséről tudósíthat.

Ebben az akcióban 19 európai ország, köztük Magyarország müködik együtt, hogy minden partner a saját tudását, müszereit latba vesse egy közös cél érdekében: ismerjük meg minél alaposabban a cellulózrost azon tulajdonságait, meíyek felelősek a papírgyártás során a rostok viselkedéséért. A végső cél pedig a minél jobb minőségű papír előállítása.

Alapító főszerkesztőnk, Dr. Vámos György biztos örömmel venné kézbe ezt az újságot, mely a klasszikus kutatás nemzetközi együttmüködésben létrehozott eredményeit mutatja be.

Személy szerint számomra külön öröm, hogy a konferencia során az akció olyan résztvevőivel is találkozhattam, akikkel a 90-es évek elejétől több mint 10 éven át – Magyarország COST képviselőjeként – együttmüködhettünk számos közös kutatásban az életciklusanalízistől az elfolyásmentes papírgyártásig stb, melyek mindegyikének eredményei alapvető fontosságúak a papírgyártásban.

Magyar olvasóinknak biztosan feltűnik, hogy az újság szerkezete eltér az utóbbi időben megszokottól. Az akció és a konferencia beosztása szerint munkacsoportonként mutatjuk be 12 előadás rövidített változatát angolul, illetve magyar összefoglalóval azok számára, akiknek az angol szakszöveg esetleg gondot okozna.

Ez a szám különleges tehát, de a következő is feltehetően is az lesz, mert semmi sem örök, csak a változás.

Újságunk jövő évi megjelenése – gazdasági és szakmai okok miatt – nagy valószínűséggel sok újdonsággal szolgál majd olvasóink számára.

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Special issue

It is an honour for the journal of our Association „PAPÍRIPAR" to report on the session of an international research co-operation (COST Action E54) held in Budapest on 16-17 October 2008. There are 19 European countries including Hungary co-operating so that each partner contributes his knowledge, instruments serving one common goal: to be more and more familiar with the properties of the cellulose fibre that are responsible for the behaviour of fibres during papermaking. The final objective is the production of paper of the possible highest quality.

Our founder and editor-in-chief, Dr. George Vámos would be happy to take this journal in his hands demonstrating the results achieved in international co-operation of a classic research. For me personally it is a special privilege that during the conference I could meet participants of the Action whom I had the chance, in my capacity of Hungary's COST-representative, to work together over more than ten years from the beginning of the nineties, in several joint research projects, from "life cycle assessment" through "papermaking towards zero liquid effluent" etc., the results of which are of basic importance in papermaking.

Our Hungarian readers will probably realize that the structure of the journal differs from that of the ordinary appearance. According to the Action and Conference schedule an abbreviated version of twelve papers will be introduced by Working Groups in English and with summary in Hungarian for those whom the understanding of the English technical text would cause difficulties. This issue will be thus a special one but presumably the next one will be the same since nothing is eternal but the changes.

The appearance of our journal in the next year, due to economic and professional reasons will, most probably, furnish our readers with lot of novelties.

Éva Polyánszky
redactor in chief
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A Dunapack-Hamburger dunaújvárosi gyárának és az új csomagolópapírt gyártó gép projektjének bemutatása

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Szikla Zoltán

A Prinzhorn csoport bemutatása vezeti be az előadást. Bemutatásra kerül a magyarországi papírgyártásban és papírfeldolgozásban való domináns szerepe. Az elmúlt évben a csoport árbevételének több mint 28%-a származott más közép- és kelet-európai Dunapack leányvállalatoktól. Az előadó a Dunaújvárosi telephely jelenlegi és jövőbeli struktúráját mutatja be. Itt a Hamburger Hungária Kft. új gépének felfutása után a jövő évben 520.000 t/év papírgyártó kapacitás áll rendelkezésre. A 205 millió eurós beruházás szíve a 7,8 m széles papírgép, konstrukciós sebessége 1.500 m/perc, barna 70–150 g/m² hulladékalapú csomagolópapírokat fog gyártani. A technológia néhány technikai részlete mellett a hallgatóság a hulladékpapír-forgalomról is kap adatokat.

Gyárlátogatás a COST E54 programjában

A Cost 54 akcióprogram magyarországi ülése során az érdeklődők közel 40 fős csapata meglátogatta a Dunapack Ltd Dunaújvárosi Gyárát. A látogatás aktualitását az adta, hogy pont az ülés megnyitását megelőző napokban tartották Közép-Kelet Európa legnagyobb papíripari beruházásának bokrétaünnepségét. A gyárlátogatás során a látogatók meggyőződhettek a meglévő egység működési körülményeiről, mely éppen akkor 100 g/m²-es hullámosított réteget 900 méter feletti sebességgel gyártott, valamint megtekinthették az új papírgép építészeti eredményeit is. Meggyőződhettek arról, ahogy az alábbiakban idézett kiadott sajtóközlemény nemcsak reálisan ambiciózus célokat fogalmazott meg, hanem

annak határidős megvalósítása a legjobb ütemben halad.

Bokrétaünnepség

Az október 14-i bokrétaünnepségen – amelyen a tulajdonos Thomas Prinzhorn is részt vett – *Galli Miklós*, a Dunapack Zrt vezérigazgatója arról is beszélt, hogy a pénzügyi válság közvetetten érintheti ugyan a céget, de a beruházást semmiképpen.

Braunecker Antal, a társaság értékesítési igazgatója pedig azt hangsúlyozta, hogy a régióban szükség van egy ilyen kapacitású gyár felépítésére. Magyarországon ugyanis ma kb. 500.000 tonna hulladékpapírt gyűjtenek be. Az új gyár évente 400.000 tonnát hasznosít majd, az ország hulladékpapír termelésének nagy részét feldolgozza.

Bencs Attila projektvezető a bokrétaünnepségen felidézte, hogy az új üzem alapkövét tavaly novemberben rakták le, idén szeptemberben pedig megkezdődött a gyártó berendezések telepítése, szerelése. A próbaüzemelést jövő év májusára tervezik a szakemberek, 2009. júliusában pedig a tervek szerint elindul a papírtermelés.

Ez a fejlesztés az eddigi legnagyobb magánerős környezetvédelmi beruházás Magyarországon, amelynek révén az ország teljesíteni tudja az Európai Uniós irányelvekben Magyarországra meghatározott hulladékpapír-hasznosítási kötelezettségét.

Az új papírgép a felhasználók igényei szerint különlegesen vékony és könnyű csomagolópapírt fog gyártani – 70 és 150 g közötti négyzetméter-súlyban –, közel nyolc méter szélességű tekercsekben, a termékek széles skálájának biztonságos csomagolására.

Az üzem mintegy 280 főnek biztosít munkát közvetlenül, de a beruházás megvalósulása révén a térségben további mintegy 600 fő számára oldódik meg a foglalkoztatottság.

Paper Industry in Hungary

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Introduction

The Prinzhorn Group is an international private owned paper and packaging producer. Its turnover amounted last year to 1094 million €. The production capacities reach 1.150.000 t containerboard, 565.000 t corrugated products and 183.000 t label paper. The concern employs 3.779 people in 9 European countries. The Dunapack Group's share from the total capacity is 26% in the paper business and 59% in the converting business. In Hungary there are two paper mills totally with 310.000t/a containerboard capacity and three corrugating mills with 155.000 t/a capacity.

In 2007 Dunapack's Hungarian share was above 55% both in the total paper production and in the corrugated production. The change of the Hungarian paper and board production and consumption in the last few years is shown in **Fig. 1. Fig. 2** shows figures of the corrugated board industry in the same period.

The biggest still running papermachine in Hungary is the PM3 in Dunaújváros/Dunapack. The annual capacity for 100% recycled corrugated medium is 170.000 t. The corrugating machine at that site had a capacity of 61 million qm. At the Dunaújváros site of Dunapack 250 people are employed.

Investment of Hamburger Hungaria Ltd in Dunaújváros

At that site the investment of the new papermachine of the Prinzhorn Group is on stream. The project is managed by the subsidiary Hamburger Hungaria Ltd. The main items and targets of the project are a paper machine with 350.000 t/a capacity for Wellenstoff, Testliner 2 and 3, Schrenz in the range of 70-150 g/qm, a waste paper and a finished good store for approx. two weeks of production. The planned production speed reaches 1350 m/min with 7,8 m trimmed width. Foundation works started in November 2007 and start up is targeted in June 2009. The investment costs reach 205 million €. The machinery takes about 60% of that. The main suppliers are

Item	Supplier
Paper machine	Voith
Slitter-winder	Metso
System planning	TMB/BMH
Transformators	Siemens
Drive, motors	ABB

The new stores of the mill will have a direct connection to the existing systems on both sides, to the recovered paper side and to the automatic roll warehouse. The stock preparation – with a conventional pulper, high and low consistency cleaning, fractionating – has elements which have already been approved in the existing mills. The paper machine has a Duo-
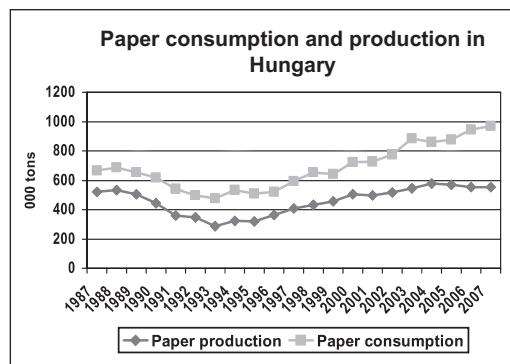
Fig. 1.
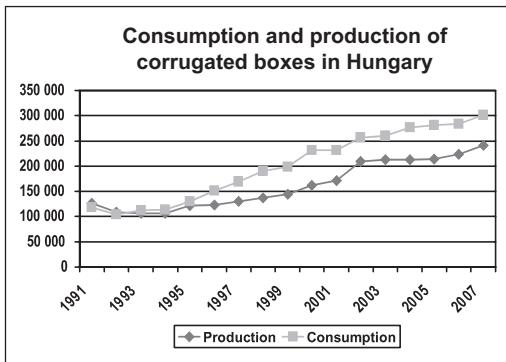
Fig. 2.
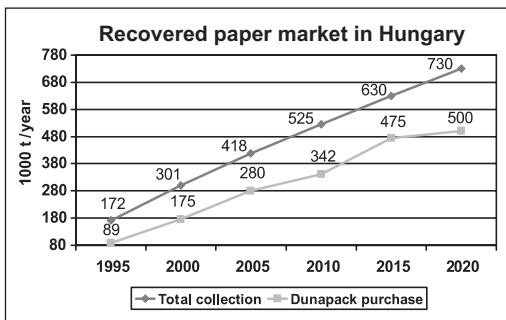
Fig. 3.
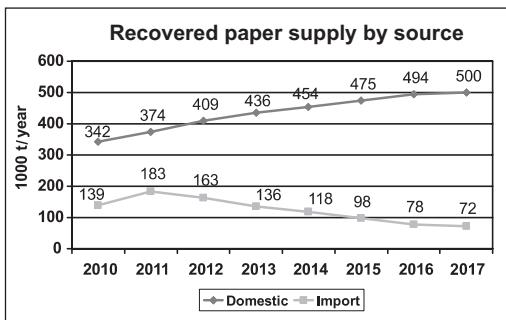
Fig. 4.

Former Masterjet II former, a three nip Nipcoflex press with shoe press nip, combined drying with one and two raw drying cylinder, a Speed Sizer as filmpress.

With this new machine – the only new one in the last decades in the Central-Eastern-European region- a big gap will be closed for the packaging industry. The lightweight container-board production will come nearer to the market where the biggest growth is forecasted for the common years. The investment involves environmental goals, too. As the **Fig. 3** shows Dunapack/Hamburger will certainly remain the biggest user of the domestic packaging waste in Hungary, even in the case, if the volume of the collected recovered paper will grow in measure represened in the figure.

The increase of the collection of recovered paper shows that after a shorter period of import necessity the Hungarian collection and the closed region can cover the demand of the new machine on commodity grades. **See Fig. 4.**

Conclusion

The growth of the recovered paper collection, the containerboard and corrugated board production, consumption was since the middle of the nineties continuous. The increasing demand on modern packaging makes necessary to start production of new light weight RCCM grades in the region. The trend and the must of growing recovered paper collection makes possible to use Hungarian tradition of papermaking at Dunaújváros in economical size with the new PM7 from Hamburger Hungaria ltd.

Kutatási tevékenység a cellulózrostok finomszerkezetének területén a Papíripari Kutatóintézetben (PKI) Budapest

Hernádi Sándor – Lele István

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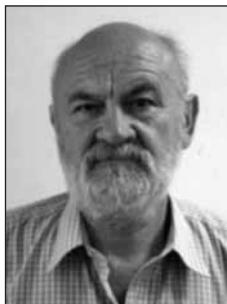
Hernádi Sándor   *Lele István*

A Papíripari Kutatóintézetet 1949-ben alapították mint önálló kutatási szervezetet, amely a cellulóz- és papírgyártás, nyomtatás és a kapcsolódó iparágak területén fellépő problémákkal foglalkozott.

Az intézetet 1991-ben magántulajdonú céggé alakították.

Jelenleg az intézet a következő szolgáltatásokat nyújtja a cellulóz- és papíripar, papírfeldolgozás és nyomtatás területén működő vállalatok és intézmények számára:

– Kutatás és fejlesztés
– Vizsgálatok, szakértői mérések
– Műszaki és tudományos információs szolgáltatás
– Statisztikai és piaci információs szolgáltatás
– Elméleti és gyakorlati oktatás, részvétel főiskolai és egyetemi képzésben
– Szabványosítással kapcsolatos munkákban való részvétel

A rostok szerkezetét vizsgáltuk többek között

– Higany poroziméterrel
– Letapogató elektronmikroszkóppal (SEM)
– Különböző módszerek használatával a rost-víz kölcsönhatás tanulmányozásával.

Különböző alapanyagok, valamint papírok és töltőanyagok pórusszerkezetét vizsgáltuk. Különböző facellulózok és egynyári növények póruseloszlását és pórusátmérőjét mértük. Majd a papírlapok pórusait osztályoztuk méret szerint. Megállapítottuk, hogy a papírlapok három különböző pórussal, makropórussal, mikropórussal és szubmikropórussal rendelkeznek.

SEM technikát alkalmaztunk a cellulózrostok felületének vizsgálatához:

– öregítést
– különböző kezeléseket, illetve
– rostfrakcionálást követően.

Példaként néhány képet mutatunk az öregített papírfelületre és papírlapokra, melyeket Bauer McNett frakcionátoron frakcionált rostokból állítottunk elő.

A rost-víz kölcsönhatást

– Klemm szerinti vízfelvétellel
– Vízbe történő bemerítés utáni vízfelvétellel
– A papír felületére ejtett víz felszívódásával
– PDA készülékkel mért, rövid ideig tartó papírnedvesítéssel vizsgáltuk.

Research activity in the field of fine structure of cellulose fibres in PRI

Alex Hernádi and Istvan Lele

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Introduction

History of the Hungarian pulp and paper research.

Foundation of the research institute: 1949, its transformation into private company: 1991.

Based on its almost 60 years experience the Hungarian Paper Research Institute offers its services for companies and institutions, operating in the pulp and paper, paper converting, packaging, printing and related industries, as well as in trade and education.

We offer the following services:

– research and development in the area of pulp and paper production, paper and board converting**,** gluing, printing, environmental protection, collection and service of market, trade, production and technical data.
– tests, certifying measurements
– service of technical and scientific information
– service of statistical and market information
– theoretical and practical training, vocational education
– contribution to the formation and introduction of standarts

Experimental

The structure of fibres was investigated by

– Mercury porosimetry
– Scanning electron microscopy
– Studying fibre- water interaction using different methods

Results and discussion

MERCURY POROSIMETRY

One method for measurement of porosity of fibres and paper sheets is the mercury porosimetry. The clue of this method is that the mercury does not wet fibres and under pressure fills their pores

$$p = -2\gamma \cdot \cos\theta / r$$

there γ – surface tension of mercury,
θ – contact angle of mercury on the solid surface

Pore volume and pore size distribution can be calculated from capillary resistance and outer pressure.

A Carlo Erba mercury porosimeter measures the total pore volume in the range $0,1 – 100$ cm^3/g. The applied pressure during measurement changes between $10^4 – 10^8$ Pa.

Average pore radii of different fibres are given in **Table 1.**

• *The pore structure of paper [1]*
Paper itself contains a cluster of voids of different types and origin. The void system is incorporated in and amongst the components of solid network. Different methods can be used to investigate the effect of raw materials, rate of delignification, mechanical treatment (beating and pressing) on the pore volume and pore radii. It was established that the cellulose fibre has at least three different pore

Sample	Averge pore radii, µm	
	Micropores	Macropores
Linter	3,4	22
Black pine TMP NSSC Chemical pulp Bleached chemical pulp	3,2 3,1 3,4 3,3	10 17 17 28
Poplar TMP NSSC Chemical pulp Bleached chemical pulp	3,4 3,3 1,2 1,4	24 36 24 32
Beech Chemical pulp	3,4	30
Straw Chemical pulp Bleached chemical pulp	1,7 1,0	34 31

Table 1. Pore radii

system depending on the form of existence of fibres:

- submicropores, which exist only in swollen state between lamellas of microfibrilles,
- micropores, which are in the fibre wall and in the lumen and in pitch hole etc.,
- macropores which are the interfibre voids existing only in paper sheet and disappearing in pulp slurry condition

SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was used to investigate the surface of cellulose fibres after

- ageing,
- different treatments,
- fractionating of fibres.

Some pictures can be seen on the next pictures:

paper from 1797   *paper from 1609*
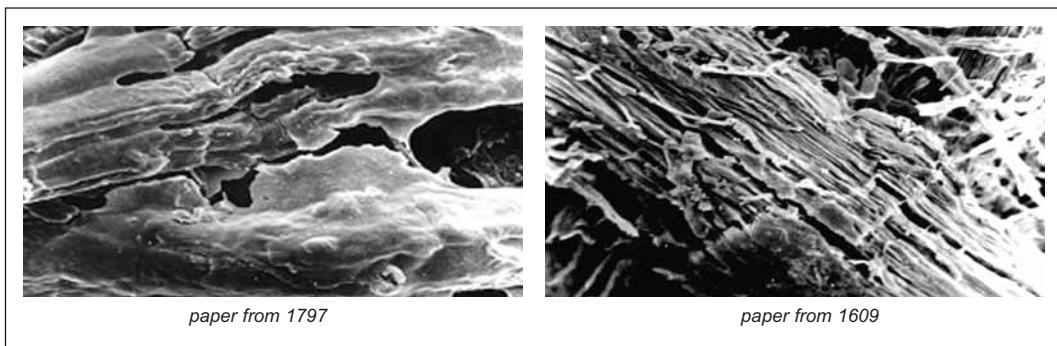
Fig. 1.: SEM pictures of ancient papers
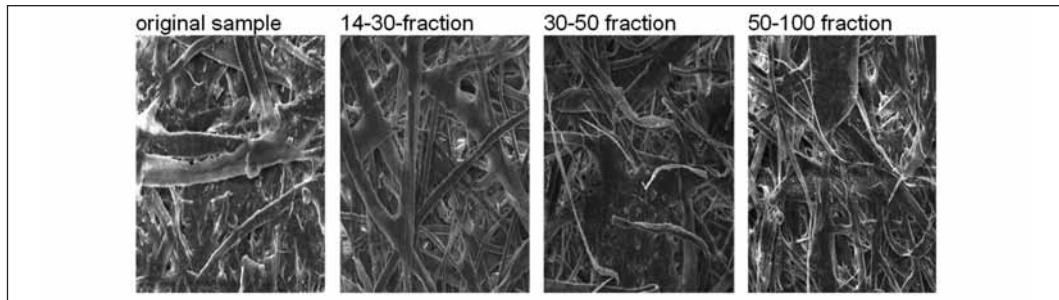
Fig. 2.: SEM picture of different fractions of OCC fibres
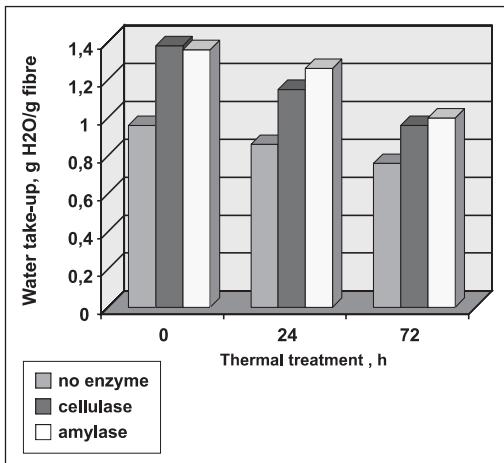
Fig. 3.: Water take-up of enzimatically treated aged paper

Fig. 4.: Measuring principle of PDA device

STUDYING FIBRE-WATER INTERACTION BY

– water take up by Klemm **Fig. 3.**
– water take up after immersion into water
– suction of water dropped onto the paper surface
– short time wetting of paper measured by PDA device (**Fig. 4**)

Results of short time wetting of paper measured by PDA device are shown in Fig. 5. **[2]**

Fig. 5.: Some curves of short time wetting on different paper surfaces

Summary

PRI as an industrial applied research institution uses special methods of research for the solution of industrial problems
– Beside this PRI also takes role in academic research and in the education
– Staff of the institute is involved into the education of students and PhD students
– Scientists of the institute participate on national and international conferences and symposia

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Pirolízis gázkromatográfia-tömegspektrometria és a módszer használata fa, farost, szálasanyagok és ezek származékainak vizsgálatára

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Tánczos Ildikó

A pirolízis gázkromatográfia-tömegspektrometria (Py-GC/MS) egy gyors és rendkívül hatékony módszer komplex szerkezetű szintetikus, s főleg természetes polimerek analízisére, valamint többkomponensű összetett rendszerek, mint pl. a papír is, vizsgálatára. A termikus vagy a reaktív pirolízis termékeit gázkromatográf segítségével választjuk szét, s tömegspektrumuk alapján azonosítjuk. A bomlástermékek analíziséből indirekt módon kapunk információt az eredeti mintáról.

Erősen poláris anyagok pirolízisekor gyakran a keletkező termékek is erősen polárosak, melyek nehezen jutnak át a pirolizátorból a gázkromatográfra, s direkt kromatográfiás analízisük is igen problematikus. Mellékreakcióként pedig dekarboxileződés fordulhat elő.

Ezen hátrányok kiküszöbölésére vezette be Challinor a 90-es években a tetrametil-ammóniumhidroxid (TMAH), mint reaktív ágens használatát a pirolízisben. A TMAH segíti a nagy molekulájú anyagok lúgos hidrolízét és közepes metilező hatása révén segíti a bomlástermékek kromatográfiás analízisét. A módszer leginkább elterjedt megnevezése: termikusan segített hidrolízis és metilezés – rövidítve THM.

Mi a linzi egyetemen vizsgáltuk a TMAH analitikai és technológiai alkalmazásának bizonyos aspektusait.

Az analitikai alkalmazásban tanulmányoztuk különböző fa-, lignin és cellulózminta, valamint számos modellvegyület reaktív pirolízisét. Magyarázatot találtunk a fa- és ligninminták THM pirogramjaiban korábban megfigyelt intenzív benzoesav-metilészter származékok megjelenésére. Modellvegyületekkel végzett kísérletekkel bebizonyítottuk, hogy a pirolízis körülményei között a ligninből tipikusan keletkező benzaldehidek a jelenlévő TMAH hatására Cannizzaro reakcióban vesznek részt, ahol az ekvimolárisan keletkező sav és alkohol párosból a benzoesavak rögtön teljes mértékben metileződnek észterekké, az alkoholok pedig kémiai szerkezetüktől függően csak részben alakulnak át metil-éterré.

A cellulóz és hemicellulózok hagyományos pirolízise rendkívül sok terméket eredményez, ami „fingerprint" (ujjlenyomat) jellemzésre nemigen alkalmas. A TMAH-ot Fabbri alkalmazta először mono-, di- és poliszacharidok pirolízisében. A hagyományos pirolízistől eltérő és kevesebb terméket kapott, közöttük a cukrok lúgos reakciójára jellemző szacharinsavak metilezett származékait. Mi uronsav THM analízisének alkalikus bomlásra jellemző származékát találtuk és azonosítottuk a pirogramban.

Az analitikában, különösen a lignin hidrolízisében jól bevált TMAH-t technológiai folyamatokban is kipróbáltuk. A fafeltárásban a nátrium-hidroxid helyett alkalmazva, ugyanolyan moláris koncentráció és hőfok mellett, jelentősen alacsonyabb kappa szám és könnyebb fehéríthetőség volt elérhető a cellulóz minőségének és hozamának csökkenése nélkül. Kraft feltárásban TMAH megfelelő arányú alkalmazása NaOH helyett lehetővé teszi a szulfidítás csökkentését, miközben a kitermelés akár nőhet is. Lo-solids® folyamatokban rögtön az első, az impregnációs fázisban alkalmazva mutatkozik meg előnyös hatása. A TMAH cellulózra gyakorolt hatásának vizsgálata során megállapítottuk, hogy 2 mol/l koncentráció fölött jóval erősebben duzzasztja a cellulózt, mint a NaOH, ugyanakkor a cellulóz késlelteti a TMAH termikus bomlását.

A Py-GC/MS technika rendkívül egyszerű módszernek mutatkozott fa- és cellulózszármazékok analízisére. Újonnan kidolgozott eljárással, izopropenil-acetát segítségével acetilezett vagy acilezett származékok acilezési fokának, a szubsztituensek arányának mintaelőkészítés nélküli gyors meghatározását teszi lehetővé.

Pyrolysis-Gas Chromatography-Mass Spectroscopy and its use for the analysis of wood, pulp, fibers and their derivatives

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Summary

The Pyrolysis Gas-Chromatography Mass-Spectrometry is a very quick and high-power method for the analysis of complex structure of wood, fibres and papers. The use of tetramethyl-ammonium hydroxide (TMAH) in the pyrolysis significantly increases the efficiency of the method. The thermally assisted hydrolysis and methylation (THM) was applied in the analysis of different wood and lignin samples as well as for lignin model compounds. The origin of benzene carboxylic acid methyl esters in the pyrograms of lignin and wood was declared. On the field of carbohydrates the pyrolysis of uronic acid was emphasized. TMAH, the chemical agent of the reactive pyrolysis, was applied also in technical processes as pulping of wood and swelling of cellulose. The Py-GC/MS proved to be very useful in the analysis of variously acylated wood samples, too.

Introduction

In spite of the great development in the analytical equipments, the analysis of natural materials as wood and fibres is difficult due to their complex structure and the high molecular weight of the components. Instead of a direct analysis, the analysis of their pyrolytic decomposition products provides an alternative possibility.

The products evolving at the pyrolysis will be separated by gas chromatograph and analyzed by mass spectrometry (Py-GC/MS). The original structure will be concluded from the decomposition products. The modern multifunctional pyrolysis systems enable evolved gas analysis, flash pyrolysis, reactive pyrolysis, thermal desorption and double-shot analysis [1].

The Py-GC/MS is a quick and high-power method especially for the chemical characteriza-tion of complex structures, both synthetic and natural polymers even in different composites (for example wood, wood composites, fibres, paper with additives, etc.).

Very small amount of samples are needed and in a very short time characteristic fingerprints can be obtained from the samples without being isolated their components.

However, pyrolytic analysis of highly polar samples may lead to incorrect conclusions if highly polar products are evolved which are difficult to transfer from the pyrolizer to the GC and are almost impossible to chromatograph. Furthermore, as unwanted thermal reaction decarboxylation may occur.

At the beginning of the nineties John Challinor [2] suggested the usage of tetramethylammonium hydroxide (TMAH) as reactive agent in the pyrolysis to avoid the above mentioned limitations. The TMAH is a strong base and a moderate methylating agent (**Fig. 1**).

The naming of the reactive pyrolysis method is not uniform. It is referred in the literature as:

- Pyrolysis in the presence of tetramethyl-ammonium hydroxide
- Pyrolysis-methylation GC/MS
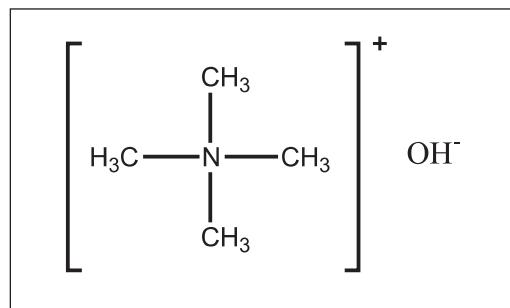
Fig.1. Tetramethylammonium hydroxide

- Thermochemolysis
- TMAH thermochemolysis and
- Thermal Hydrolysis and Methylation (THM)

Advantages of the THM analysis:

- Alkaline media helps the hydrolysis of polymers
- Fewer decomposition products – but different from the conventional pyrolysis
- The product yields are higher
- Lower temperature is enabled due to the chemical hydrolysis
- Pyrolytic decarboxylation may be avoided
- The evolved free carboxylic acids will be methylated
- Organic alcohols may be also methylated
- The methylated products are in most cases better to characterize and give sharper GC signals due to their increased volatility

The method is sensitive to the parameters of the analysis: temperature, TMAH/sample ratio, solvent of TMAH (methanol or water), sample preparation (incubation time of TMAH/sample mixture, etc.).

Analytical use of TMAH in reactive pyrolysis

THM analysis of wood

All components of wood have been already analyzed:

1. most studied is the THM analysis of lignin and the easiest to identify the decomposition products [3,4,5]
2. analysis of the cellulose and hemicelluloses: the decomposition pattern is more complicated and difficult to identify the decomposition products. Sensitive to the sample preparation [6].
3. Less work has been done with the extractives.

THM analysis of lignin

In contrast to the conventional pyrolysis the THM analysis of wood or lignin resulted always in relatively high amount benzene carboxylic acid methyl esters. They were absent in conventional pyrolysis. Mono-, di- and trimethoxybenzenecarboxylic acid methyl esters were detected. For

many years the origin of these α-carboxylic acids was not clear.

Martin and his co-workers [4] ascribed the presence of the benzene carboxylic acid methyl esters first of all to the technique since it avoids the decarboxylation, on the other hand to oxidation of some structural components of lignin.

Hatcher and his colleges [5] supposed that TMAH assists in the production of these acids but they did not find a possible reaction mechanism to explain the presence of them.

We succeeded to prove and demonstrate [7,8] that benzene carboxylic methyl esters can be produced from benzaldehydes that are typical side chain cleaved products in lignin pyrolysis. Benzaldehydes evolved in the pyrolysis (as aldehydes having no α-hydrogen) in the presence of TMAH can undergo to a Cannizzaro reaction producing in equimolar amounts the corresponding benzylic alcohols and benzene carboxylic acids – that is immediately a salt of the acid. Under the circumstances of the pyrolysis there is a second step in the reaction, the methylation of the evolved products (**Fig. 2**).

In the lignin pyrograms – also from different researchers - beside a given benzaldehyde the corresponding products of the Cannizzaro reaction can be really observed. To determine the importance of this reaction during the pyrolysis three factors must be considered:

1. the yield of the Cannizzaro type reaction of the evolved aldehydes
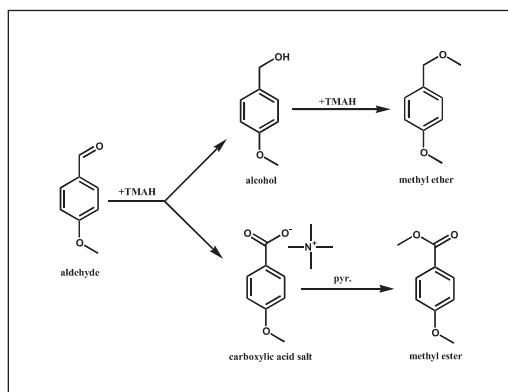
Fig. 2.: Cannizzaro reaction of benzaldehydes evolved in the pyrolysis of lignin

2. the yield of the methylation by TMAH
3. detectability of all compounds in the Py-GC/MS system.

Investigations with different aldehydes common in the lignin pyrolysis showed that the disproportionation is strongly effected by the substituents and the position of substituents in the aromatic ring, for example OH-group in the p-position has a blocking effect – as in the case of vanillin [7].

THM analysis of cellulose and hemicelluloses

The pyrolytic analysis of cellulose and hemicelluloses is more complicated. Fabbri [6] was the first who explored the behaviour of various monosaccharides combined with 1,4-linked carbohydrates. As characteristic products of monosaccharides, such as xylose, glucose, mannose, arabinose, C5 and C6 meta-saccharinic acid methyl esters were identified under the products. In contrary to the monosaccharides, iso-saccharinic acid methyl ester isomers were detected as primary products of the glycosidically linked cellulose.

The glucuronic acid groups are important constituents of the xylan backbones of hemicelluloses. We studied the thermochemolysis of uronic acid, too (**Fig. 3**). In the pyrogram we could observe two significant new peaks [9]. Applying the generally accepted reaction mechanism of the effect of strong bases on reducing sugars to glucuronic acid we assigned the new peaks as epimers of the corresponding permethylated deoxy glucaric acids.

Technical use of TMAH in delignification and swelling

Delignification of wood using TMAH instead of NaOH – Quatam process

At the analysis of wood or pulp, the decomposition products of lignin are dominant in the THM pyrogram. We thought TMAH had to be a very good agent in the alkaline hydrolysis of lignin. So we tried it as a reactive agent in wood pulping instead of sodium hydroxide: in Soda, Sulfite, Kraft and Lo-solids® processes.

The experiments in laboratory and later in semi-pilot plants confirmed our assumption [10,11,12] The tetramethylammonium hydroxide showed a significantly better pulping effect than the commonly used sodium hydroxide both in hardwood and softwood pulping under the same circumstances. In Kraft pulping the sulfidity could be drastically reduced without a decrease in the pulp quality. In Lo-solids® process the highest efficiency could be achieved if TMAH was used in the impregnation stage.

1:   2,4-dimethoxybutanoic acid methyl ester
2/3: C5 methylated metasaccharinic acid methyl esters
4:* unknown
5/6: we assigned as tri-O-methylated-3-deoxy-glucaric acid dimethyl esters
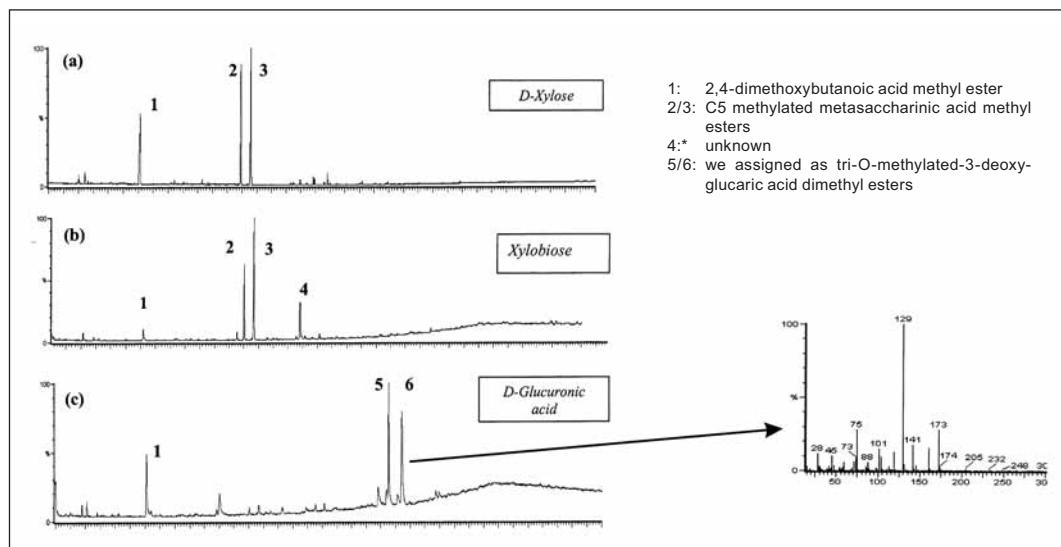
Fig.3.: THM pyrogram of glucuronic acid compared to the those of xylose and xylobiose [9]
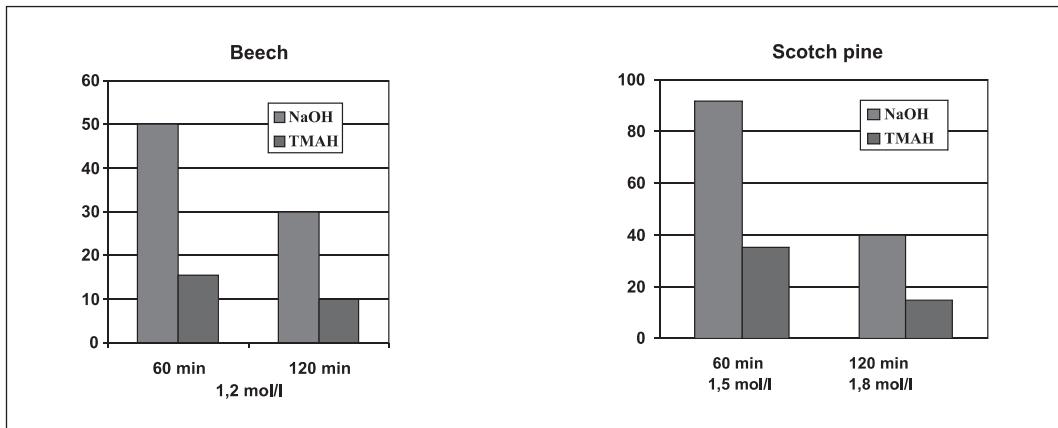
Fig. 4.: Kappa numbers of pulps obtained in Soda and Quatam process under the same circumstances.

Where may be the differences between the effect of NaOH and TMAH? Both physical and chemical factors must be considered as size of the cation, hydration, solvation, penetration, adsorption, desorption as well as degradation reactions of lignin and hemicelluloses, secondary/condensation reactions and methylating effect of TMAH **[11]**.

Using different quaternary ammonium hydroxides it is obvious that the pulping effect is decreasing with increasing molecular weight (increasing alkyl chains in the molecule) in the sequence TMAH > tetraethylammonium hydroxide > benzyl-trimethylammonium hydroxide **[13]**.

Swelling of cellulose

TMAH proved to be a more effective swelling agent of cellulose than NaOH. The difference between their swelling effects starts to be significant at about 2 mol/l concentration **[14]**. This result was assigned to the large size and non-polar part of TMAH able to penetrate into the non-polar sheets of cellulose, furthermore, to the abnormally high activity coefficient of TMAH in aqueous solution (**Fig. 4**).

The decomposition pattern of TMAH itself is also changed. TMAH bounded on the cotton fabric contains hardly crystal water anymore and the cellulose stabilizes TMAH. The molecular interaction between TMAH and cellulose results in formation of cellulose-tetramethylammonium: $CellO^-$ $[N(CH_3)_4]^+$ which retards the

decay of TMAH. The temperature range of the decomposition is shifted from 134°C to about 230 °C.

Py-GC/MS analysis of acylated wood

The acetylation of wood using isopropenyl acetate (IPA) is a new technique, developed in the Universität Linz **[15]**. The acylation process was extended also for products containing higher carboxylic acid rests **[16]** (**Fig. 5**).

Py-GC/MS is a high-performance method for the analysis of wood derivatives, especially in our case for the analysis of acylated wood containing different carboxylic groups. Not only the grade of
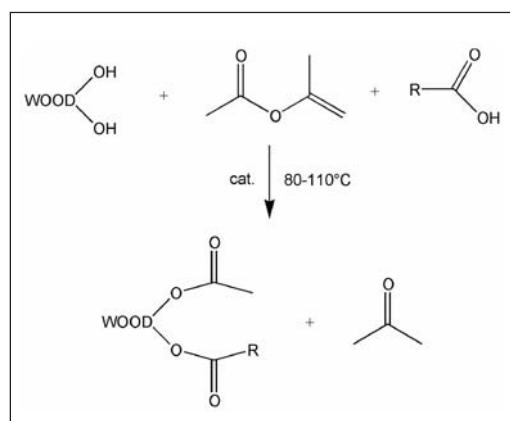
Fig. 5. Acylation of wood with IPA+carboxylic acid mixture

acylation but immediately the ratio of the different carboxylic groups in the samples could be quantitatively determined.

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Mechanikailag leválasztott fehérítetlen és fehérített eukaliptusz kraftcellulóz rostok felületi rétegeinek elemzése

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A fasejtfal középső lamellájának és elsődleges falának maradványalkotórészei befolyásolják a cellulózrost felületi rétegének összetételét. Várható, hogy ez hat a cellulózrostok fehéríthetőségére is. Jelen munkánk célja az volt, hogy hidromechanikai leválasztási technikákkal szétválasszuk az eukaliptusz fehérítetlen kraftcellulóz rostjainak felületi rétegeit, majd a szétválasztott (lehámozott) rétegeket enzimes fehérítéssel dolgoztuk fel, a peroxid – xilanázkezelés – lúgos extrakció – peroxid P[1]-X-E-P[2] sorrendnek megfelelően. Mind a fehérítetlen, mind pedig a fehérített rostfalfrakciók összetételét UV/látható spektroszkópiával és az oxidált cellulóz funkciós csoportjainak fluoreszkáló jelölésével elemeztük, melyet GBC-MALLS követett.

Annak érdekében, hogy a maradék lignin és oxipoliszacharidok által előidézett UV-abszorpcióképesség között különbséget tudjunk tenni, 0,5%-os és 10%-os lúgos extrakciót alkalmaztunk NaOH-dal. A teljes NaOH-os oldhatóság fehérítetlen felületi rétegekre 40 súlyszázalék volt, a rostfalak fő részére pedig 19%. Az UV spektrum megmutatta, hogy a lignin és hexénuronsav tartalom 3-4-szer magasabb a rostok felületi rétegeiben az átlagértékekkel összehasonlítva. A (hetero)aromás vegyületek (furanoidok/furángyanták) és oxipoliszacharidok tartalma is sokkal magasabb volt a becslések szerint a felületi frakcióban. Fehérített frakciók esetében a teljes NaOH-os oldhatóság csökkent, és 25 súlyszázalékot tett ki a rost felületi rétegei, és 15%-ot a rostfal fő része esetében. A felületi komponensek frakciókról történő abszorpciójának csökkenése a teljes spektrális tartományon belül megfigyelhető volt.

A fluoreszkáló jelölés és GPC-MALLS megmutatták, hogy a felületi réteg frakciójának molekuláris súlyeloszlása lényegesen különbözött a tömbfázisú rostokétól, leginkább az alacsony molekulasúlyú frakciókban. A belső réteg frakciói megegyeztek a tömbfázisú rost molekuláris súlyeloszlásával. Ugyanez volt igaz a molekulasúlyra és a karbonilcsoport-tartalomra. A felületi rétegekből nyert frakcióra gyakorolt fehérítési hatás nagyon hangsúlyozott volt. Fehérítés után a molekulasúly csökkent, és a karbonilcsoportok pedig, ahogy ez várható volt, az összes vizsgált mintában növekedtek. A rostok felületi részét azonban még komolyabban érintette. A felületi rétegben a karbonilcsoport háromszorosára nőtt, összehasonlítva a belső rétegben vagy a tömbfázisú rostban történő kétszeres növekedéssel.

A rostfalfrakciók kémiai összetételében végbemenő meglehetősen radikális változások ellenére az elkülönített felületi rétegek ISO-fehérsége sokkal alacsonyabb maradt a rostok fő részéhez viszonyítva. Ez 50%-os ISO-fehérséget jelentett a rostok fő részeinek 67%-os ISO-fehérségéhez viszonyítva.

Analysis of surface layers of mechanically peeled unbleached and bleached eucalyptus kraft pulp fibres

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Summary

The objective of the present work was to separate the surface layers of eucalyptus unbleached kraft pulp fibres by hydromechanical peeling techniques and to proceed with enzyme-aided bleaching of the separated layers according to the sequence peroxide – xylanase treatment – alkaline extraction – peroxide P_1-X-E-P_2. The composition of both unbleached and bleached fibre wall fractions was analysed by UV/Vis spectroscopy and fluorescence labelling of oxidized cellulose functionalities followed by GPC-MALLS.

UV spectra revealed the content of lignin and hexenuronic acids to be 3-4 times higher in fibre surface layers as compared to the average values. The content of heteroaromatic compounds (furanoids / furan resins) and oxypolysaccharides was also estimated to be much higher in the surface fraction. For the bleached fractions the decrease of the absorbance of the components from surface fractions occurred over the whole spectral range.

Fluorescence labelling and GPC-MALLS showed that the molecular weight distribution of the surface-layer fraction differed significantly from that of the bulk fibre, mostly in the low molecular weight fraction. The inner-layer fractions equaled the molecular weight distribution of the bulk fibre. The same held true for molecular weight and carbonyl group content. The impact of bleaching on the fraction obtained from the surface layers was very pronounced. After bleaching molecular weight and carboxyl group content are decreased in all analyzed samples. Again, the surface-layer fraction exhibits a different behaviour than bulk sample and inner-layer fractions.

In spite of the rather exhaustive changes in the chemical composition during the fibre wall fractions, the ISO brightness of the isolated surface layers remained much lower as compared to the main part of fibres. It provided 50% ISO as compared to the 67% ISO brightness for main part of fibres.

Introduction

It is established by several researchers that the residual constituents of middle lamella and primary wall of wood cell walls affect the composition of pulp fibre surface layers. It is expected that this translates into the pulp fibres' bleachability. In order to perform bleaching trials directly with separated fibre surface layers (P and S_1) and the main part of the secondary wall (S_2 and S_3) as well as with intact pulp fibres, hydromechanical peeling of eucalyptus unbleached kraft pulp fibres was accomplished. Unbleached fibres (the sample for integrated analysis by participants of the COST Action E41) were acquired from the industrial digester before oxygen delignification stage.

Materials and methods

The hydromechanical peeling techniques was applied to separate the surface layers of eucalyptus unbleached kraft pulp fibres [1]. The peeling of the surface material was monitored by „Lorentzen&Wettre Fiber Tester" and digital microscope „Leica DM5500", separation of the fractions was done by wet fibres shaker „Retzsch AS200" following by centrifugation and freeze-drying. The peeling process was interrupted before the fragmentation of the fibres had started. The degree of the exposure of the secondary wall S_2 layer usually reaches 30-50% as a consequence of the suspension of the procedure. Separated fibre wall fractions, i.e., rather clean surface layers (P+S_1) and conditionally the main part of secondary layer (S_2+S_3), were analysed by standard TAPPI methods and subjected to the enzyme-aided bleaching of the isolated layers according to the sequence peroxide – xylanase treatment – alkaline extraction – peroxide P_1-X-E-P_2. The composition of both unbleached and bleached fibre wall fractions was analysed by UV/Vis spectroscopy. In order to differentiate the UV-absorbance derived by residual lignin and oxypolysaccharides, sequential alkaline extraction with 0.5% and 10% NaOH was applied. The total NaOH solubility was 40% by weight for unbleached surface layers and 19% for the residual part of the fibre wall. Fluorescence labelling of oxidized cellulose functionalities followed by GPC-MALLS was performed according to [2],[3].

Results and discussion

In order to elucidate the distinctions in the chemical composition of the fractions before the bleaching, the UV-spectra (**Fig. 1**) and the 1st derivative of the spectra were analysed. When 0.5% NaOH solution is applied, the absorbance values at 218, 290, 330, 350, 386 and 390 nm are attributed to lignin. Strong absorbance of the alkaline extract from fibre surface layers at 245 nm and weaker UV-absorbance at 244, 254, 266 and 276 nm for the alkaline extract of the fraction enriched in S_2 and S_3 layers indicate the presence of the heteroaromatic compounds of the furanoid (pyranoid) type. In 10% NaOH extracts, the absorbance at 235 is attributed to hexenuronic acids (HexA). From UV spectra analysis we conclude that the content of lignin and hexenuronic acids is 3-4 times higher in fibre surface layers as compared to the average values. The content of heteroaromatic
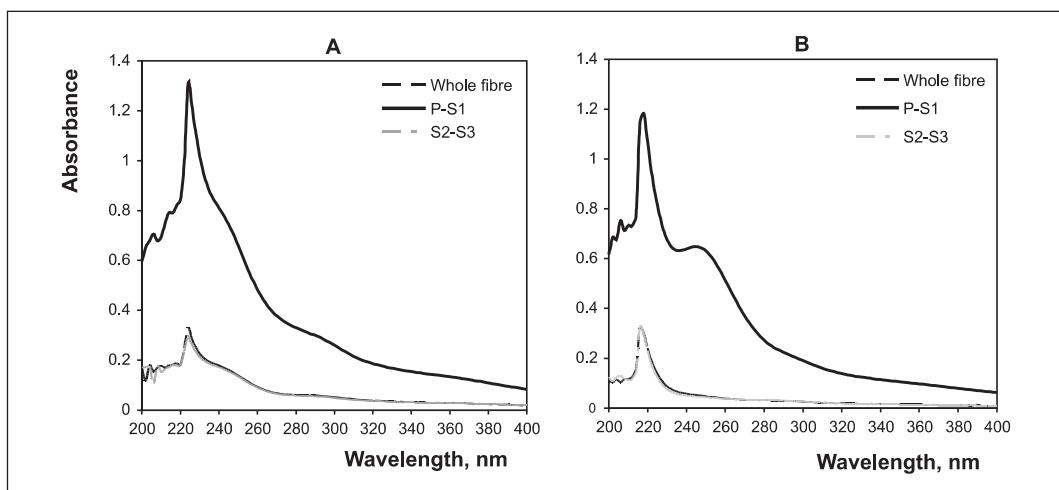

Fig. 1. The UV-spectra of the alkaline extracts from unbleached P-S$_1$ (upper curves) and S$_2$-S$_3$ fractions (lower curves) (A – 0.5% NaOH; B – 10.0% NaOH).

compounds (furanoids / furan resins) and oxy-polysaccharides is also estimated to be much higher in the surface fraction.

For the bleached fractions the total NaOH solubility decreased and was 25% by weight for the fibre surface layers and 15% for the main part of fibre wall. The decrease of the absorbance of the components from surface fractions occurred over the whole spectral range. The absorbance drop at 218 nm and 250 nm by 45% and 63%, respectively, in the 10% NaOH extract of the surface P-S_1 layers indicates the destruction of the heteroaromatic compounds possibly incorporated in the furan resins. The decrease of absorbance at 280-300 nm and around 340-360 nm indicates the elimination of both carbonyl groups and double bond conjugated structures in the surface layers. The

main part of the fiber walls, the S_2-S_3 layers, has lost most of the easily accessible fraction of hemicelluloses and HexA during the bleaching procedure. It is indicated by the decrease of the absorbance around 235 nm. At the same time an increase of the absorbance at 235 nm in the case of the polyoses from S_2-S_3 layers soluble in strong alkali points to some increase of HexA at the bleaching conditions used (no acidic stage).

The brightness values of the eucalyptus kraft pulp separated surface (P-S_1) and main secondary wall layers as well as whole fibres after bleaching were measured [**Fig. 2**]. In spite of the rather exhaustive changes in the chemical composition during the fibre wall layers bleaching, the ISO brightness of the fibre surface layers remains much lower as compared to the S_2-S_3 layers. It makes up 50% ISO as compared to the 67% ISO brightness for both secondary wall layers and whole fibres.

The molecular weight distribution of the P-S_1 layer shows a distinct and well separated hemicellulose peak (**Fig. 3 left**). In the unbleached samples the amount of carboxyl groups, which corresponds predominantly to the uronic acid moeities in the xylan of the eucalyptus pulp used is comparable in the whole sample and the S_2-S_3 layer (**Fig. 3 right**). Interestingly, the free uronic acid content in the surface layer is significantly lower compared to the S_2-S_3 layer. A possible explanation is the engagement of the
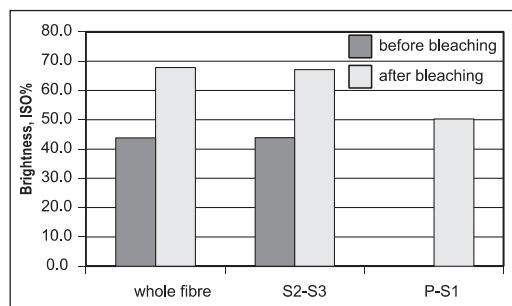
Fig. 2. Brightness values for eucalyptus kraft pulp fibrer and separated fibre wall layers.
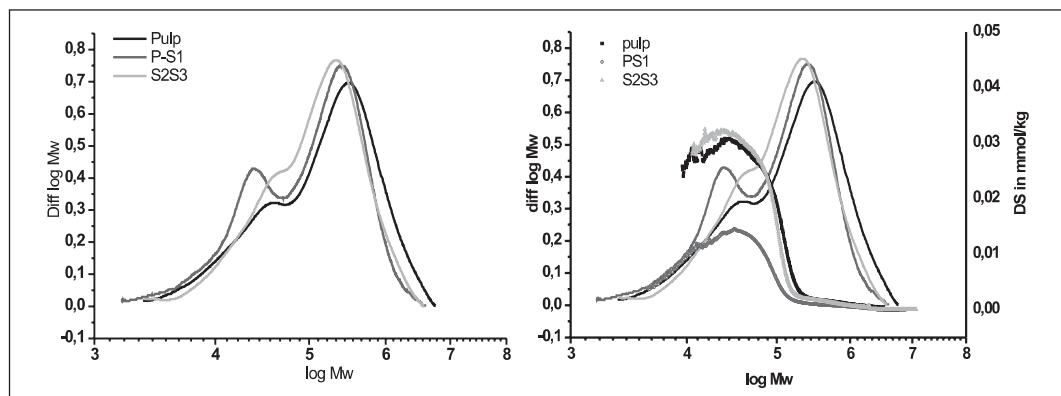
Fig. 3. Molecular weight distribution of bleached (left) and unbleached (right) pulps In addition, the figure on the right shows the distribution of carboxyl groups in relation to the molecular weight.

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	Whole pulp μmol/g	P-S$_1$ layer μmol/g	S$_2$-S$_3$ layer μmol/g
Unbleached COOH	60.1	30.1	63.8
Bleached COOH	41.3	-	40.9
Bleached* C=O	16.1	28.4	16.9

*Determination of carbonyl values in bleached samples was not possible due to fluorescence quenching of lignin.

Table. 1: Amounts of carboxyl and carbonyl groups in unbleached and bleached samples

uronic acid group in lignin-carbohydrate complexes, which corresponds well to the increased UV activity within the surface layer (cf. **Fig.1**). In the mild labeling protocol the ester linkages are not cleaved and only free uronic acid groups are labeled. The bleached samples showed a significantly higher carbonyl group content in the surface layers than in the bulk sample and in the S$_2$-S$_3$ layer, also indicating the presence of a more complex chemical structure.

Conclusions

- Composition of the papermaking (pulp) fibres surface layers differs from that of the secondary wall.
- In spite of rather exhaustive changes during bleaching, ISO brightness of the isolated surface layers remained much lower.
- Carboxyl groups in surface layers are engaged in lignin-carbohydrate complexes.

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Újonnan kifejlesztett módszer az egyedi rost rugalmasságának méréséhez

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Új módszer került kifejlesztésre az egyedi rost rugalmasságának/kezelhetőségének meghatározására szuszpenzióban. A vízben szuszpendált rostokat egy plexiből készült átlátszó áramlási cellában nyíróerőknek tették ki. A rostok reakciójának megfigyeléséhez transzmissziós fénymikroszkópon alapuló nagysebességű képelemzési rendszert használtak. A maximálisan elkészített képek száma 500 kép volt másodpercenként. Az optikai felbontás 7,63 [μm/pixel]. Képelemzés alapján egy-egy rost képe maximum ötször vehető fel a nagy nyíróerejű zónában.

Rene Eckhart

Az egyedi rostnak a hidrodinamikus terhelésre mutatott reakciója lesz az adott rost rugalmassága meghatározásának az alapja.

Az áramlási cellát az Áramlástani és Hőátadási Intézettel együttműködésben fejlesztették ki a Grazi Műszaki Egyetemen.

Az eredmény egy olyan cella, amelyben azonos áramlási sebességgel rendelkező két áramot egymással szemben vezetnek. Ezáltal elegendő nyíróerő keletkezik ahhoz, hogy látható rostdeformáció keletkezzen lamináris áramlási rendszer feltételei mellett.

A pulzálás elkerülése érdekében (a pulzálások befolyásolnák vagy akár rombolnák is a lamináris áramlási mezőt) a szuszpenziót sűrített levegő alkalmazásával a transzparens cellán keresztül átszivattyúzzák.

Az áramlási mezőt az Áramlástani és Hőátadási Intézetben szimulálták folyékony anyag (FLUENT) alkalmazásával. A sebességkomponensek x és y irányban, valamint gradienseik 30 m-es térbeli felbontással ismertek.

Erre a szimulációra alapozva elérhetők azok a hidrodinamikus feltételek, melyeknek a rostok az áramlási mezőben ki vannak téve. A rost rugalmassági modulusban kifejezett rugalmasságának kiszámításához a folyadékáram miatt a rostra ható valódi erők szükségesek. Ezeket az erőket a rost és a folyadék közötti sebességkülönbség határozza meg. Ez a sebességkülönbség nem számítható ki egyszerűen, mivel a folyadékáramlási feltételek, amelyek között a rostot használják, drámai módon változhatnak két egymást követő kép között.

A rostrugalmasság/merevség meghatározásának általunk követett koncepciója a rost és egy ideálisan rugalmas partner összehasonlításán alapszik. Az egyedi rost áramlási mezőben való reprezentálása alapján kiszámítjuk ennek a rostnak a helyzetét és megjelenését a következő képen, feltéve, hogy a rostok középvonalában lévő minden egyes pont ideális módon követi az áramlási mezőt. Ennek az ideálisan rugalmas rostnak a referenciarosttal összehasonlított változását értékeljük az alak összehasonlításával. Az alak hasonlóságát a rost alakját leíró, több paramétert tartalmazó vektorok közti euklideszi távolság alkalmazásával számítjuk ki.

A valós rost deformációját hasonló módon értékeltük (a referenciarostot hasonlítottuk valódi reprezentációjához a következő képen). A valós rost deformációja és az ideálisan rugalmas rost deformációja közti arányt alkalmaztuk rugalmassági paraméterként.

A Newly Developed Method for Single Fibre Flexibility Measurement

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Summary

A new method for single fibre flexibility measurement in suspension was developed at the Institute for Pulp, Paper and Fibre Technology at Graz University of Technology.

A flow cell with suitable channel geometry is used to induce a flow field with high shear forces in flowing suspension. These shear forces are strong enough to deform pulp fibres under laminar flow conditions. A high speed image acquisition system is used to acquire several images of a fibre while passing the transparent flow cell. Thereby the deformation of the fibre due to the shear forces is recorded.

To gain access to the defined flow conditions at any point in the sheared region the flow field was simulated in FLUENT.

The fluid flow is then linked with the fibres reactions. Thereby a flexibility parameter for every evaluated fibre is determined.

Introduction

Fibre flexibility/conformability is an important pulp parameter during stock preparation, sheet forming, in fiber to fiber bonding and thus for the resulting paper properties.

Several fibre flexibility measurement methods are mentioned in the literature. Some are based on single fibre manipulation and apply bending beam theory to determine a modulus of elasticity. These methods are rather tedious and or can not treat all fibres in a given pulp sample but are restricted to rather long and undamaged fibres **[1]**. Others are based on the fibres ability to conform to a wire/ glass fibre/another pulp fibre after settling on to a glass slide. These methods determine a "conformability" that is closer to the fibre property relevant for

the fibre to fibre contact in a sheet **[2]**. Still, neither of these methods can be applied on line.

Today pulp morphology parameters like for example fibre length, width, curl or kink **[3]** are to an increasing extent determined using commercially available flow cells with high on line applicability. Highly diluted fiber suspension is pumped through a transparent cell and photographs of individual fibers are taken by means of transmitted light microscopy. Automated image analysis is used to detect and evaluate the fibres in these images.

Two fibre flexibility measurement methods show at least theoretical on-line applicability in such a flow cell. Kuhn et.al. **[4]** described a method where fibres are photographed while exiting a capillary tube into a main channel. The fibres are deformed due to the load of the fluid flow of the main channel. The deformation of the fibres exiting the tube is compared to that of fibres of defined flexibility, simulated under the same flow conditions. This method was never implemented in a commercially available device.

Another method was patented by STFI in 1992 **[5]**. The fiber curl of a large number of fibers is registered at two different flow velocities. As the shear rate in the flow cell is higher at increased fluid velocity the fibers are straightened in the second run. Fibre flexibility is not determined for every single fibre but defined as the relationship between the average fibre curl values of the two measurements. The method is implemented in the commercial fiber analyzer FibreMaster.

The goal was to develop a flow cell based method that delivers flexibility values for every evaluated fibre. That way not only average flexibility values but distributions of fibre flexibility should be accessible. Such distributions of fibre flexibility might deliver beneficial information concerning for example the earlywood-latewood ratio or the number of fibres reached during a refining process.

Approach

The idea is to use an appropriate flow cell geometry to generate shear forces strong enough to provoke fibre deformation under the boundary condition of a laminar flow regime. A high speed image acquisition system is used to record the movement of single fibers in the sheared region. Based on the fibres deformation due to the fluid forces a flexibility parameter is determinable for every evaluated fibre.

The Flow Cell

The flow cell was developed in cooperation with the Institute of Fluid Mechanics and Heat Transfer of Graz University of Technology (**Fig. 1.**) .

Several channel geometries were tested but only the one described in the following induced shear forces strong enough to provoke visible fibre deformation under the boundary condition of a laminar flow regime. Two fluid streams of identical flow rate and velocity are headed against each other in a crossing. The average flow velocity in the ingoing channels is 1,4 [m/s]. No turbulence or mixing of the fluid streams headed against each other occurs. Fig. 1a shows schematically the transparent flow cell made of Plexi Glass. To avoid pulsations (pulsations would affect or destroy the laminar flow field) in the fluid flow, suspension transport is done using a pressure resistant glass bottle equipped with a stand pipe and a compressed air connection. Thereby the suspension is pumped through the flow cell by air pressure.

The flow conditions in the flow field were simulated by the Institute of Fluid Mechanics and Heat Transfer using FLUENT. Experiments have shown that the fibres tend to move in the centre plane of the flow channel. Furthermore the z-direction of the channel is not accessible in the images. Therefore only the centre plane of the channel was simulated. The velocity components in x- and y-direction as well as their gradients are known with a spatial resolution of 30 μm. As an example Fig. 1b shows a contour plot representing the velocity magnitude in the flow cell.

Based on this simulation, the hydrodynamic conditions in the flow field are accessible and can be linked to the fibres reactions.

Images are acquired using a Basler A504k high speed camera. It allows a frame rate of 500 images per second. Thereby each fibre passing the cell is acquired 2 to 3 times in the region of highest shear forces. The optical resolution is 7.63 [μm/Pixel]. Illumination is done using one red high power LED.

Automated image analysis is used to evaluate the acquired images. Two main tasks have to be accomplished by the image analytical algorithms: fibre segmentation and fibre tracking through the consecutive images, where fibre tracking means relocating a specific fibre in the consecutive image.

The segmentation process starts with a background correction to delete impurities in the optical path and eventual uneven illumination. In the next step binary images of the fibres are calculated. Based on these binary images the corners of the fibre are detected and the fibre is reduced to its centreline. Fibre length as well as the centre of gravity is calculated.

Tracking of the fibres through the consecutive images is done using the flow field data and the fibres length. The region where the centre of gravity of a detected fibre should most likely emerge in the following image can be calculated. If a fibre within a certain distance to this calculated region shows
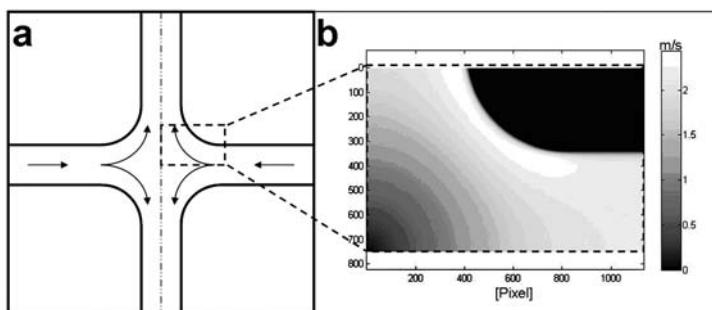

Fig. 1: The flow cell made of Plexi glass with the two streams meeting in a crossing and the profile of the velocity field in the region of high shear forces (one of the symmetric quarters)

an adequate fibre length it is selected as a second representation of the specific fibre. That way up to five representations of a fibre can be captured for flexibility determination.

Determination of Fiber Flexibility

For a calculation of fibre flexibility in terms of an elasticity modulus the real forces acting on the fibre due to the fluid load would be necessary. These forces are determined by the speed difference between fibre and fluid. In our concept this speed difference is not determinable as the fluid flow conditions a fibre is exerted to can change dramatically between two consecutive images. Even an estimation of the translational and the rotational part of fiber movement would demand a higher framerate. Therefore an approach using bending beam theory and the forces acting on the fibre to determine the modulus of elasticity seemed inappropriate.

The concept for the determination of the fibres flexibility/rigidity is based on a comparison of the fibres behaviour with that of a calculated ideally elastic counterpart.

Two consecutive images of the same fibre are taken into account for the determination of its flexibility. The first image of the specific fibre in the region of high shear forces is used to calculate position and appearance of the fibre in the following frame, provided that every single point along the fibres centreline follows the flow field ideally. The result is an ideally elastic fibre following the fluid flow without any restrictions (bright gray in **Fig. 2**). The deformation this ideally elastic fibre

undergoes compared to the reference fibre in the first image is evaluated using a comparison of shape. The Euclidian distance between vectors containing several shape parameters and thereby describing the shape of the reference fibre and of the calculated ideally elastic one represents the deformation of the ideally elastic fibre and thereby determines the "load" acting on the fibre.

The deformation of the real fiber in the high shear zone is calculated likewise based on the reference fibre (the one that was used to calculate the ideally elastic one) and the same fibre in the consecutive image. The deformation of the real fibre due to the fluid forces determines the "reaction" of the fibre.

The ratio between the deformation of the real fiber and the ideal one, the ratio between "reaction" and "load" is used as a parameter for the fibres flexibility.

The method delivers promising results e.g. for softwood fibres with different drying history or for fibres treated in a laboratory refiner to increase fibre flexibility step by step.

Acknowledgements

Fig. 2: Two schematic representations of a fiber as it is photographed in the high shear zone and the calculated, ideally elastic counterpart (bright grey); scaling in pixels (7,36 µm/pixel)

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Cellulóz szupramolekuláris szerkezetének szilárd fázisú NMR és Röntgen-diffrakciós összehasonlító vizsgálata fenyő kraftcellulóz roston

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A COST E54 akció keretén belül közös rost-mintákat használtak. Egy fehérítetlen fenyő kraftcellulózt és egy fehérített fenyő kaftcellulózt bocsátottak az összes akcióban résztvevő rendelkezésére. A COST E54 akció keretén belül szilárdfázisú NMR (CP/MAS ^{13}C-NMR) és Röntgen diffrakciós adatok (XRD) eredményeit rögzítették.

Az azonos anyagokkal végzett vizsgálatok a műszeres mérések széles körének alkalmazásával ritka alkalmat teremtenek a módszerek interkalibrálásához és az adatok értelmezéséhez használt modellek érvényességének vizsgálatához. Ebből a célból a Röntgen-diffrakció és NMR mérések eredményeinek összehasonlításáról döntöttek.

Az összehasonlítás fő célja a cellulóz I szupramolekuláris szerkezete, azaz a cellulóz nativ formája volt. Az NMR és Röntgen-diffrakció alapvetően különböző mérési technikák, melyek adatokat hoznak létre; ezek közül

néhány a meglévő modellek keretén belül összehasonlítható. A Röntgen-diffrakció és az NMR különböző természete miatt különböző modelleket alkalmaztak az adatok értelmezésére, ami bizonyos mértékig megnehezítette az összehasonlítást. Az cellulóz I, lévén félkristályos anyag, amely a rostfal komplex morfológiájába rendezett biopolimerekből áll, nem igazán optimális anyag az NMR vagy Röntgen-diffrakciós mérésekhez.

Az összehasonlítás az eredmények három kategóriájára történt: cellulóz I látszólagos krisztallitmérete, a kristályosság foka és a rostfalban lévő cellulóz cellulóztartalma. Ez a három tulajdonság, közvetve vagy közvetlenül, rendelkezésre áll mind a Röntgen-diffrakcióból mind az NMR mérésekből.

A Röntgen-diffrakció és NMR működési elveinek különbözősége miatt az **1. táblázatban** bemutatott eredmények közti egyezőség a kiválótól a jóig értékelhető. A cellulóztartalom becslésében megállapított különbség várható volt, mivel tudott, hogy az NMR módszer nem veszi figyelembe a hemicellulóz jel intenzitását. Mindkét módszer enyhe növekedést mutat fehérítés után a látszólagos krisztallitméretben, míg a kristályosság foka változatlan marad.

	Fehérítetlen Röntgen-diffrakció	Fehérítetlen NMR	Fehérített Röntgen-diffrakció	Fehérített NMR
Látszólagos krisztallitméret (nm)	3.0	3.2 (0.1)	3.2	3.4 (0.1)
Kristályosság foka (%)	60	55 (1)	59	56 (2)
Cellulóztartalom (%)	86	90	84	90

1. táblázat: A cellulózmintákon rögzített Röntgen-diffrakció és NMR eredmények Az NMR esetében a látszólagos krisztallit-méreteket a mért átlagos laterális fibrilla-méretből becsülték, figyelmen kívül hagyva a fibrilla-felületi polimereit. A glükánlánc átlagos laterális mérete 0,57 nm volt. A kristályosodás fokának NMR becslése tartalmazza a parakristályos formákat is.

A comparative CP/MAS ^{13}C-NMR and XRD study of the cellulose supra-molecular structure in softwood kraft pulp fibers

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Abstract

Cross Polarization Magic Angle Spinning (CP/MAS) Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) spectroscopy and X-Ray Diffraction (XRD) has been used to study cellulose I structural characteristics. Both methods were applied to the same set of samples, unbleached and bleached softwood kraft pulps. Despite the differences in principles of operation the two measuring techniques give some estimates of material properties that can be compared. In this study the focus was on the cellulose I fibril dimensions, degree of crystallinity and the cellulose content of the materials. Within the models used for interpreting the measured data good agreement between the two methods were found for fibril dimensions and degree of crystallinity. Estimates of cellulose content were in qualitative agreement, which was expected since the NMR method tends to over estimate the cellulose content in the presence of hemicellulose.

Introduction

CP/MAS ^{13}C-NMR spectroscopy has been shown to be a versatile tool for the study of cellulose supra-molecular structure (VanderHart 1984 [8], Larsson 1997 [5], Wickholm 1998 [9], Hult 2001 [3]). Measured spectra can be used to obtain estimates of cellulose allomorph composition, degree of crystallinity, lateral dimensions for both cellulose fibrils and for cellulose fibril aggregates. In cellulose I isolated from softwoods cellulose I fibrils are typically 4 to 5 nm thick and cellulose fibril aggregates thicknesses range from 15 to 30 nm depending on isolation procedure.

The most known method of determining the structure characteristics of cellulose substrates is the study of their X-ray diffraction, in the small as well as wide angle region. The X-ray diffraction in the wide angle region (beyond $2\theta = 6$ degrees) allows the determination of the degree of crystallinity, the degree of orientation and from the width at the half maximum intensity of the meridional and equatorial reflections, the crystallite length and width dimensions, respectively (Krässig 1993 [4],Teeaar 1987 [7]).

The average size of the crystallites can be evaluated using the well-known Scherrer equation while the degree of orientation can be obtained through calculation of the Hermans orientation function (Cullity, Stock 2001 [2]). Other characteristics related to the material crystallinity can be also obtained (Anderson 2003 [1], Popescu 2007 [6]). Unfortunately this method can not reflect the hydrogen bonding patterns, allomorph composition in cellulose crystallites and the integrity of the crystallite (J. Xe 2007).

Both NMR and XRD methods are dependent on models for the interpretation of recorded data. Due to the fundamental differences relating to how data is acquired, different conceptual models are used for interpretations. In the case of estimates of lateral dimensions as obtained from the two methods it is necessary to impose some assumptions in order to obtain comparable results. Further, the interpretation of NMR

spectra includes separate signal intensity from so-called para-crystalline cellulose, domains of highly ordered glucan polymers interior in the fibril (Larsson 1997 **[5]**, Wickholm 1998 **[9]**). Currently it is not clear whether or not the para-crystalline form contribute to the degree of crystallinity as observed by XRD.

Experimental

Materials: The unbleached and the bleached pulps were commercial pulps supplied by Södra Cell Värö, Sweden. The spruce (*P. abies*) to pine (*P. sylvestris*) ratio was 79:21. The pulp was batch cooked and TCF-bleached. The bleaching sequence was Q OP Q+Paa PO where Q represents a chelator and Paa is per-acetic acid. The kappa-numbers were 26.8 and 3.2 respectively for the unbleached and the bleached pulps.

X-ray diffraction (XRD): The analysis was done using a Bruker diffractometer equipped with a Kristalloflex 760 sealed-tube copper anode generator, operated at 40 kV and 40 mA, and a two-dimensional position-sensitive wire-grid detector (Bruker AXS) pressured with xenon gas. Collimation was effected by a graphite monochromator with a 0.8-mm pinhole, the sample-to-detector distance was 9 cm. Samples were placed in sealed Mark-Röhrchen glass capillaries (Charles Supper) of 1.0 mm inner diameter (1200 scans).

NMR spectroscopy. All samples were wetted with deionised water (40 to 60% water content) and packed uniformly in a zirconium oxide rotor. The CP/MAS ^{13}C-NMR spectra were recorded using a Bruker Avance AQS 300 WB instrument operating at 7.04 T. All measurements were performed at 290 (+/- 1) K. The MAS rate was 5 kHz. A double air-bearing probe was used. Acquisition was performed with a CP pulse sequence,

using a 4.3 µs proton 90° pulse, 800 µs ramped (100 – 50%) contact pulse and a 2.5s delay between repetitions. A TPPM15 pulse sequence was used for ^{1}H decoupling. Glycine was used for Hartman-Hahn matching procedure and as external standard for the calibration of the chemical shift scale relative to tetramethylsilane ($(CH_3)_4Si$). The data point of maximum intensity in glycine carbonyl line was assigned a chemical shift of 176.03 ppm. The software used for spectral fitting was implemented at STFI-Packforsk AB and is based on a Levenberg-Marquardt algorithm (Larsson 1997) **[5]**.

Results and discussion

The main target for the comparison was the supra-molecular structure of cellulose I, the native form of cellulose. NMR and XRD are fundamentally different measuring techniques that generate data, some of which are directly comparable within the limits of existing models. Due to the different nature of XRD and NMR different models are used for interpreting data, which to some extent complicates the comparison. Cellulose I being a semi-crystalline material made up from bio-polymers arranged into a complex morphology of a fibre wall is not the optimal material for NMR or XRD measurements.

The comparison was made for three categories of results: cellulose I fibril lateral dimensions, the degree of crystallinity and the cellulose content of the fibre sample. These three properties are directly or indirectly available from both XRD and NMR measurements.

Table 1 shows the results of the comparison of estimates from NMR and XRD. A slight increase in apparent crystallite size due to the bleaching is observed using both NMR and XRD. Further the agreement in lateral dimension

	Unbleached XRD	Unbleached NMR	Bleached XRD	Bleached NMR
Apparent crystallite size (nm)	3.0	3.2 (0.1)	3.2	3.4 (0.1)
Degree of crystallinity (%)	60	55 (1)	59	56 (2)
Cellulose content (%)	86	90	84	90

Table 1. XRD and NMR results recorded on the pulp samples. In the NMR case the apparent crystallite sizes was estimated from the measured average lateral fibril dimension by neglecting fibril surface polymers. The average lateral dimension of a glucan chain was set to 0.57 nm. The NMR estimates of the degree of crystallinity include contributions from para-crystalline cellulose forms.

estimates between NMR and XRD is excellent. Results obtained from NMR spectral fitting give estimates for the lateral fibril dimension (LFD) which includes the fibril surface glucan chains. The procedure used to translate LFD measures to apparent crystallite size (the lateral dimension of the highly ordered fibril interior) was to remove the contribution of surface glucan from the LFD. This gives a reduction in LFD measures with 1.14 nm. These are the NMR values quoted for apparent crystallite size in Table 1.

Due to the occurrence of para-crystalline (PC) signal intensity in NMR spectra recorded on cellulose I (Larsson 1997 **[5]**, Wickholm 1998 **[9]**), a question arises whether or not this form of cellulose I will be detected as crystalline cellulose I during XRD measurements. In the studied samples the cellulose I forms classified as crystalline and para-crystalline were about 20% and 35% respectively according to NMR, typical for cellulose I isolated from softwood. It is obvious from the comparison with XRD data that the relevant basis for comparison consists of the sum of crystalline and para-crystalline NMR signal intensity adding up to some 55%.

Conclusions

Given the differences in principle of operation between XRD and NMR the agreement between similar results is judged as excellent to good. The difference found in the estimates of cellulose content is expected since the NMR method is known to discriminate hemicellulose signal intensity. Both methods indicate a slight increase in the apparent crystallite size after bleaching while the degree of crystallinity remains unchanged. Further, the comparison of the degrees crystallinity determined by NMR and XRD indicate that the NMR signal intensity interpreted as para-crystalline cellulose is detected as a crystalline form during XRD measurements.

Acknowledgements

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Cellulózrostok vizsgálata sósavval, foszforsavval és cellulázzal

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Az új sósavas módszert haszáltuk különböző lucfenyő, erdeifenyő, nyírfa, eukaliptusz és TMP-rostok összehasonlítására. Néhány eredményt az **1. táblázatban** mutatunk be: a gyári rostok savra sokkal érzékenyebbek voltak, mint a laboratóriumi rostok, és a nagyobb lucfenyő-erdeifenyő arányú rostanyagok is sokkal érzékenyebben reagáltak a savra. A szinergetikai hatás miatt az N342 és a Celluclast az összes rost nagyon erős hasadását eredményezte. A cellulázok azonban **nem** mutattak különbséget a gyári és laboratóriumi rostanyagok között. A HCl a fenti rostokat 0.7-1.7 µm között duzzasztotta, míg az N342 és a Celluclast a rostszélességet 1–3 µm-rel csökkentette. A HCl bocsátotta ki a legtöbb xilózt (0.1 g/l) és nagyon kevés glükózt (0.015 g/l). Ez arra utal, hogy a HCl 80–82°C-nál az összes sejtfalrétegen áthatol, ezzel degradálva főként a hemicellulózokat. Így a xilán és a glükomannán sav hatására történő degradációjának van bizonyos jelentősége a gyári és laboratóriumi rostanyagok közötti különbségekben. A – főként a rost felületén aktív – nagy cellulázmolekulák esetében a glükóz volt a kibocsátott legnagyobb mennyiségű cukor, ami nagy EG + CBH katalitikus tevékenységet tükröz 0.8 g/l glükóz adagolása mellett.

Az **1. ábra** lucfenyő teljes hasadását mutatja 1N HCl jelenlétében. A **2. ábrán** 79%-os foszforsav hatására bekövetkező gömbduzzadás és felcsavarodott

S1 „gyöngysor" láthatók. A gömbduzzadás a rostok tulajdonságaitól függ.

Vizsgáltuk a HCl hatását eukaliptuszra és nyírcellulóz rostokra. Ezek az eredmények azt mutatják, hogy a nyír kraftcellulóz rostjai sokkal inkább ellenállnak a savnak, mint az eukaliptuszrostok. A hosszabb nyírrostok (cca 1 mm) ellenére, ezek a rostok kevésbé hasadtak, mint a 0.65 mm hosszú eukaliptuszrostok. (hasadás 0.22-0.35 vs 0.835-1.40). Ebben az eltérésben az edények és a parenchimaszövet is szerepet játszanak.

Következtetés

A sósavas kezelés, a rosthosszúság meghatározása és a rostonkénti hasadás (viszonyítva a

Rost-anyag típusa	Luc-erdeifenyő aránya	HCl Hasadás/rost	N476 Hasadás/rost	N342 Hasadás/rost	Celluclast 1.5L Hasadás/rost	Celluclast 1.5L Hasadás/rost
Gyári I	33:67	1.93 ± 0	0.42 ± 0.07	8.40 ± 0.08	*5.59 ± 0.09	---
Labor I	33:67	0.935 ± 0.24	0.32 ± 0.07	9.31 ± 0.24	*5.73 ± 0.60	---
Gyári II	84:16	4.16 ± 0.02	0.22 ± 0.03	9.98 ± 0.42	*5.91 ± 0.08	**9.93 ± 0.23
Labor II	84:16	1.23 ± 0.02	0.23 ± 0.04	9.95 ± 0.68	*5.59 ± 0.75	**9.62 ± 0.34

*1. Táblázat. Gyári és laboratóriumi kraftrostok hasadása HCl (81°C, pH 0) és különböző celluláz keverékek hatására 50°C-nál. A celluláz N476-nál pH értéke 7 volt, és a többinél pedig 5. *0.3 ml; **0.6 ml enzim.*

Testing of pulp fibres with HCL, phosphoric acid and cellulase

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Abstract

HCl treatment, determination of fibre length and cleavage per fibre was found to differentiate between pulps made in the laboratory and mill even though the same batch of spruce wood fibres was used. This was not the case for cellulase fibre cleavage. The reason is due to better penetration of fibre walls by the acid at a higher temperature with release of hemicellulose sugars, while cellulase activity is mainly restricted to the fibre surfaces, except in dislocations, with release of glucose as the main sugar. Phosphoric acid probably penetrates through cracks and dislocations of the S1 wall and swells the S2 fibre cell wall creating balloons. The number of balloons and degree of swelling reflects the history of the pulp fibre such as bleaching and mechanical treatment.

Introduction

The new pulp fibre testing method called the HCl-method can be used to compare different spruce, pine, birch, Eucalyptus and TMP pulp fibres by allowing calculation of the number of fibre cleavages in dislocations and other weak points [1,2]. Here fibre cleavage using HCl and cellulase treatments are further evaluated regarding differences in cleavage pattern, in degradation of the different fibre cell walls and in sugar release [3]. For more background see [4]. The use of phosphoric acid and fibre balloon swelling as a test of fibre quality is also shortly described.

Experimental

Pulps

Source and properties of kraft and TMP pulp fibres are given in [1,2]. Four kraft pulps were from two Scandinavian mills and called Mill I & Lab I (spruce:pine relation 33:67) and Mill II & Lab II) (spruce:pine relation 84:16) [3]. Spruce kraft pulp samples along a kraft pulp fibre line were: I. After cook; II. After Wash press; III. After O2; IV. After EOP; V. After D2. L_0-values are from each sampling point before HCl-treatment [2].

HCl-treatment and calculation

Final version of the HCl-method is given in [2,4]. In short, never-dried fibres are swelled in 20 ml water and 20 ml 2N HCl added to give pH 0. Incubation is then carried out for 4h at 80-82°C with cleavage completed during cooling using a stirring bar for 30 min. Finally the fibres are washed with phosphate buffer at pH 7 to remove the acid. Fibre length determination was done using a FibreMaster or a Kajaani instrument. *Calculation:* Cleavage per fibre = $(L_0 / L) - 1$ were L_0 is length weighted fibre length distribution in mm for control in water (or for untreated fibres), and L is length weighted fibre length distribution in mm for HCl-treated fibres.

HCl and Cellulase treatment

The four kraft pulps Mill I & Lab I and Mill II & Lab II were tested with HCl as above and with Novozym 476 (monocomponent endoglucanase EG), Novozym 342 (multicomponent endoglucanase + cellobiohydrolase CBH) and Celluclast 1.5L (EG + CBH from *Trichoderma reesei*) at 50°C [4].

Sugar analyses

Arabinose, galactose, glucose, mannose and xylose in fibre filtrates were determined at M-real/MoRe Research, Örnsköldsvik using ion chromatography and pulsed amperometric detection [4].

Phosphoric acid swelling

Balloon swelling of fibres was performed using 79% ortho-phosphoric acid as described earlier [5-7]. Some balloon swelling tests were also done with 8% LiCl in DMAC, copperethylenediamine and Fe(III)-tartrate [7].

Light microscopy. For polarized light microscopy, a Leica DMLB or DMLS coupled to an Image-Pro Plus
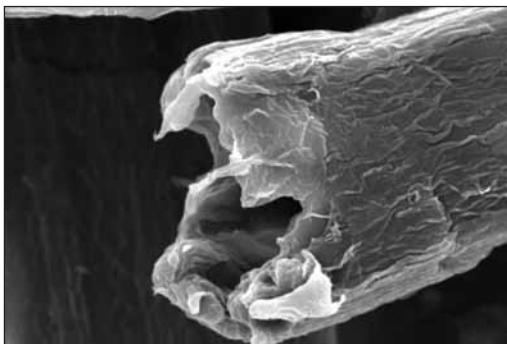
1.ábra. Lucfenyőrost HCl hatására bekövetkező teljes hasadása, feltárva a sejt belsejét

2.ábra. Lucfenyőrost gömbduzzadása foszforsavkezelés után

diszlokációk számához) különbséget tesznek a laboratóriumban vagy gyárban előállított rostanyagok között, még akkor is, hogyha ugyanazt a lucfenyőrostot alkalmaztuk. Ugyanakkor ezt nem tapasztaltuk cellulázos rosthasításban. A nyírfarostok nagy ellenállást mutatnak a sósavval szemben. A foszforsav valószínűleg behatol a S1 fal repedéseibe és az elmozdulások közé, és megduzzasztja az S2 rostsejtfalat, ezáltal gömböket hoz létre. A gömbök száma és a duzzadás foka tükrözi a cellulózrost múltját, mint például fehérítés és mechanikai kezelés.

image analysis program was used. Dislocations are most easily seen in latewood fibres.

Scanning electron microscopy

Pulp fibres and fragments (free of buffer) following HCl or cellulase treatments were prepared and gold sputtered as described [4,7]. Electron microscopy instruments used were Philips ESEM XL 30 or Hitachi 4500 FE-SEM.

Results and discussion

Dislocations as light bands are most easily seen in latewood fibres in polarised light and one example is shown in **Fig. 1.** It was reported in Riga 2004 [8] and in [1] that industrial (Mill) pulps, both from early thinnings and final cutting, were significantly more sensitive to HCl cleavage indicating more dislocations than in laboratory (Lab) produced kraft pulps from the same spruce wood batch. Thus the HCl-method is a valuable tool in Strength Delivery studies [1,2]. These results have been confirmed for many kraft pulps and one example is given in **Fig. 2.** In a comparison between bleached pine and spruce kraft pulps, it was shown that pine pulp fibres were less sensitive to HCl cleavage than spruce kraft pulps (**Fig. 3**). A similar result was obtained for pine and spruce TMP pulps.

Influence of hemicellulose

Bleached spruce pulp fibres (PH, RDH, ITC, PS) containing 8.1, 15.9, 17.0, and 20.8 % hemicellulose, respectively were tested with the HCl-method [2]. The corresponding cleavage per fibre were: 4.90, 3.42, 3.10, 2.43 (R^2 = 0.965). Thus hemicelluloses, mainly glucomannan, may protect the cellulose from acid cleavage.

Fibres from a kraft pulp fibre line

Pulp fibre samples were taken along a pulp fibre line. Strong cleavage was obtained after the wash press in point 2 indicating fibre compression and mechanical effects in the wash press [2]. In samples 3-5, the cleavage numbers gradually decreased probably due to removal of HCl-vulnerable structures already in the bleaching process. Thus the HCl-method can be used to study all kinds of pulps and to evaluate pulping processes (**Fig. 4**).

Comparison of fibre cleavage by HCl and Cellulase

Four pulps (see **Table 1**) were tested with HCl and the cellulases N476 (EG), N 342 and Celluclast 1.5L

Fig. 1. Spruce latewood fibre showing dislocations in pol. light
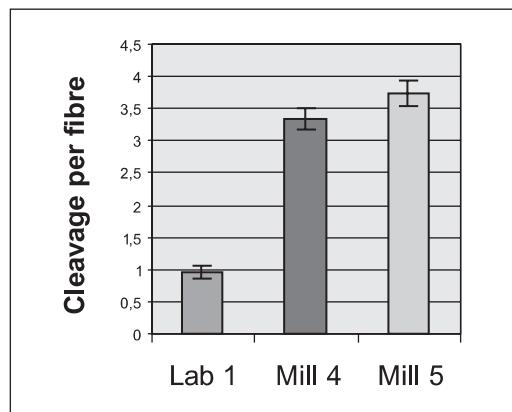
Fig. 2. Cleavage of Lab and Mill spruce fibres by HCl.
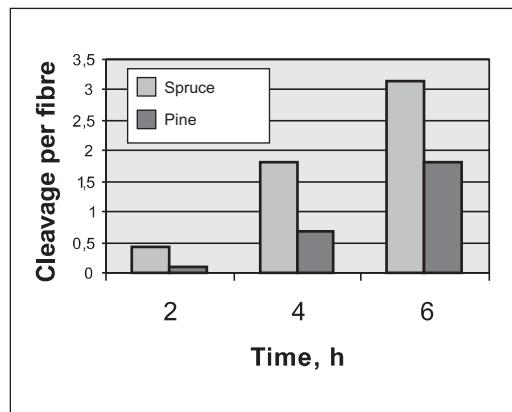
Fig. 3. Cleavage of bleached pine and spruce fibres by HCl

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(both with EG + CBH). The last two cellulase mixtures gave good fibre cleavage in dislocations but only HCl could differentiate between Mill and Lab pulp fibres (*Table 1*). N476 containing only endoglucanase had little cleavage activity.

Some interesting points from *Table 1*: Mill fibres were more sensitive to acid than Lab fibres, and pulps with a larger spruce to pine relationship were also more acid sensitive. Due to the synergistic effect, N342 and Celluclast gave very strong cleavage of all pulp fibres. The cellulases, however did **not** distinguish between Mill and Lab pulps. HCl swelled the above fibres between 0.7-1.7 µm, while N342 and Celluclast decreased fibre width by 1-3 µm (not shown) indicating removal of S1 and the outer part of S2 fibre cell walls by cellulase **[4]**. Furthermore, HCl released most xylose (0.1 g/l) and very little glucose (0.015 g/l). This indicates that HCl at 80-82°C is penetrating all cell wall layers mainly degrading hemicelluloses. Thus degradation of xylan and glucomannan by the acid seems to be of some importance for the differences obtained between Mill and Lab pulp fibres. For the large cellulase molecules acting mostly on the fibre surface; a supposition supported by the
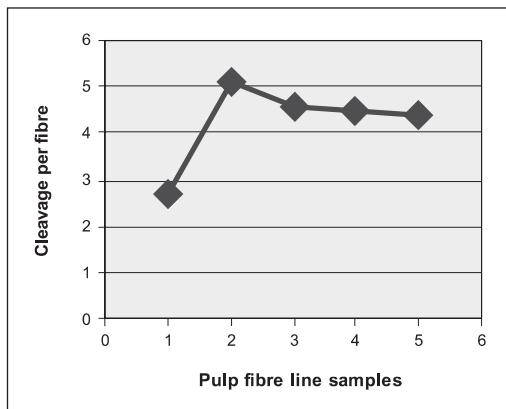
decreased fibre width, with glucose beeing the major sugar released reflecting the catalytic activity of EG + CBH giving up to 0.8 g/l of glucose.

Balloon swelling of pulp fibres

The morphology of balloons produced by 79% phosphoric acid swelling **[5]** was studied in light- and electron microscopy (SEM and TEM). The goal was to evaluate balloon swelling as a method for characterization of spruce kraft pulp fibres **[5,7,9]**. The studies showed that phosphoric acid was the best swelling agent as compared with LiCl/DMAc giving a slimy substance on the fibre, which hindered electron microscopy studies. Very stable balloons, possible to study in EM, were obtained in fibres with 3-4% lignin. Cellulase-treated, bleached or mechanically affected fibres gave rapid ballooning and further dissolution of the fibre. The reason for the remarkable regularity of swelling in the form of "string of pearls" or if dislocations are involved is not known with certainty. Eckhart et al. **[9]** developed an image analysis method to study fibre swelling in copperethylenediamine and calculated degree of swelling in percent of the total fibre length. In this way an indication of outer fibre wall damage for pulps of similar type was obtained. Dislocations may be involved in this fibre swelling.

Le Moigne et al. **[10]** recently investigated swelling of bleached cotton fibres, Na-sulfite pine pulps and Ca-bisulfite spruce pulps in N-methylmorpholine-N-oxide – water mixtures and in NaOH-water. It was suggested that both the primary wall and the outer part of the S1 wall are important in balloon swelling and formation of "unswollen sections" between the balloons (similar as in **Fig. 7**). This is partly in contrast to our opinion **[6,7]** after using spruce kraft pulp without primary wall, which if present, is only 0.1-0.2 µm thin. We suggested that it is mainly the S1 wall, which is rolled off the balloons creating the "collars" shown in Fig. 7. In COST Action E54 we want to continue cooperation to clarify further the mechanisms of balloon swelling of different


Fig. 4. HCl cleavage of fibres from a pulp fibre line.

Pulp type	Relation Spruce: Pine	HCl Cleavage/fibre	N476 Cleavage/fibre	N342 Cleavage/fibre	Celluclast 1.5L Cleavage/fibre	Celluclast 1.5L Cleavage/fibre
Mill I	33:67	1.93 ± 0	0.42 ± 0.07	8.40 ± 0.08	*5.59 ± 0.09	---
Lab I	33:67	0.935 ± 0.24	0.32 ± 0.07	9.31 ± 0.24	*5.73 ± 0.60	---
Mill II	84:16	4.16 ± 0.02	0.22 ± 0.03	9.98 ± 0.42	*5.91 ± 0.08	**9.93 ± 0.23
Lab II	84:16	1.23 ± 0.02	0.23 ± 0.04	9.95 ± 0.68	*5.59 ± 0.75	**9.62 ± 0.34

Table 1. Cleavage of Mill and Lab kraft pulp fibres by HCl (81°C, pH 0) and by different cellulase mixtures at 50°C.
*Cellulase N476 was run at pH 7, and the others at pH 5. *0.3 ml; **0.6 ml enzyme.*
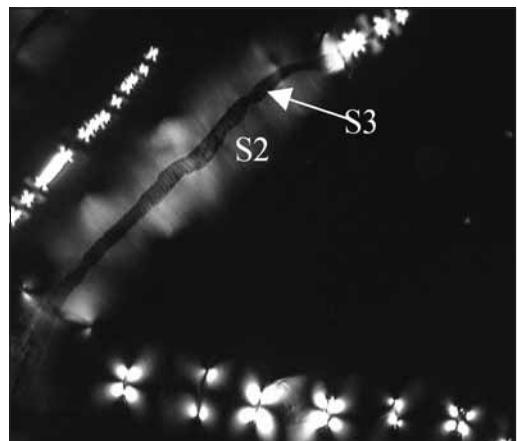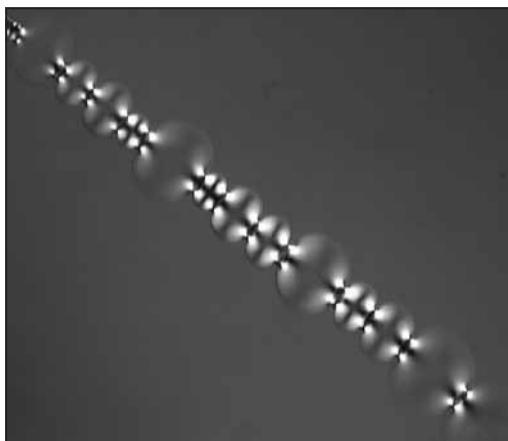
Spruce fibre balloon swelling in phosphoric acid **[6,7]**.
Figs 5-6: Polarized light microscopy, S2 and S3 cell walls are shown in Fig. 6.

cellulose and wood fibres. Another line of investigation is to use Raman spectroscopy to see whether phosphoric acid is converting cellulose I to cellulose II in bleached fibres **[11]**.

HCl-effects on Eucalyptus and birch pulp fibres were also tested **[12]**. These results indicate that **birch** kraft pulp fibres (ca 1 mm) are more resistant to HCl than the 0.65 mm long **Eucalyptus** fibres. Despite longer birch fibres, they were poorly cleaved as compared with Eucalyptus fibres (cleavage 0.22-0.35 vs 0.835-1.40). Vessels and parenchyma may be involved in these differences.

Conclusions

– The HCl-method can be used to determine dislocations and other weak points in different pulp fibre types and may be a complement to wet zero span measurements and other paper tests.
– Fibre length determination in Fibermaster or Kajaani or other instruments can be done in many paper and fibre research laboratories.
– Spruce pulp fibres are more sensitive to HCl than pine pulp fibres.
– Pulp samples from fibre lines can be studied with the HCl-method.
– Hemicellulose degradation by HCl seems to be of importance for the differentiation between Mill and Lab pulp fibres, while cellulases mainly release glucose from the fibre surfaces causing decreased fibre width.

Spruce fibre balloon swelling in phosphoric acid **[6,7]**.
Fig. 7. SEM micrograph of balloons and rolled off S1 "collars".

– HCl penetrates deeply into the fibre cell walls, while cellulases act mostly on the fibre surfaces and only penetrate the fibre to a certain extent in dislocations, that are supposed to be of a more amorphous character.
– Dislocation cleavage and/or cleavage of β-1,4-glucosidic bonds in cellulose by HCl or cellulase give little sugar release and the amount of sugars cannot be used to differentiate between Mill and Lab pulp fibres.
– Fibre swelling and ballooning in phosphoric acid or copperethylenediamine coupled with image analysis may be used for pulp fibre characterisation.

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Egyedi cellulózrostok mikromechanikája

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Különböző típusú rostanyagokat, beleértve fenyő-, lombos, fehérített és fehérítetlen cellulózokat vetettünk alá szakítási vizsgálatoknak. Az egyedi rostok vizsgálatához papírkeretbe rögzített rostokat alkalmaztunk. A cellulózrostok törékeny természete miatt a javasolt egyedi rost vizsgálatok nem hoztak ígéretes eredményeket. Az egyedi rost sejtfalának MTS Nano indenterrel [*alakváltozást, bemélyedést mérő* szerkezet] végrehajtott keménységi vizsgálata a sejtfal elhelyezésének nehézsége miatt nem volt sikeres. Jelenleg a sejtfal keménységét Tribo nanoindenterrel mérjük, amelyre AFM van felszerelve, és a rost hosszanti irányában a bemetszéseket MTS nanoindenterrel végezzük, és mindkettő kiváló eredményeket mutatott az előzetes vizsgálatok során.

Micromechanics of single pulp fibres

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Pulps of various grades including softwood, hardwood, bleached, unbleached were subjected to tensile testing. Paper frame set-up was adopted to test the single pulp fibres. Due to the brittle nature of pulp fibres, proposed single fibre tests did not yield promising results. Hardness measurements on single fibre cell-wall using MTS Nano indenter were not successful due to the difficulties in locating the cell-wall. Presently cell-wall hardness is measured using Tribo nano indender equipped with AFM and indents on the fibre longitudinal direction is performed using MTS Nano indenter, both revealed excellent results during preliminary tests.

Az egyedi rost-rost kötések kötési felületének mérése

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Ez az előadás az egyedi rost-rost kötések kötési felületének meghatározási módszerét mutatja be mikrotommal történő sorozatos szeletelés és képelemzés alapján. A kötési terület méretét és háromdimenziós struktúráját a keresztmetszeti rostmorfológiával együtt értékeltük. A lyukakat és átfedett, de nem kötött éleket pótlólag mértük.

Az egyedi rost-rostkötések hidegen polimerizálódó gyantába vannak beágyazva. Kezelés után a kötési terület háromdimenziós struktúráját elemeztük automatikus mikrotom rendszer alkalmazásával. A mikrotommal három mikrométer vastagságú szeleteket vágtunk le, és a vágási területet minden egyes vágás után automatikusan megjelenítettük. Ez a rost keresztmetszetéből számos képet eredményez, amely a rost-rost kötés háromdimenziós alakját reprezentálja.

Minden egyes vágásnál képelemzéssel határoztuk meg azt a vonalat, ahol a rostok érintkeznek, és megmértük ennek hosszát. A kötési területet úgy számítottuk ki, hogy a kötésvonal hosszát megszoroztuk a vágás vastagságával (3 μm).

A kötési terület mellett a rostok számos morfológiai paraméterét és kötési területét mértük képanalízissel. A rostkeresztmetszet, a rostkerület, rostfal vastagsága, a rost összeomlása, a rost szélessége, és a nem tökéletes kötés foka átfogó képet adnak a rost-rost kötésről.

87 rost-rost kötést elemeztünk lineáris korrelációval, amely megmutatta, hogy a rostszélesség ad magyarázatot a kötési terület majdnem 50%-ára. Ugyanakkor a többi morfológiai paraméter (rostfal vastagsága, rostkerület, rostkeresztmetszet területe), 2 rost keresztezésének szöge és a nem tökéletes kötés is fontos szerepet játszanak, és nem hagyhatók figyelmen kívül. Ezek az eredmények csak egyszerű korreláción alapulnak, a további elemzésekhez lineáris regressziós modellezést kell végezni, hogy megtaláljuk a kölcsönkapcsolatokat és redundanciákat.

Measuring the bonded area of individual fiber-to-fiber bonds

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Summary

This paper presents a method for the determination of bonded area of single fiber-to-fiber bonds, based on microtome serial sectioning and image analysis. The size and three dimensional structure of the bonded area are assessed together with cross sectional fiber morphology. Holes and overlapping but unbonded edges are measured additionally.

87 fiber-to-fiber bonds of unbleached and unbeaten softwood Kraft pulp were analyzed. Correlations between bonded area and morphological parameters show influences on size of bonded area. In this study only single correlations were performed, so linear modelling and analysis of interrelations and redundancies will be part of future work.

Introduction

Paper strength depends on the strength of single fibers and the strength of the fiber-to-fiber bonds. The strength of the fiber-to-fiber bonds again depends on the size of the bonded area and on the specific bonding strength. Measuring the actual size of the bonded area helps to understand the governing factors for fiber-to-fiber bond strength. In this study we investigate the distribution of the bonded area for individual fiber-to-fiber bonds. We propose a novel method for the determination of bonded area based on microtome serial sectioning. Analysis of geometrical and morphological parameters of 87 single fiber-to-fiber bonds will help to explain the governing factors for the size of bonded area.

Measurement of bonded area

The method for the determination of the bonded area is based on microtome serial sectioning and image analysis. It yields the size of bonded area together with the three-dimensional structure of the bonded area and morphological fiber parameters.

The samples are embedded in a gelatine capsule using a cold-polymerizing resin. After curing, the three dimensional structure of the bonding region is analyzed using an automated microtomy system **[1]**. Slices with a thickness of 3 μm are repeatedly cut off the embedded sample with the microtome and the cutting area is imaged automatically after every cut with a pixel size of 0,161 μm. This yields a stack of images of the fiber cross section, representing the three-dimensional shape of the fiber-to-fiber bond.

Three exemplary light microscope images at different cutting positions are given in **Fig. 1.** The first image (a.) shows the edge of the bond, the fibers contact region is small. The left fiber is fully collapsed and folded, the right fiber on the other hand is fully collapsed and unfolded. The following two images (b. and c.) proceed deeper into the bond. Because of the irregularity of the fold the contact between the fibers is
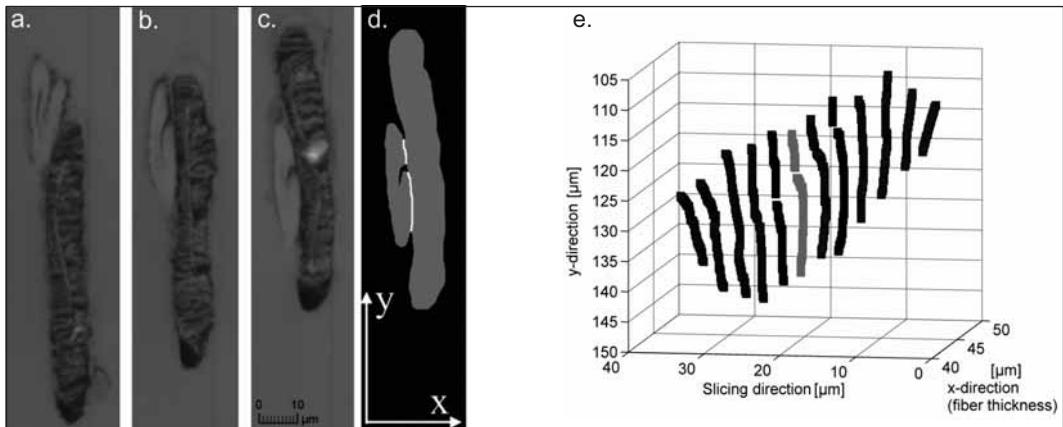
Fig 1 a., b., c.: Microscope images of fiber-to-fiber bond cross sections. d.: Segmented fibers of c. with bonding line. e.: 3-dimensional representation of bonded area by plotting the bonding lines.

interrupted. Fig. 1 (b.) shows, that the fibers are only partly bonded. In the upper part of the bond the fibers are separated. In the next image (c.) the fibers are in contact over a greater length, but the contact is interrupted.

Segmentation of the fiber regions is performed by the operator, the fiber outline is drawn into the microscope image by hand (Fig. 1 d.).

From these fiber outline images the morphology of the bonding region and the fibers is determined using image analysis.

For bonded area measurement we consider these fiber regions to be bonded, where the fibers in the microscope images are in direct contact. This region is determined image analytically, yielding a bonding line for every cut, as it is indicated by the white line in Fig. 1 (d.).

Bonded area is calculated from bond line length multiplied with the cut thickness (3 μm). A 3-dimensional representation of the bonding region is obtained by plotting all lines of one bond (Fig. 1e.). The rightmost line corresponds to the length where the fibers were in contact in the first cut (a.). The line which is marked gray belongs to the cut of the label image (d.). The interruption caused by the fold of the left fiber can be seen. The distance between the lines is equivalent to the cut thickness (3 μm).

In addition to bonded area several morphological parameters of fibers and bonding region are measured image analytically using a proce-dure described by [2]. Fiber cross sectional area, fiber perimeter, fiber wall thickness, fiber collapse, fiber width and incomplete bonding give a comprehensive picture of the fiber-to-fiber bond.

Results

Bonded area and morphological parameters of 87 fiber-to-fiber bonds of unbleached unbeaten softwood Kraft pulp were analyzed. We tried to find linear correlations between bonded area and morphology.

The mean value for bonded area is 1130 μm² and standard deviation is 602 μm². **Fig. 2** shows a histogram of all values for bonded area, the distribution is positively skewed.
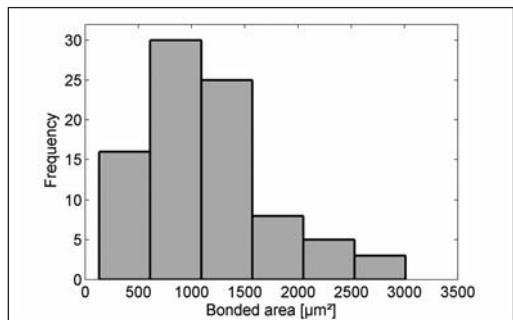

Fig. 2 Histogram of values for bonded area, mean=1130 μm², variance=602 μm², skewness=0.9495.

Determining factors for bonded area

The influencing factors on the size of bonded area will be discussed in the following section, based on the results for bonded area and morphological parameters.

Fig. 3 shows correlations between bonded area and morphological parameters, the R^2 value is given in each diagram.

Fig. 3 (a) shows that fiber width has the biggest impact on size of bonded area. The drawing in **Fig. 4** illustrated this relationship. Bigger fiber width leads to larger bonded area.

The influence of fiber width is also reflected in fiber perimeter (Fig. 3c), as bigger fiber width leads to a bigger fiber perimeter. The same correlation is also valid for fiber cross sectional area (Fig. 3b).

Incomplete bonding (Fig. 3d) also seems to be important for the size of bonded area. This shows that only consideration of morphological fiber parameters is not enough, as in some
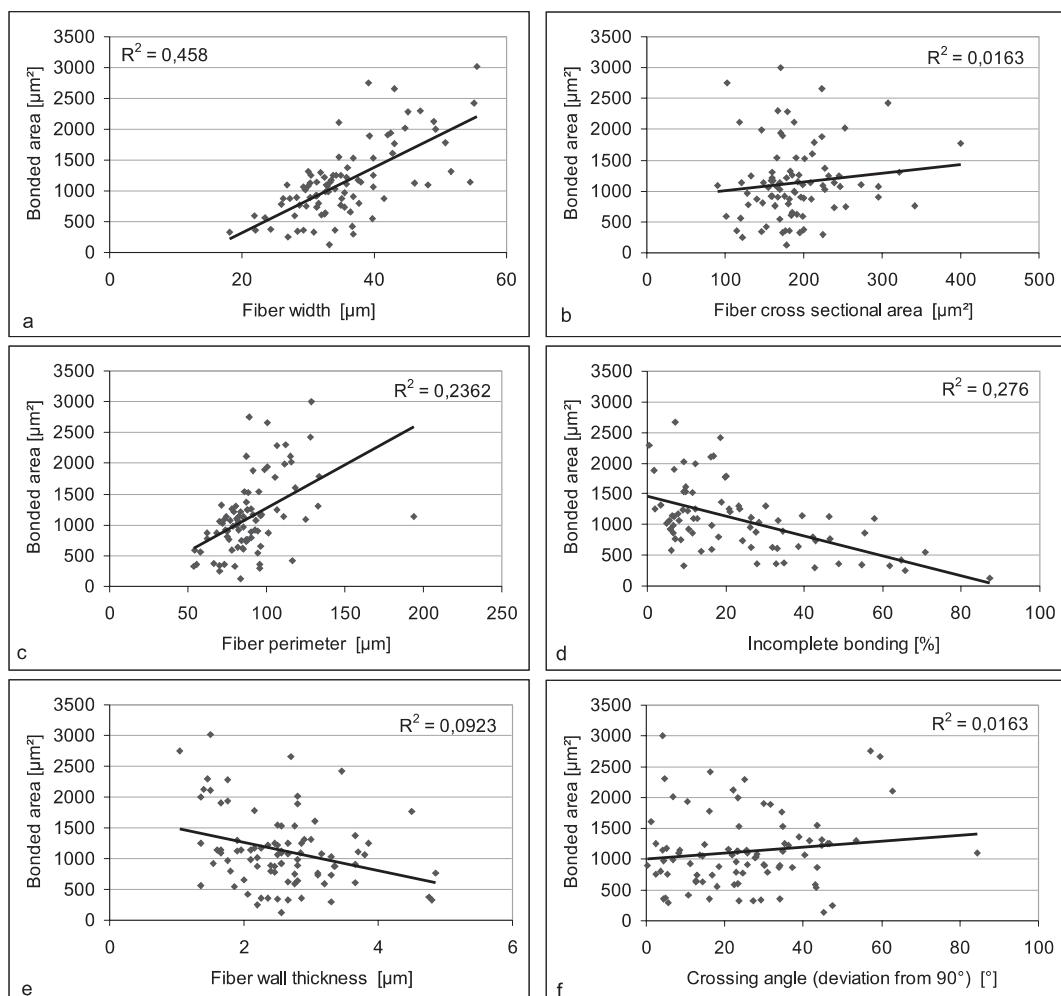

Fig. 3 Correlations between bonded area and morphological parameters (fiber width, fiber cross sectional area, fiber perimeter, incomplete bonding, fiber wall thickness and crossing angle)

cases quite large unbonded areas have to be considered.

Fiber wall thickness (Fig. 3e) is closely related to conformability. Summerwood fibers with a thick fiber wall cannot conform so well to each other and so bonded area gets smaller, though the influence is far smaller than the influence of fiber width.

The deviation of the crossing angle from right angle also has an influence on size of bonded area (Fig. 3f). Bigger deviation from right angle leads to bigger bonded area, as can also be seen in Fig. 4.

Conclusions

The method introduced in this paper seems to be a useful tool to investigate bonded area together with the morphology of the fiber cross sections and the bonding region. The method is able to measure incomplete bonding (holes and overlapping but unbonded regions at the border of the bond). This combined measurement of fiber morphology and bonded area morphology might contribute to a comprehensive understanding of fiber-to-fiber bonding.

The analysis of 87 fiber-to-fiber bonds showed that fiber width explains almost 50 % of bonded area. Also other morphological parameters (fiber wall thickness, fiber perimeter, fiber cross sectional area), crossing angle and incomplete bonding play an important role and have to be considered.

Please note that only single correlations were analyzed in this study. Linear modeling will have to be performed in order to investigate interrelations and redundancies.

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Fig. 4 Influence of fiber width and crossing angle on size of bonded area.

Rostanyagok víztelenítése és az őrlés hatékonyságának javítása celluláz kezeléssel

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A papír- és karton gyártásában a leginkább energiaigényes folyamat az őrlés és a rostanyagok szárítása. A celluláz termékek alkalmazása az egyik legkorszerűbb módszer a víztelenítés és az őrlés hatékonyságának javítására. Ha az őrlés előtt adagolunk enzimet, annak hatása eltérő lesz az őrlés utáni kezelés hatásától. Az őrlés előtti alkalmazás jobb őrlési hatékonyságot eredményez, míg az őrlés utáni kezelés nagyobb őrlésfokot eredményez. Tény, hogy a celluláz a gél formájú struktúrák lebomlásához vezet. Ezeket a víztelenedés javítására lehet alkalmazni hidrolízis révén a rostokban, finomanyagokban és oldott kolloidanyagokban jelenlévő cellulóz- és hemicellulóz leginkább hozzáférhető részeiben. A megfelelő módon alkalmazott cellulázok növelhetik vagy helyreállíthatják a rostszilárdságot, csökkenthetik az őrlési időt, és növelhetik a rostok közti kötést fibrilláción keresztül.

Ennek a munkának a célja az, hogy vizsgáljuk az új celluláztermékeknek az őrlésre, a víztelenedésre és a rostanyag szilárdsági tulajdonságaira gyakorolt hatását.

A vizsgálatokat a Bulgáriából, az „Duropack-Trakia-Papír" AD – Pazardjik által biztosított OCC rostanyaggal, a „Mayr-Melnhof" AD –Nikopol által biztosított festéktelenített rostanyaggal, a Svilocell AG által biztosított fehérített cellulózzal, valamint fehérített brazil eukaliptusz rostanyaggal végeztük.

Az enzimes kezelést a Novozymes AS FiberCare® D celluláz termékével végeztük, amely nagyon hatékony, de ugyanakkor kíméletes a rostokkal.

0,05–0,2% enzim 20–45%-kal javítja az OCC-rostanyag víztelenedését, illetve max. 25%-kal az őrlésfokot. Nagyobb négyzetmétertömegű termékek gyártásában a szárító gőzfogyasztása akár 4%-kal is csökkenhet. Az enzimes kezelés kapott eredményeit a másodlagos rostok kolloid anyagainak részleges destrukciójával lehet értelmezni. Ez a gélfrakció megtartja a vizet, és a másodlagos rostok lassú víztelenedését okozza. A hulladékpapír FiberCare® D kezelése lassan növeli a rostanyag szakadási hosszát, míg a tépő- és repesztési mutató csökken.

Az „Mayr Melnhof" AD által szállított festéktelenített rostanyag víztelenedésében vizsgált cellulázhatás kisebb enzimaktivitást mutat, amely nagyobb FiberCare® D terhelést tesz szükségessé ugyanolyan víztelenedés eléréséhez.

Az oldatban a redukált cukrok vizsgálatának eredményei körülbelül 0,4-0,5%-os rostveszteséget mutatnak, ami a kolloid anyagok oldódásával kapcsolatos. A papír minőségek és a rostanyag víztelenedése közötti optimális egyensúlyt alacsony szintű enzimterhelésnél lehet elérni.

A FiberCare® D hatása az őrlés előtti kémiai rostanyagkezelésben elősegíti az őrlésfok növekedését 14°SR-rel eukaliptuszra, és 24°SR-rel a Svilocell rostanyagára. Az enzimadagolásnak a két rostanyag típus szilárdsági tulajdonságaira gyako-

Pulp dewatering and refining efficiency improvement by cellulase treatment

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Summary

Refining and pulp drying are the most energy-intensive processes in the production of paper and boards. The usage of cellulases products is one of the modern methods to improve dewatering and refining efficiency.

The enzyme treatment was performed with the Novozymes AS cellulase product FiberCare® D.

The carried out investigation shows the positive effect of enzyme treatment on the secondary fiber dewatering. The obtained results of enzyme action can be interpreted by partial destruction of colloidal substances of secondary fibers.

The effect of enzyme treatment on the pulp strength properties shows insignificant increasing of breaking length, while the tear index and the burst index decrease. Probably the FiberCare® D action at low enzyme charge contributes an improvement on the paper structure independent of fiber destruction processes. Optimal balance between paper qualities and pulp dewatering is reached at low level enzyme charge.

The pre-refining cellulase treatment of Svilocell and eucalyptus bleached pulp significant improves beating efficiency without pulp strength properties loss. The influence of enzyme treatment on the pulp yield and waste water pollution are not significant.

FiberCare® D is able to waste paper dewatering improvement and is a prerequisite for dryer steam consumption decreasing, refining energy costs saving and paper machine capacity increasing.

Introduction

Cellulase pulp treatment has been investigated for several years, with the goal of achieving improved refining efficiency and fibre dewatering. There are two methods for enzyme treatment. Addition of enzyme prior to refining has a very different effect compared with a post-refining treatment. Pre-refining application results in improved refining efficiency, while a post-refining treatment results in increased furnish freeness. A combination of the two can provide optimized strength and drainage benefits [1]. Beating and refining are mechanical processes that enhance fibrillation and inter-fiber bonding. Properly applied, cellulases can enhance or restore fiber strength, reduce beating times, and increase inter-fiber bonding through fibrillation. A correctly applied enzyme treatment provides a tool that can improve recycled paperboard operations. This is accomplished by treating the refined stock with an enzyme blend to recover a portion of the freeness typically lost through refining. A pre-refining enzyme treatment can help the papermaker meet strength tests more readily through improved refining efficiency. Mill experience has shown that a combination of these two methods can provide strength and drainage benefits.

Distinguishing feature of secondary fibers is the breaking down of cell walls, causing liberating fine particles, which grow swollen and change in gel form. They retain water, slow down the dewatering, impede drying, and causes over consumption of chemicals in the paper production. It is a standing fact that cellulase lead to breaking down the gel form structures [1, 2]. They can be applied to improve the drainage by hydrolyse the most accessible parts of the cellulose and hemicellulose present in the fibers, fines and dissolved colloidal substances [3].

Jackson et al. [4] suggest that enzymes can either flocculate or hydrolyse fines and remove fibrils from the surface of large fibres. According to these authors, the enzyme-aided flocculation occurs when a low enzyme dosage is used. In this case, fines and small fibre particles aggregate with each other or with the larger fibres, decreasing the amount of small particles in the pulp and consequently improving pulp drainage. For higher enzyme concentration, flocculation becomes less significant, and fragmentation of the fibres begins to predominate. Numbers of authors observe pulp strength proper-

rolt hatását vizsgálva javulást mutattak ki a szakadási hosszban, míg a tépési mutatóra a FiberCare® D alacsony mennyiségben nem gyakorolt negatív hatást. Azt is megfigyeltük, hogy az eukaliptusz rostanyag 40°SR őrlésfokát 20 perccel hamarabb értük el FiberCare® D kezeléssel. Ugyanakkor a rostanyag szilárdsági tulajdonságainak függése a tépési mutatók és a szakadási hossz esetében hasonló. Ezért az elért jelentős őrlésjavulás adott őrlésfokon, FiberCare® D kezeléssel 0,05%-os alacsony enzimadagolás mellett nem befolyásolja a rostanyag szilárdsági tulajdonságait, melyeket kisebb őrlési energiaigénnyel is el lehet érni. A FiberCare® D optimális adagolása mellett (0,025% a Svilocell rostanyag és 0,05% az eukaliptusz rostanyag esetében) 0,2%-nál kevesebb cukor keletkezik. Ezért az enzimes kezelés eredményeként a hozamveszteség és a szennyvíz szennyezettsége nem jelentős.

A másodlagos rostanyagok FiberCare® D celluláz kezelésével folytatott vizsgálatok lehetőséget mutatnak a rostanyag víztelenedésének jelentős javulására.

Optimális enzimadagolás mellett a szakadási hossz javulását figyeltük meg, mivel a celluláz főleg az oldott kolloidanyagokra van hatással, és csak enyhén csökkenti a rostanyaghozamot.

A FiberCare® D-hatékonysága a másodlagos rostok típusától függ, és az enzimaktivitás töltőanyagok és rostanyag-adalékok jelenlétében csökken. Az őrlés előtti enzimes kezelés lényegesen javítja az őrlés hatékonyságát anélkül, hogy rontaná a rostanyag szilárdsági tulajdonságait. Az enzimeknek a rostanyag őrlésére vagy a papírhulladék víztelenedésére gyakorolt hatásának kialakítása előfeltétele annak, hogy csökkenjen a szárító gőzfelhasználása, illetve őrlési energiaköltség-megtakarítást és papírgépi kapacitásnövekedést tudjunk elérni.

WG-meeting

ties decreasing by rise of enzyme quantities and by increase reaction time **[5, 6, 7]**.

Surface properties may be modified, not only because of enzymatic hydrolysis of the outer layers of the fibre, but also because of the adsorption of enzyme molecules onto the fibre surface. It could be speculated that changes in fibre–water interaction, induced by the presence of enzyme molecules, might be the factor responsible for drainage and strength modification **[8]**.

The purpose of this work is to investigate the effect of the new cellulase product on the refining and dewatering improvement and on the pulp strength properties.

Experimental

The investigations were performed with OCC pulp supplied by "Duropak – Trakia-Papir" AD – Pazardjik, deinking pulp provided by "Mayr-Melnhof" AD – Nikopol, bleached pulp supplied by Svilocell AD – Bulgaria and with bleached Brazilian eucalyptus pulp.

The enzyme treatment was performed with the Novozymes AS cellulase product FiberCare® D, which is designed to be effective, yet gentle on fibers. This is accomplished because FiberCare® D takes advantage of Novozymes' proprietary mono-component cellulase technology, resulting in a product that is highly specific and targeted in its action.

The enzyme treatment conditions were as follows: pulp consistence 6 and 10%, temperature 60°C, reaction time 60 min., enzyme charge 0.025 – 0.5 % and pH 4 – 7.

The reducing sugars were determined according to a DNS method **[8]**.

Pulp beating was performed with Jokro mill according to ISO 5264-3 at duration from 10 to 50 min.

The degree of refining was determined on the Schopper Riegler device according to ISO 5267. The rate of dewatering was determined on the same device.

Pulp strength properties: breaking length, tear index and burst index were determined according to the ISO 1924, ISO 1974 and ISO 2758 respectively.

Results and discussion

The effect of FiberCare® D treatment on the dewatering time and refining degree of Duropak - Trakia-Papir OCC pulp is shown on **Fig. 1** and **Fig. 2.** The enzyme charge 0.05–0.2% improves the pulp dewatering by 20–45% and refining degree up to 25% respectively. In the production of the heavier weight, dryer steam consumption is able to decreased by over 4%.

The obtained results of enzyme action can be interpreted by partial destruction of colloidal substances of secondary fibers. That gel fraction retains water causing slow dewatering of secondary fibers.

Similar study of cellulase action on the pulp dewatering is conducted with deinking pulp supplied by "Mayr-Melnhof" AD. Typical feature of that pulp is the present of fillers (basic $CaCO_3$), pulp additives and mechanical fibers. It is found a lower enzyme activity with respect to that pulp, which determines on the higher FiberCare® D charge for achievement the same dewatering.

The effect of enzyme treatment on the pulp strength properties is present in **Table 1.** As it is

Fig 1. Influence of enzyme charge on the pulp dewatering rate, (pH 5, T=60°C and t = 60min)
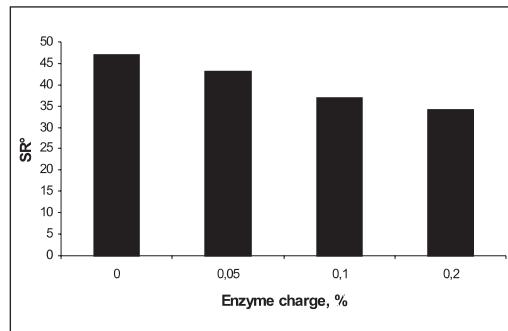
Fig 2. Effect of enzyme charge on the pulp refining degree, (pH 5, T=60°C and t = 60min)

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Enzyme charge, %	Duropak - Trakia-Papir OCC pulp			Mayr-Melnhof – Nikopol deinking pulp		
	Breaking length, m	Tear ind., mN.m²/g	Burst ind., kPa.m²/g	Breaking length, m	Tear ind., mN.m²/g	Burst ind., kPa.m²/g
0	2720	4.5	2.7			
0.05	2740	4.4	2.7			
0.1	3040	3.7	2.5	2790	4.0	2.5
0.2	3000	3.3	2.2	3130	3.6	2.3
0.5				2970	3.2	2.1

Table 1. Effect of FiberCare® D charge on the waste paper strength properties
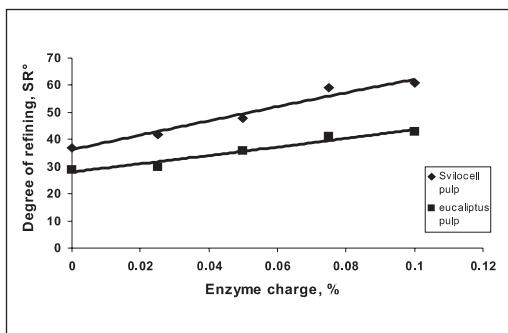

Fig. 3. Influence of enzyme charge on the refining efficiency
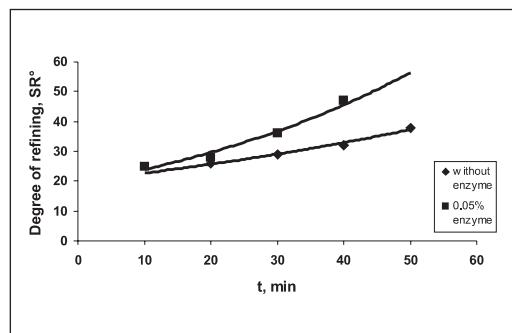
Fig. 4. Effect of enzyme treatment (pH 4.5, T=60°C, t=60min) on the rate of eucaliptus pulp beating

Enzyme charge, %	Svilocell pulp, pH 6.5, T=60°C, t = 60min			Eucaliptus pulp, pH 4.5, T=60°C, t = 60min		
	Breaking length,m	Tear ind., mN.m²/g	Burst ind., kPa.m²/g	Breaking length, m	Tear ind., mN.m²/g	Burst ind., kPa.m²/g
0	5200	5.0	4.2	7800	5.2	5.6
0.025	5300	5.1	4.2	7900	5.2	5.7
0.050	5400	4.9	4.3	8200	5.3	6.4
0.075	5450	4.7	4.3	8200	4.8	6.1
0.1	5600	4.4	4.4	8100	4.6	6.0

Table 2. Influence of pre-refining cellulase charge on the pulp strength properties
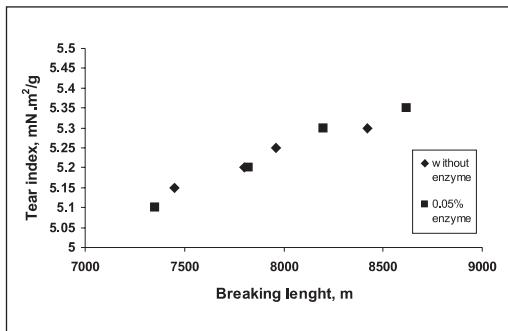
Fig. 5. Influence of enzyme treatment on the eucalyptus pulp breaking length - tear ind. dependence
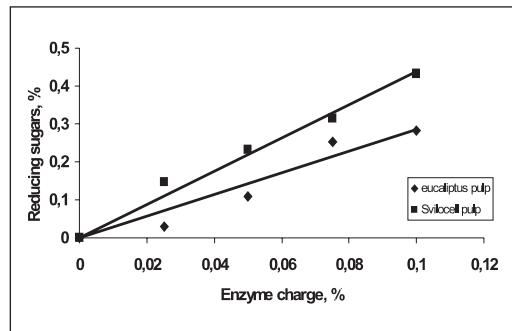

Fig. 6. Effect of enzyme charge on the reducing sugars formation

shown the breaking length slowly increases by the enzyme charge, while the tear index and the burst index decrease. Probably the FiberCare® D action at low enzyme charge contributes an improvement on the paper structure independent of fiber destruction processes.

The results of analysis of reduced sugars in the solution show fiber losses about 0.4–0.5 % which are connected with dissolving of colloidal substances. Optimal balance between paper qualities and pulp dewatering is reached at low level enzyme charge.

It is studied the effect of cellulase charge in pre-refining chemical pulp treatment on the pulp beating efficiency. The results obtained for the two types of bleached pulp, presented in **Fig. 3**, show a total refining degree increase with 14°SR and 24°SR for eucalyptus and Svilocell pulp respectively. The performed investigation on the effect of enzyme charge on the strength properties of the two types of pulp show improvement on the breaking length, while the tear index is not adversely affected by FiberCare® D at low dosage (**Table 2**).

The influence of enzyme action on the rate of eucaliptus pulp beating can be seen on the **Fig. 4**. It is observed that pulp refining degree 40^0SR is reached for 20 min. less in the case of FiberCare® D treatment. In the same time the pulp strength properties dependence between tear index and breaking length is a common relation for enzyme treated and untreated pulp. (**Fig. 5**).

Therefore the obtained significant beating improvement to a given refining degree by FiberCare® D treatment at low enzyme dosage up to 0.05% is not affected on the pulp strength properties, which can be developed with less refining energy requirements.

The obtained reducing sugars as a result of cellulase treatment are in the range up to 0.4 % based on pulp in relation of enzyme charge and type of pulp (**Fig. 6**). At optimal dosage of FiberCare® D (0.025% for Svilocell pulp and 0.05% for eucaliptus pulp) the generated sugars are less of 0.2%. Therefore in the result of enzyme treatment the yield loss and waste water pollution are not significant.

Conclusion

The carried out investigations on cellulase treatment of secondary fiber materials by FiberCare® D show opportunity for significant improvement of pulp dewatering.

It is observed breaking length improvement in the optimum enzyme dosage as the cellulase affects mainly on the dissolved colloidal substances and slightly reduces the pulp yield.

FiberCare® D efficiency depends on the type of secondary fibers and enzyme activity decreases on the presence of fillers and pulp additives.

The pre-refining enzyme treatment significantly improves beating efficiency without pulp strength properties deterioration. At optimal FiberCare® D dosages 0.025%–0.05% the yield loss and waste water pollution are not significant.

Established enzyme effect on the pulp beating or waste paper dewatering is a prerequisite for dryer steam consumption decreasing, refining energy costs saving and paper machine capacity increasing.

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Hogyan hat az enzimes kezelés a rost tulajdonságaira?

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Az enzimek világszerte nagy mennyiségben és számos alkalmazásban használt vegyi anyagok. Ezeket elsősorban az élelmiszeriparban és mezőgazdaságban használják. Az enzimek előállításában jelenleg végbement fejlődés lehetővé tette, hogy tiszta egynemű komponenseket állítsunk elő. Így lehetővé vált az enzimek felhasználása a rostelőállítás folyamataiban is.

Rostanyag szuszpenziókhoz különböző enzim típusokat adagoltunk annak érdekében, hogy meghatározzuk, milyen lesz a hatás az ilyen vegyszerekkel kezelt rostok esetében. A cellulóz viszkozitásváltozásait mértük eukaliptusz és fenyőfa cellulózokon. Az enzim típusától függően a kezelés következményei eltérőek voltak. A fenyőcellulóz viszkozitása volt a leginkább érintett cellulázzal történő kezeléskor, összehasonlítva az eukaliptusszal. A maximális veszteség fenyőnél 20% volt, míg az eukaliptusznál csak 10%. Minél több cellulázt adtunk hozzá, annál alacsonyabb lett a viszkozitás, ami a cellulózlánc gyakoribb hasadását jelenti. Ha azonban 3 cellulázt vizsgáltunk, az egyiknek nem volt hatása a viszkozitásra még nagyobb koncentráció esetén sem. Következésképpen elmondható, hogy a celluláz szó nem jelentette ugyanazt, a márkanévtől függően. Endo- és exo- glükanáz-aktivitást kell specifikálni annak érdekében, hogy azonosítani lehessen a celluláz alkalmazásának következményeit. Eközben a vizsgált hemicelluláz csak korlátozott tevékenységet mutatott a cellulóz-

láncok irányában. Ez igazolta azt a feltevést, hogy ezek az enzimek meglehetősen tiszták, és hogy működésük a hemicellulózok irányában korlátozott volt. A cellulázkoncentráció hatása a viszkozitás csökkenésében mutatkozott meg. 25%-os csökkenést figyelhettünk meg a legalacsonyabb koncentrációnál. 1.000-szer több celluláz adagolásával a viszkozitás megfeleződött. A cellulózlánc hasadása nem volt arányos az enzimkoncentrációval. Az enzimmobilitás és a rost mentén a degradációra rendelkezésre álló helyek is szerepet játszottak és hatással voltak az enzim hatékonyságra. Őröletlen cellulóz tulajdonságait mértük próbalapokon, ami jobb kötési potenciált mutatott cellulázok alkalmazásával, és tisztán mutatta a vízretenció értéknek növekedését. Eközben nagyobb fehérséget is mértünk hemicelluláz alkalmazásakor. Őrlés után a különbségek nőttek. Az alkalmazott enzimtől függően a szakadási hossz maximum 25%-kal volt magasabb, a tépési mutató 10%-kal, hasonló energiafogyasztás mellett.

How do enzymatic treatments affect fibre properties?

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Summary

Enzymes are catalysts used worldwide, in large scale and for many applications. They are mainly used in food industry and in agriculture. Recent developments in enzyme production made it possible to produce pure monocomponent. So that, it became possible to use enzymes in fibres production processes.

Different enzymes were added to pulp suspensions in order to determine the impact on fibres characteristics, fibres structure and pulp quality. Cellulose degree of polymerisation or pulp viscosity was also considered to understand the enzyme effect on fibre ultrastructure. Depending on the enzyme type, consequences were different. Softwood pulp viscosity was the most affected by treatment with cellulase compared to eucalyptus one. Maximum losses were 20% and 10% for softwood and eucalyptus pulps, respectively. The more the cellulase charge, the lower the viscosity, meaning the more cellulose chain cutting. However, between the 3 tested cellulases, one did not affect the pulp viscosity, even at the highest charge. As a consequence, it could be said that "cellulase" name had not the same sense depending on production origin. Endo- and exo-glucanase activities should be specified in order to identify cellulase effects. Cellulose chain cutting was not proportional to enzyme concentration. Meanwhile, tested hemicellulases presented only limited action towards cellulose chains, confirming that those enzymes were rather pure and that their action was limited towards hemicelluloses. Enzyme mobility and fibre locations available for degradation played both role and impacted on enzyme efficiency.

Unrefined pulp properties showed a better bonding potential using cellulase and also a clear increase in water retention value, revealing increased fibrillation and fibre hydration. Besides, a higher brightness was enhanced by hemicellulases treatment. Refining enhanced differences. Depending on enzyme applied, breaking length was increased by 25% and tear index by 10% for similar energy consumptions.

Introduction

Enzymes are used in many processes. Main applications are in food industry (starch modification, wine fermentation…), agriculture or chemistry (chemical synthesis, fuel, bio-ethanol, …).

Nowadays, various enzymes are introduced or are ready to be used in pulp and paper processes. Most advanced applications are bleaching of virgin pulps, deinking, pitch control, effluent treatment and energy savings in mechanical pulping.

The objective of this work was to study the impact of various enzymes on commercial chemical pulps quality and fibre characteristics before and after refining.

Materials and methods

Commercial bleached kraft pulps were considered in this study: eucalyptus one and softwood one. Five commercial enzymes were used: 3 cellulases, 1 mannanase and 1 xylanase. Pulps were treated with the different enzymes at 40°C, pulp pH at 5% consistency for 30 minutes in a slusher. Pulp quality was analysed on Rapid Köthen handsheets according to ISO standard.
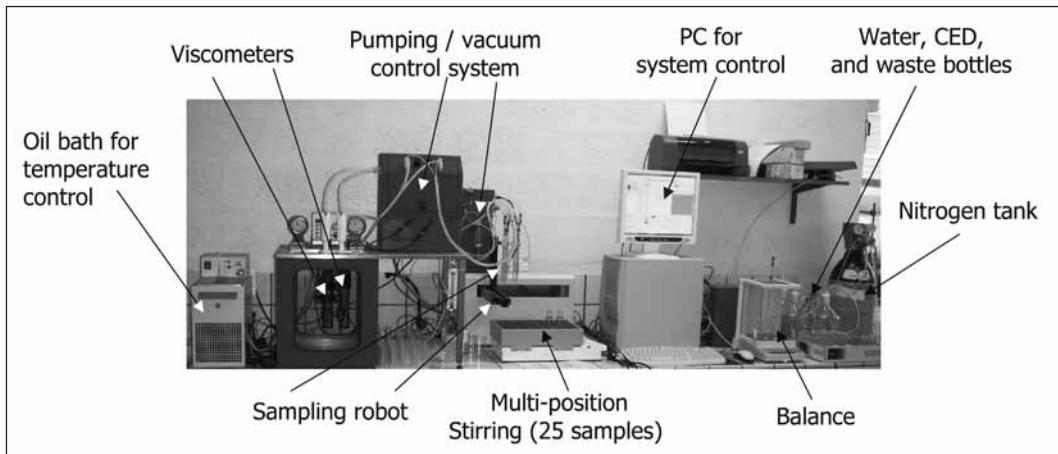
Figure 1: Automatic viscometer supplied by Rheotek (UK)

Pulp intrinsic viscosity (SCAN method) was measured with an automatic viscometer supplied by Rheotek (**Figure 1**).

Refining was carried out at low consistency with a 12" single disc refiner pilot plant in order to reach different drainage levels.

Results

Firstly, pulp viscosity was analysed on eucalyptus kraft pulp at different refining levels and with two different drying methods (**Figure 2**).
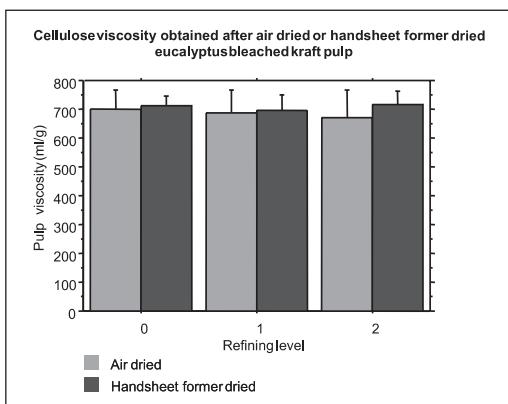

Figure 2: Comparison of pulp viscosity measured on air-dried or sheetformer dried eucalyptus pulps

The pulp drying method did not affect pulp viscosity. Besides, pulp viscosity measurements were also unaffected by refining level. As a consequence, viscosities were assumed to be similar whatever drying method or refining level. So that, it was decided to carry out the intrinsic viscosity measurements on handsheets.

Effects of enzymatic treatments on pulp viscosity are presented in **Figure 3** and **Figure 4.** Hemicellulase action was limited on pulp viscosity. As expected, those enzymes did not affect cellulose chains, because the main target structure for hemicellulases are hemicelluloses. If some small differences were observed, they could be due to small amounts of cellulase that may be contained in enzyme solution. In the case of eucalyptus bleached kraft pulp (**Figure 3**), none of differences were significant. But some trends were identified: the more the cellulase A, the lower the viscosity. Results were different with softwood bleached kraft pulp (**Figure 4**) as significant differences between cellulase A and B were found. A clear impact of cellulase charge was also observed with cellulase A, contrary to cellulase B. Cellulase E did not affect this property. Therefore, cellulase reaction mechanisms were different in these 3 cases. As these 3 cellulases solutions present a similar action, it could be concluded that other mechanism was involved and needed to be
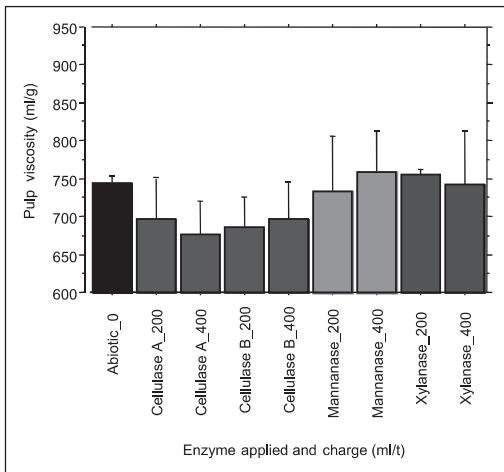
Figure 3: Pulp viscosity obtained on eucalyptus bleached Kraft pulp after various enzymatic treatments
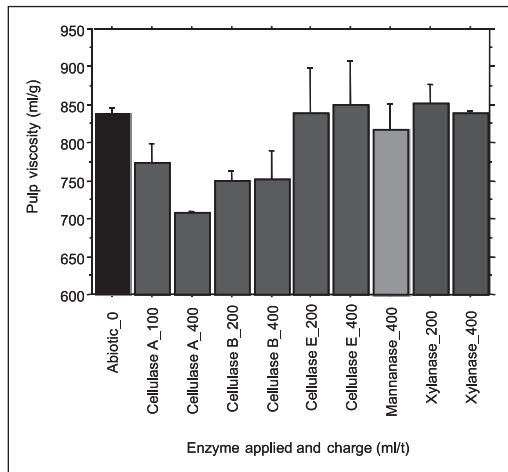
Figure 4: Pulp viscosity obtained on softwood bleached Kraft pulp after various enzymatic treatments
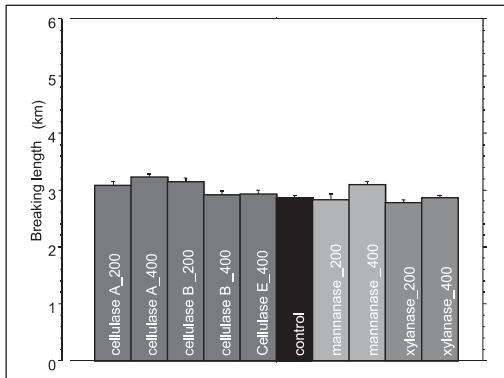

Figure 5: Breaking length of eucalyptus bleached kraft pulp after enzymatic treatments before refining
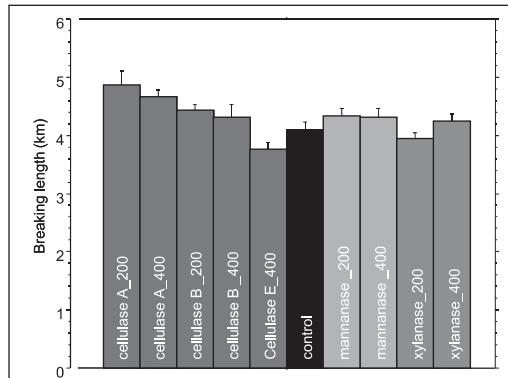
Figure 6: Breaking length of eucalyptus bleached kraft pulp after enzymatic treatments and refining (50kWh/t applied)

characterised. Cellulases activity and protein composition seemed to be important parameters to be considered.

Mechanical properties, and more particularly breaking length, measured on eucalyptus kraft pulp before and after refining, confirmed the observed differences in enzyme efficiency (**Figure 5 and Figure 6**).

Before refining, breaking length was affected by enzymatic treatments (Figure 5). Hence, the highest improvements were obtained with cellulase A and also mannanase treatment at the highest concentrations. The other enzymes

did not affect significantly this property. After refining, a strong improvement was measured and differences observed before refining were changed (Figure 6). Hence, cellulase A at the lowest charge presented the highest breaking length. It was significantly improved compared to control and hemicellulases treatments, which all were similar. Other cellulase treatments led also to an improvement, but at a lower degree. However, cellulase E showed the lowest breaking length. This was in agreement with that was observed on pulp viscosity for softwood pulp treated with cellulase E.

Conclusion

In the enzyme treatment of kraft pulps, different behaviours of pulp viscosity were observed depending on enzyme.

For hemicellulases, their actions were rather limited. Viscosity measurements on eucalyptus and softwood bleached kraft pulps were not significantly affected by either xylanase or mannanase. In the case of eucalyptus kraft pulps, impact on breaking length measured before or after refining was rather limited, indicating that the hemicelluloses had a lower impact on inter-fibre bonding.

For cellulases, totally different behaviours were observed. Cellulases treatments had various consequences on pulp viscosity, depending on their origins and treated substrate. Softwood kraft pulp was strongly affected: a maximum drop in viscosity of 22% was observed. Meanwhile, for the same condition, eucalyptus kraft pulp presented a loss of 11% only. Among the 3 considered cellulases, none of them had a similar behaviour. Hence, one cellulase impacted differently pulp properties, depending on concentration. Another one led to the same results whatever the applied charge was. The last one had a very limited impact compared to control, and even an opposite one.

As a consequence, the enzyme name was not sufficient to characterise an enzymatic solution and its potential efficiency. An enzyme presents a specific action devoted to catalyse the cleavage of a given structure linkage. The most common way to characterise the enzyme activity is to evaluate the amount of sugar released after treating the corresponding pure component. For example, in the case of xylanase, enzyme activity to degrade xylose can be evaluated by colorimetric method and modelled at various pH and temperature (**Figure 7**).

However, commercial bleached chemical pulps are composed of different polysaccharides, cellulose and hemicelluloses, with in some cases a very limited amount of residual lignin. So that, the expected enzyme actions might be precised in order to determine the result to look after and to unexpected pulp degradations. Cellulases and/or hemicellulases could be interesting alternatives to enhance the pulp properties and to save some electrical energy during refining.
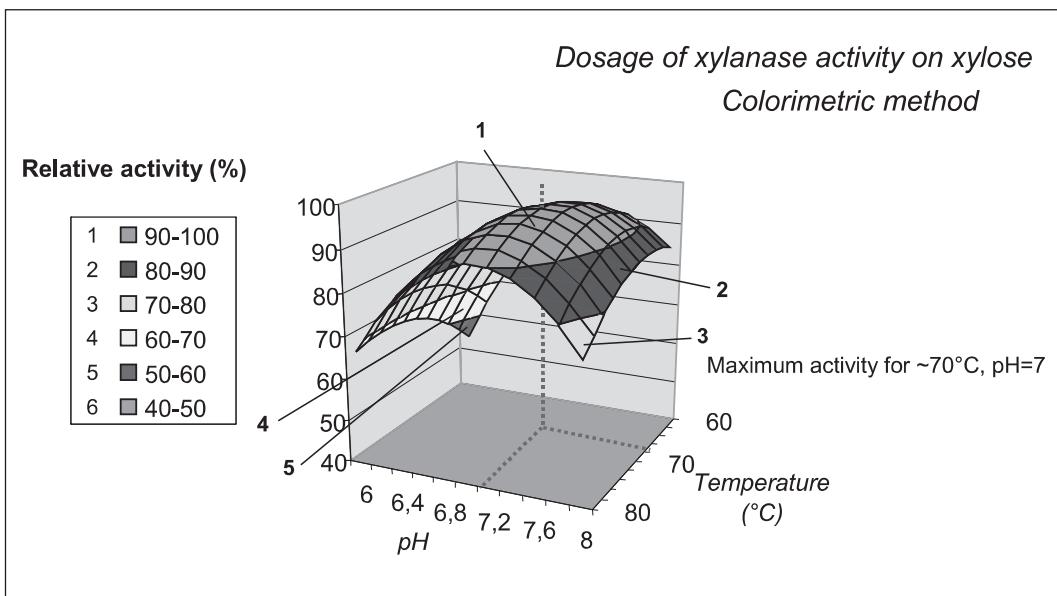

Figure 8: Dosage of xylanase activity by dosing sugar released after 1h treatment

Cellulózrostok finomszerkezetének viselkedése papírgyártási vizsgálatokban

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A papírszilárdságot, több más paraméter mellett, a cellulózrostok finomszerkezete is befolyásolja. Az őrlés során rostfibrilláció történik, és ez növeli a rostok felületét. Ez nem csak a végső papírszilárdságot befolyásolja, hanem a lapképzés során a víztelenedési tulajdonságokat is. Ebben a munkában a mikrofibrillált cellulóz (MFC) lapképzésre és a végső papírtulajdonságokra gyakorolt hatását vizsgáltuk. MFC hozzáadása után a Schopper-Riegler érték drámai növekedését figyeltük meg. Ugyanakkor a papírszilárdság is növekedett az MFC nanoméretű tulajdonságai miatt. A papírlapok letapogató elektronmikroszkópos vizsgálata megmutatta, hogy az MFC a rostok közötti kapcsolódási pontokon filmszerűen aggregálódik. Nehéz azonban megérteni és megmérni ezeknek a cellulóz finomszerkezeteknek a viselkedését a lapképzés során és a végső papírszerkezeten belül. Azért, hogy több információt tudjunk feltárni a cellulóz finomszerkezeteinek viselkedéséről, egy fentről lefelé történő megközelítést alkalmaztunk a makro szintről a nanoszintre, a rostmorfológia, víztelenedési tulajdonságok és a Page egyenlet alapján. A relatív kötési terület (RBA) és a kötésszilárdság kiszámításához egy egyszerűsített referencia rosthálózatot feltételeztünk. Ennek a modellnek az alapján következtetést lehetett levonni a hatékonyságról. A hidrodinamikai felületet az SR és a fajlagos felület (SSA) közötti korrelációra alkalmazott empirikus módszerrel határoztuk meg. Az MFC retenciót az eredeti rostháló és az SR mérése után a dezintegrált rostháló SSA értékeinek különbségéből határoztuk meg.

182.79 m²/g hidrodinamikai felületet számítottunk az MFC-re. Az őrölt rosthoz 5% MFC hozzáadásával a cellulóz felülete 3.6 m²/g-ról 12.56 m²/g-ra nőtt. Az SSA-ből származtatva, az MFC retenciót 63,5%-ra becsültük. A mért papírtulajdonságokkal kapcsolatban azt a következtetést vontuk le, hogy az MFC viselkedése és hatékonysága nem hasonlítható össze az őrlés során keletkezett finomanyagokkal, mert csak kisebb növekedést észleltünk a látszólagos sűrűségben az MFC következtében. Az egyszerűsített referencia rosthálózat alapján azonban a rostok közti kötési szilárdságot 9 MPa-nál számítottuk 5% MFC adagolásakor, ami kétszer annyi, mint a kiindulási anyagként használt cellulózban.

Az alkalmazott modell-feltételezés és a mért papírtulajdonságok alapján azt a következtetést lehet levonni, hogy az MFC a hidrogénkötések számában növekedéshez vezet a kontakt területeken a rostok között a magas SSA miatt, mert a látszólagos sűrűségre és, ezzel együtt, az RBA-ra szinte semmi hatással sincs az MFC. Ennek következménye a kötési szilárdság növekedése. Az MFC viselkedése azonban bizonytalan és nehezen magyarázható, mert a fényszórási tulajdonságok csökkenése az RBA növekedését jelzi, főleg a látszólagos denzitás növekedéséhez kapcsolódva.

Behaviour of cellulose fine structures in papermaking tests

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Summary

In this work the influence of microfibrillated cellulose (MFC) on sheet forming and final paper properties was investigated. In order to reveal more information about the behaviour of these cellulose fine structures a top-down approach from macro- to nano-scale was used based on fibre morphology, dewatering properties and the Page equation. A hydrodynamic ´specific surface area (SSA) of 182.79 m²/g was calculated for MFC. By addition of 5% MFC to the refined pulp the surface area of the pulp was increased from 3.6 m²/g to 12.56 m²/g. Derived from SSA, MFC retention was estimated at 63.5%. In connection with the paper properties measured, it was concluded that behaviour and effectiveness of MFC are not comparable with those of fines produced during refining because only a minor increase in apparent density was observed due to MFC. However based on the simplified reference fibre network the bonding strength between fibres was calculated at 9 MPa for an addition of 5% MFC, which is twice as much as in the pulp used as starting material.

Introduction

The paper strength is influenced, among other parameters, by the fine structure of pulp fibres. Refining is the method most frequently used in papermaking to change the fine structure of fibres. Fibre fibrillation takes place during refining and increases the surface area of fibres. At the same time different types of fine structures are produced. This influences not only the final paper strength but also optical properties and the dewatering properties during sheet forming. Fines are commonly defined as the fraction that passes through a 200 mesh screen. The largest fines particles are fibre fragments and the smallest are fibrils whose size can be below 1µm. In this work we investigated the influence of micro-fibrillated cellulose (MFC) as a special cellulosic fine material on sheet forming and final paper properties. MFC is completely different to commonly known pulp fines, because of its much smaller size and the material properties associated with it. MFC was invented by Herrick and Turbak in the early 1980ies through mechanical disintegration of the fibre wall down to the cellulose fibril aggregates as building blocks of the fibre wall [1, 2]. Since then many patents have been granted and applications introduced on the basis of MFC. However, due to the high energy consumption for fibre wall homogenization, the preparation of MFC has been less attractive in view of cost effectiveness. The main breakthrough for reducing the energy consumption has been made by Lindström and co-workers in recent years – by improving the pulp preparation before final homogenization [3]. Today MFC is one of the most interesting nano-materials not only to papermaking scientists, but also in the field of composite materials.

Although MFC is also a cellulosic fine material derived from fibre walls, it is completely different to primary or secondary fines because MFC is a fibrillar network of entangled fibrils. The size of the fibrils varies across a wide range from 20-30 nm in width, but larger fibril bundles are present as well. Alince and co-workers compared the behaviour and effects on paper properties of MFC, fines of high and low specific surface area, and microcrystalline cellulose. Their results indicate that the strength prop-

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erty improvement is much greater with MFC. A different type of action was observed particularly with bleached kraft pulp, because the light scattering coefficient was almost unaffected by MFC in contrast to other fines, where increasing light scattering coefficients indicated that a higher relative bonded area (RBA) was responsible for the improvement in strength properties [4]. Due to the nano-scale level and similarity of MFC to other fines and fibres it is difficult to characterize the mechanisms and effectiveness of MFC in sheet forming. In order to reveal more about the effectiveness and interaction of MFC with fibres a top-down approach was used, supported by model assumption and calculation methods. The bonding strength was calculated based on the PAGE equation; and the hydrodynamic mass-specific surface area (SSA) of MFC was calculated as well.

Materials

A mixture of dried bleached hardwood and softwood pulps (ratio 4:1) was used as pulp source together with 2% suspension of micro-fibrillated cellulose (MFC) supplied by STFI-Packforsk in Sweden. MFC was prepared according to Pääkkö and co-workers [5]. In order to support the retention of fines and MFC a retention aid based on high-molecular polyethylene imine (PEI) was used.

Methods

Technical methods
The dried market pulp was disintegrated in water for 15 minutes, at 40°C and a consistency of 5%. The resulting pulp suspension was then refined in a pilot refiner at a consistency of 4%, using a specific refining energy of 65 kWh/t and a specific edge load of 0.1 Ws/m. After refining the fibre dimensions were analyzed by means of a Fiberlab 3.0 device. A special method was used to characterize the fibre fraction and dimensions of collapsed and dried fibres in the fibre network according to

Meinl and Erhard [6]. Sheets were formed in a Rapid Köthen former according to ISO 5269-2 at a consistency of 0.3%. The MFC used was stirred for 10 minutes at 0.2% consistency and treated with an ultra-turrax blender for 2 minutes. MFC was added to the stock container of the Rapid Köthen former sheet per sheet, to a pulp consistency of 0.3%. When PEI was used as a retention aid, it was also added in the stock container after the MFC addition. Before sheet forming the SR value was measured. The dried sheets were characterized according to standard methods for light scattering coefficient S_y, Scott bond z-strength, apparent density, tearing resistance, tensile index, and air permeability.

Mathematical methods
The mass-specific surface area (SSA) – an empirical formula based on the SR value – was used for calculation.

$$SSA = c_{SSA} \times \sqrt{\frac{SR-4}{100-SR}} \qquad (Eq.\ 1)$$

The factor c_{SSA} is about 6,24 when applying corresponding known values of SR and SSA from Heinemann [7, 8]. *Eq. 1* is only valid if no chemical additives are used which could influence the pulp viscosity). The SSA value is additive. If SSA_{Pulp} / SSA_{MFC}, are the specific surface areas of the pulp / microfibrillated cellulose and w_{MFC} is the mass-weighted MFC share then the specific surface area SSA_{MFC}:

(Eq. 2)

$$SSA_{MFC} = \frac{SSA_{Total} - (100\% - w_{MFC}) \times SSA_{Pulp}}{w_{MFC}}$$

To estimate the relative bonded area (RBA) – a critical value for applying the PAGE equation – in a given sheet, one can use a regular fibre network reference which is made up of the same fibres and which has the same apparent density as the original fibre network. The RBA was assumed as ratio between bonded area (A_B) and total area (A_T) according to the following equation:

$$RBA = \frac{A_B}{A_T} = \frac{4D^2}{4d \times D + 4d \times H} \qquad (Eq.\ 3)$$

The values D (diameter) and H (height) of collapsed and dried fibres in the network were calculated by means of the fibre morphology data from FIBRELAB 3.0 according to Meinl and Erhard [6]. We have yet to calculate the distance d (distance between neighbouring fibres in a layer, which equals the length and width of the elementary cell) according to (Eq. 4). This equation ensures that the apparent density of the elementary cell equals the apparent density ρ of the sheet.

$$d = \frac{D \times \rho w}{AD} \qquad (Eq.\ 4)$$

The bonding strength b can now be calculated via the Page equation [9] for given values of mean fibre length FL, tensile index T and zero-span tensile index ZI. The cross sectional fibre area A_{CSA} equals $D \cdot H$ and the fibre perimeter P equals $2(D+H)$. For the zero-span tensile index a value of 150 Nm/g was assumed.

$$\frac{1}{T} = \frac{9}{8ZI} + \frac{12 \times A_{CSA} \times \rho_W}{b \times P \times FL \times RB_A} \qquad (Eq.\ 5)$$

Results and discussion

The sheet properties are listed in **Tab. 1.** As expected, pulp mat dewatering was deteriorated. The SR value has increased dramatically from 28 to 86 at 5% MFC. The addition of PEI caused MFC and fines to agglomerate on fibre surfaces, thus helping to reduce the SR value. At the same time, strength properties have been improved to the same extent. But it is obvious that not all MFC has been retained in the paper sheet, because the PEI containing sheets had always higher strength levels than sheets containing no PEI - due to better fines and MFC retention. The tensile index has increased by up to 70% , and also the Scott Bond z-strength by up to 170% in comparison to the reference pulp. However one can see that the apparent density has remained almost unaffected, indicating that the strength improvement is not due to a higher RBA as usually expected from common fines. But – by contrast – the light scattering S_y as indicator of the unbonded area has been reduced.

In order to reveal more about the mechanisms and effectiveness of MFC the SSA was calculated based on dewatering properties. The calculation results of SSA are listed in **Tab. 2.** It is obvious that the SSA of the whole pulp has been increased by MFC. At 5% MFC the SSA of the pulp is 12.6 m²/g. This value is in a range usually obtained by intense refining only. This increase shows that with MFC more OH-groups are available for the formation of more H-bonds between pulp fibres. The SSA of the MFC has been calculated at 170.7 - 182.8 m²/g. This range is consistent with the results of other authors working with nanofibrillar cellulose aerogels. Hoepfner

MFC	%	0	0	1	3	5	1	3	5
PEI on dry pulp	%	0	0,25	0	0	0	0,25	0,25	0,25
Schopper Riegler		28	28	44	68	86	32	55	77
Density	g/cm³	0,61	0,59	0,60	0,62	0,66	0,62	0,63	0,66
Air permeabilty	ml/min	1873	1924	603	185	25	1203	214	19
Tensile-Index	Nm/g	36,7	37,9	44,1	49,4	57,0	42,1	50,5	62,3
Scott Bond	J/m²	229	305	345	421	453	223	463	551
Tearing resistance	mNm/m	1275	1349	1447	1533	1724	1422	1576	1833
s	m²/kg	40,6	39,1	39,8	37,1	34,3	40,3	36,8	33,6

Tab. 1: Sheet properties of MFC containing papers

and Co-workers estimated the BET surface area of freeze dried MFC at 160 m²/g and by supercritical drying in the range of 200-220 m²/g **[10]**.

Furthermore the influence of MFC on the bonding strength b between fibres was calculated according to *(Eq. 4)*. The bonding strength of the reference pulp was calculated at 4.76MPa. At 5% MFC the calculated bonding strength was increased to 9MPa. As mentioned above PEI as retention aid improves the retention of MFC. This is also reflected by the bonding strength, where b was calculated at 10.62. In **Fig. 1** the calculated bonding strength has been plotted against the Scott Bond z-strength often used to describe the bonding degree in paper sheets. Obviously, there is a clear correlation between these two different approaches to estimating the bonding properties. This indicates that the method used for calculating the bonding strength is also useful to describe the bonding behaviour

of MFC containing paper sheets. The results suggest that the high surface area and available OH-groups lead to much more H-bonds between the fibres in their contact areas. This can explain why the density and bulk properties, respectively, have remained unchanged after the application of MFC.

Conclusion

The high SSA of MFC leads to improved interactions between fines and fibres. In line with the number of H-bonds, the bonding strength is increased. It may be concluded that the bonding strength is improved not only by the greater bonding area due to better fines retention, but also by a higher number of H-bonds in the contact areas. However the behavior of MFC is ambiguous and difficult to explain, because the decrease in light scattering properties indicates an increase in RBA which is mostly connected to an increase in apparent density. But this was not observed here.

w_{MFC} %	SR_{Total}	SSA_{Total} m^2/g	SSA_{MFC} m^2/g
0%	28	3,6	-
1%	44	5,3	170,7
3%	68	8,8	177,7
5%	81	12,6	182,8

Tab. 2: Mass-specific surface area (SSA) of pulp and MFC
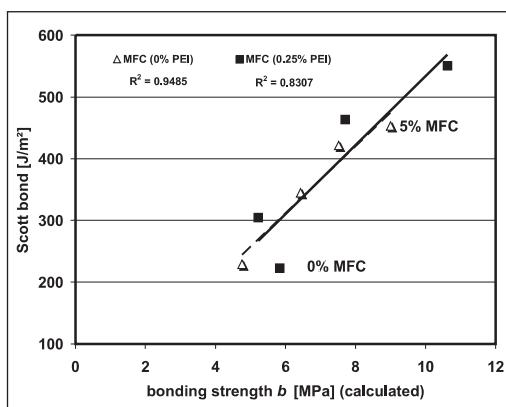
Fig. 1: Calculated bonding strength in comparison to Scott Bond z-strength

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Zárszó

Lele István

Vígh András

A *COST (European Cooperation in the Field of Scientific and Technical Research)* keretében szervezett *E54 COST ACTION 2006–2010* programban (*„Papírgyártásban használt rostok finomszerkezetének és tulajdonságainak jellemzése új technológiákkal")* 19 együttműködő európai ország vesz részt.

A program fő célja egy olyan nemzetközi fórum létrehozása, ahol lehetőség nyílik a papíripari rostok mikroszerkezete és a kész papír makroszkópikus tulajdonságai közötti összefüggésekről új ismeretek szerzésére. Ezen túlmenően különös figyelmet igényel, hogy hogyan befolyásolják a kémiai, illetve mechanikai feltárási folyamatok és utánkezelések a papírgyártásra alkalmas különböző rostok összetételét és finomszerkezetét.

A kutató munka három munkacsoportban (MCS) folyik. Témák:
- MCS1: Különböző kezelések hatása a papíripari rostok szerkezetére és kémiai összetételére
- MCS2: Egyedi rostok kezelése és jellemzésük mikrotechnológiákkal
- MCS3: Rostok finomszerkezetének hatása papírképző tulajdonságaikra, valamint kémiai és enzimatikus reaktivitásukra.

E program keretében 2008-ban két rendezvényre került sor, áprilisban Graz-ban és októberben Budapesten. A hazai rendezvényt a COST E54 Intéző Bizottságába delegált magyar résztvevők, Lele István, a Papíripari Kutatóintézet Kft K+F igazgatója és Dr. Víg András, a Budapesti Műszaki és Gazdaságtudományi Egyetem egye-temi magántanára koordinálta, együttműködve a Papír- és Nyomdaipari Egyesület (PNyME) Papíripari Szakosztálya elnökével, Szőke Andrással, valamint, az Egyesület ügyvezető igazgatójával, Pesti Sándorral.

A rendezvény három fő eseménye az Intéző Bizottság ülése, a három Munkacsoport önálló tanácskozása és az MCS-k profiljának megfelelő 12 előadásból álló Szakszeminárium volt.

A program fontos kiegészítése volt a Budapesttől 75 kilométerre levő *Dunapack Papír és Csomagolóanyag Zrt dunaújvárosi papírgyárának meglátogatása.* Dr. Szikla Zoltán elnökhelyettes ismertette a magyar papíripar helyzetét és ezen belül a Dunapack Zrt-ben folyó csomagolópapír-termelést és -fejlesztést. A Hamburger csoport Dunaújvárosban 205 millió eurós beruházás keretében 1.500 m/min sebességű, 7.800 mm munkaszélességű új papírgépet helyez üzembe, melynek évi kapacitása 350.000 t 70–150 g/m² csomagolópapír. A résztvevők megtekinthették az üzem működő papírgépét és az új beruházás elkészült építményeit.

A gyárlátogatást követően Budapesten a résztvevők baráti és szakmai kapcsolatokat erősítő kitűnő hangulatú közös vacsorán vettek részt.

Záró beszédében Prof. Dr. Arnis Treimanis a COST E54 Akció Intéző Bizottsága elnöke köszönetét fejezte ki a Munkacsoportok Koordinátorainak, az előadások szerzőinek, valamint valamennyi tisztségviselőnek és Intéző Bizottsági tagnak aktív tevékenységükért a Szakszeminárium előkészítésében és megvalósításában. Külön köszönet az Intéző Bizottság magyar tagjainak, Dr. Víg Andrásnak és Lele István úrnak, továbbá Szőke András úrnak, Pesti Sándor úrnak és Dr. Szikla Zoltán alelnök úrnak. Nagyrabecsülés és köszönet Dr. Polyánszky Éva főszerkesztő asszonynak a Szakszeminárium teljes anyagának sajtó alá rendezéséért a Papíripar c. folyóirat különszámában.

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Epilogue

The representatives of 19 European countries cooperate in the program of *E54 COST (European Cooperation in the Field of Scientific and Technical Research) ACTION 2006–2010* **"Characterisation of the fine structure and properties of papermaking fibres using new technologies"**

The main objective of the Action is to generate new knowledge on the micro- and nanostructure of papermaking fibres and properties required for the efficient and sustainable use of fibres in traditional, advanced and future products. Furthermore specific attention should be paid to the influence of the pulping processes i.e. for chemical and mechanical pulps and fibre treatment on the fine structure and composition of different papermaking fibres.

Three working groups (WG) carry out the necessary scientific activities within the program.
– WG1: Structure and chemical composition of papermaking fibres after different types of treatments.
– WG2: Treatment and characterisation of individual fibres by microsystem technologies.
– WG3: The impact of the fine structure of fibres on their papermaking properties and their chemical and enzymatic reactivity.

Two meetings have been performed within the program in 2008 in Graz, in April and in Budapest, in October.

The Hungarian meeting has been organised by the local MC members: István Lele managing director of the Paper Research Institute Ltd. and prof. Dr. András Víg Budapest University of Technology and Economics in cooperation with the Technical Association of the Hungarian Paper and Printing Industry represented by András Szőke Chairman of the Section of Paper Industry and by Sándor Pesti managing director of the Society.

The three main parts of the Meeting have been: MC meeting, meeting of the Working Groups organised separately from each other and a Workshop including 12 Scientific presentations in accordance with the activity of WGs.

The Visit of Dunapack Paper and Packaging Ltd. in Dunaújváros in distance of 75 km from Budapest has been significant additional part of the program. Detailed information about the present situation of the Hungarian paper and pulp industry as well as about the activity of Dunapack Paper and Packagings Ltd. has been performed by Dr. Zoltán Szikla vice president of the Ltd.

In Dunaújváros a new paper machine (Rate: 1.500 m/min, productional width 7.800 mm.) investment of 205 million EUR has been decided by the Hamburger Group establishing a yearly capacity of 350.000 t corrugated paper of $70-150 g/m^2$.

After getting back from the excursion a joint dinner has been organized for the participants where the excellent atmosphere did a lot for strengthening the friendly and professional relations within the international group of the experts of paper and pulp production and research.

In closing the Management Committee meeting Action Chair Prof. A. Treimanis expressed his gratitude to the Working Group co-ordinators, the authors of the presentations as well as other officeholders and MC members for their active role in preparing and performing the workshop. In particular he thanked the local organizers Dr. András Víg, Mr. István Lele, Mr. András Szőke, Mr. Sándor Pesti and to vice president Dr. Zoltán Szikla. Special thanks go to Dr. Éva. Polyánszky for preparing the Workshop Proceedings collection in form of journal "Papiripar" special edition.

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Merry Christmas and a happy New Year
Félix Navidad y próspero Año Nuevo

Frohe Weihnachten und ein glückliches neues Jahr

Buon Natale e felice Anno Nuovo
Joyeux Noël et Bonne Année

Prettige Kerstdagen en Gelukkig Nieuwjaar

Kellemes karácsonyi ünnepeket
és boldog új évet kívánunk