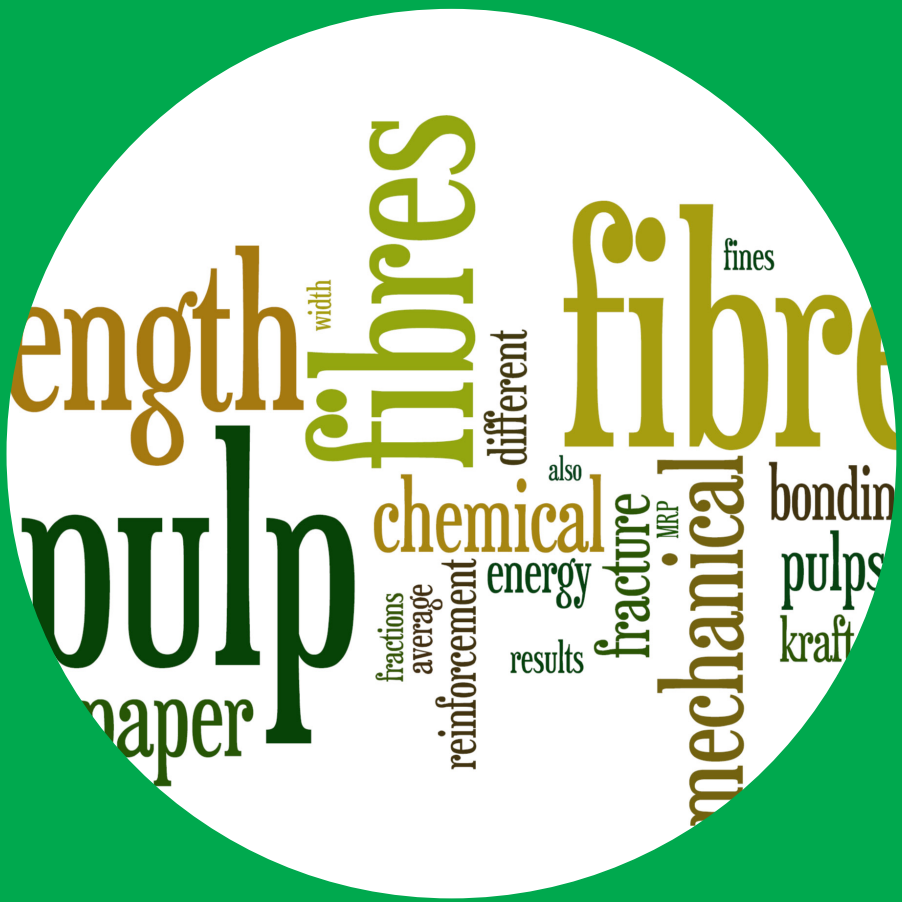
Department of Forest Products Technology

Reinforcement ability of mechanical pulp fibres

Jouko Lehto



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Reinforcement ability of mechanical pulp fibres

Jouko Lehto

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Abstract

The objective of this study was to find out the reasons why the long fibres of mechanical pulp do not seem to reinforce paper as effectively as chemical reinforcement pulp.

A preliminary laboratory trial showed that artificially increasing the average fibre length of TMP pulp by adding long fibres extracted from the same pulp increased the tear index, but decreased the tensile strength, internal bond strength and the fracture energy. Increasing the average fibre strength with chemical (NBSK) pulp fibres improved all of those properties considerably.

In the second trial fibre properties and reinforcement ability of various mechanical pulps were investigated. It was shown that fibre dimensions of mechanical pulp fibres did not differ essentially from chemical pulp fibres. The biggest differences were in the properties characterizing the cell wall structure. This was clearly seen in fibre flexibility and fibre swelling (WRV), for instance. Mechanical pulp fibres are evidently more damaged than chemical pulp fibres which is seen as a much lower fibre strength (zero-span tensile strength). The reinforcement potential, on the grounds of fracture energy, tear strength and tensile strength of handsheets was much lower for mechanical pulp fibres than for chemical pulp.

In the third trial, mechanical (MRP) and chemimechanical reinforcement pulp (CMRP) was manufactured from Norway spruce (P.abies) on a pilot scale. The focus was to increase fibre flexibility, bonding ability and maintain the fibre length and strength. The runnability of LWC base paper made from the trial pulps was tested using the KCL AHMA runnability tester. In spite of the good strength properties of the trial pulps, they did not have the same overall reinforcement ability than chemical pulp. The sulphonated trial pulp (CMRP) gave the same tensile stiffness and tensile strength as the chemical pulp. However, the fracture properties and extensibility of the paper was worse with it. The lower average length of the trial pulps did not explain the difference totally. Scaling the fibre length with the zero-span tensile strength improved the explanatory power essentially. It was concluded that the low fibre strength is the basic reason for the poorer reinforcement ability of mechanical pulps fibres over chemical ones.

Keywords Characterization, chemical pulp, mechanical pulp, refining, reinforcement ability, sulphonation, TMP

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Tiivistelmä

Tämän tutkimuksen tarkoituksena oli löytää ne syyt, minkä vuoksi mekaaninen massan pitkät kuidut eivät näytä vahvistavan paperia yhtä tehokkaasti kuin kemiallinen armeerausmassa (havupuusellu).

Alustava laboratoriokoesarja osoitti, että TMP:n kuitupituuden keinotekoinen kasvattaminen lisäämällä siihen samasta massasta erotettuja pitkiä kuituja kasvatti repäisyindeksiä, mutta heikensi vetolujuutta, sisäistä lujuutta ja murtoenergiaa. Kuitupituuden kasvattaminen kemiallisen massan kuiduilla paransi kaikkia edellä mainittuja ominaisuuksia huomattavasti.

Toisessa koesarjassa tutkittiin erilaisten mekaanisten massojen ja sellujen kuituominaisuuksia ja armeeraus-kykyä. Havaittiin, että mekaanisten massojen kuitujen kuitudimensiot eivät juuri poikenneet sellukuitujen dimensioista. Suurin ero oli kuituseinän rakennetta kuvaavissa tekijöissä, mm. taipuisuudessa ja turpoamisessa (WRV). Mekaanisen massan kuidut ovat ilmeisesti voimakkaammin vaurioituneita kuin sellukuidut, mikä ilmeni niiden alhaisena kuitulujuutena (zero-span -vetolujuus). Mekaanisen massan kuitujen armeerauskyky oli murtoenergialla ja repäisy- ja vetolujuudella arvioituna paljon heikompi kuin sellukuiduilla.

Kolmannessa kokeessa valmistettiin kuusesta (Picea abies) mekaanista (MRP) ja kemimekaanista (CMRP) armeerausmassaa pilot-mitassa. Kokeessa pyrittiin parantamaan kuitujen taipuisuutta ja sidoskykyä säilyttäen samalla kuitupituus ja -lujuus. Koemassoista valmistettujen LWC-pohjapapereiden ajettavuutta testattiin KCL-AHMA -laitteella. Niiden hyvistä lujuusominaisuuksista huolimatta ne eivät toimineet armeerausmassana yhtä hyvin kuin kemiallinen massa. CMRP antoi paperille yhtä hyvän vetolujuuden- ja jäykkyyden kuin kemiallinen massa. Tästä huolimatta sen murto-ominaisuudet ja venyvyys olivat huonommat kuin kemiallisella massalla. Koemassojen alempi kuitupituus ei selittänyt eroa kokonaan. Kuitupituuden skaalaaminen zero-span -vetolujuudella paransi selittävyyttä huomattavasti. Tästä ja muista koetuloksista pääteltiin, että alhainen kuitulujuus on yksi mekaanisen massan kuitujen huonon armeerauskyvyn perussyistä.

Avainsanat armeerauskyky, jauhatus, kemiallinen massa, luonnehdinta, mekaaninen massa, sulfonointi, TMP

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Some things in life are bad,
They can really make you mad
Other things just make you swear and curse
When you're chewing on life's gristle,
Don't grumble, give a whistle,
And this'll help things turn out for the best

Always look on the bright side of life
Always look on the light side of life

Eric Idle, Monty Python 1979

Foreword

TMP is the single most important fibre component in many value added mechanical printing paper grades, as in LWC and SC. The continuous cost pressure forces paper mills to minimize the share of chemical reinforcement pulp in these grades. In that attempt, optimizing the quality of TMP has been regarded as a very potential option.

I would like to express my gratitude to my supervisor, Professor Hannu Paulapuro, for his valuable advice during the course of this work.

This work was idle for some time after a good start not least due to changes in my position, location and building a new home. I thank Professor Hannu Paulapuro and Dr. Kari Koskenhely for tempting me to start the engine again. The deep discussion with Mikko Ylhäisi of TEKES in Savonlinna during the summer of 2008 was also very motivating.

I wish to thank my co-authors for the excellent co-operation when preparing the last three papers: Professor Paulapuro, Dr. Kari Koskenhely and Dr. Eero Hiltunen. You have given support and advice without which preparing this thesis would have been essentially more difficult. Laboratory manager Anne Pulli and the staff of UPM Research Center are thanked for the skilful testing of the numerous samples. Valkeakoski Research Center, which is history now, and its personnel I also warmly thank for testing some parts of this study and above all, offering the possibility to start this work. Jouni, TMP is good pulp, although it has some handicaps as revealed in this work!

In the early stage of this research Timo M. Koskinen had a key role as the project leader of the TEKES project, in which this research was included. Thank you Timo for offering the possibility to start the project! Annikki Vehniäinen has given me good advice when preparing the manuscript. The list of the persons to whom I'm grateful is long and it is not possible to mention everybody by name. So thank you former and present supervisors and colleagues for arranging time for this research and mental support, summer trainees for valuable pieces of work that helped me a lot! From my colleagues I liked to mention Markku Ora with whom I have had continuous change of both scientific and practical information. The service that our Information Service has given to me has been excellent. Without that this research would not have been realized. To UPM Research Center I owe much. Hopefully this work pays off!

The financial support by the National Technology Agency of Finland (TEKES) in the early stages of this thesis is highly appreciated.

Finally I wish to thank my loving wife Birgitta for patience and tremendous support during the long journey and son Lauri for offering good competition. Dad beat you to it!

Lappeenranta, May 20, 2011

Jouko Lehto

List of symbols and abbreviations

α, β, χ	geometry factors
$\varepsilon_{1/100}$	threshold strain
ρ_c	density of cellulose
σ	tensile strength of fibre, axial stress, tension
σ_b	fibre strength
$\sigma_{1/100}$	threshold tension
τ	shear strength, shear stress
τ_b	shear strength of fibre-fibre bonds
τ_c	critical value of shear strength
a, b, c	parameters
A	area
A_w	fibre wall area
A_c	fibre cross-sectional area
C	coarseness
D	diameter
Di	lumen diameter
Do	outer diameter of fibre cross-section
E	elastic modulus, tensile stiffness index
E_f	axial elastic modulus of component fibres
E_p	elastic modulus of paper
F	fracture toughness measured using the essential work of ductile fracture method
g	acceleration due to gravity
G	shear modulus, fracture energy index
G_f	shear modulus of the component fibres in the (l_a,w) plane
G_C	fracture energy
K_C	fracture toughness
l	fibre length
l_a	arithmetic mean fibre length
l_i	average fibre length of pulp i
l_l	length weighted average fibre length
l_s	zero-span scaled fibre length
l	longest dimension
L	arithmetic mean fibre length
L	contour length
m	mass, Weibull modulus
m_c	critical grammage
n	number
$n_{(\alpha°\text{-}\beta°)}$	average number of sharp bends per fibre with angles between α and β
P	perimeter, primary wall
P_i	lumen perimeter
P_o	fibre perimeter of fibre cross-section

r	radius, Pearson's product moment correlation coefficient
r_o	outer radius
R	fracture resistance
S	secondary wall, stretch at break
S_{max}	tensile stiffness
T	tensile strength, tensile index
T'	bonding term
T_0	zero-span tensile strength
w	width, mean fibre width
w_d	damage width
w_p	pull-out width
$W_2(\sigma)$	2-parameter Weibull distribution for the failure probability

AFM	atomic force microscopy
BET	Brunauer-Emmett-Teller
BIN	bonding indicator
BKP	bleached kraft pulp
BKPr	refined bleached kraft pulp
BKPu	refined bleached kraft pulp
CR	collapse resistance
CD	cross direction
CFLP	continuous laboratory fibre processor
CLSM	confocal laser scanning microscopy
CMC	carboxymethyl cellulose
CMRP	chemimechanical reinforcement pulp
CMP	chemimechanical pulp
CSF	canadian standard freeness
CTMP	chemithermomechanical pulp
DSC	differential scanning calorymetry
ESCA	electron spectroscopy for chemical analysis
FI	fibrillation index
FBW	freezing bound water
FRET	fluorescence resonance transfer
FSP	fibre saturation point
GM	geometric mean
GW	groundwood
HPC	hydroxypropyl cellulose
IPT	in-plane tear
ISEC	inverse size exclusion chromatography
ISO	International Organization for Standardization
KCL	OY Keskuslaboratorio-Centrallaboratorium AB
LEFM	linear elastic fracture mechanics
LM	light microscopy
L&W	Lorentzen & Wettre
LWC	light weight coated
MC	medium consistency
MD	machine direction
MDF	medium density fibre board
MFA	microfibril angle

MFC	microfibrillar cellulose
MRP	mechanical reinforcement pulp
NMR	nuclear magnetic resonance spectroscopy
NBSK	northern bleached softwood kraft
OPCO	Ontario Paper Company
PGW	pressure groundwood
RBA	relative bonded area
RI	rigidity index
RM_{mod}	modified Mühlsteph's ratio
RMP	refiner mechanical pulp
RR_{mod}	modified Runkel's ratio
RTS	retention temperature speed (a modified TMP process)
SC	supercalendered
SCAN	Scandinavian Pulp, Paper and Board Testing Committee
SEM	scanning electron microscopy
SFF	single fibre fragmentation
SGW	stone groundwood
TMP	thermomechanical pulp
TEM	transmission electron microscopy
ToF-SIMS	time-of-flight secondary ion mass spectroscopy
TREJr	refined TMP rejects
TREJu	unrefined TMP rejects
UPM	UPM Corporation
W	tear strength
W_z	Scott bond
WRV	water retention value
XPS	X-ray photoelectron spectroscopy
ZS	zero-span tensile strength
ZS'	relative zero-span tensile strength
zsd_i	dry zero-span tensile strength of pulp i
zsd_c	dry zero-span tensile strength of chemical pulp

List of publications

This thesis consists of a summary and the following publications (‘Papers’) which are referred in the text by Roman numerals.

I Lehto, J.H. 2003. Mechanical fibers as reinforcement pulp. 2003 International Paper Physics Conference. Victoria, B.C., Canada, 7-11 Sept. 2003, Montreal, Canada, PAPTAC, 323-331.

II Lehto, J.H. 2004. Characterisation of mechanical and chemical pulp fibres. 58th Appita annual conference and exhibition, Canberra, ACT, Australia, 19-21 April 2004, Carlton, VIC, Australia, Appita, Paper 3A13, 8 p.

III Lehto, J., Koskenhely, K., Paulapuro, H. 2007. The role of chemical and mechanical pulp fibres in LWC base paper. PTS pulp technology symposium, Dresden, Germany, 27-28 Nov. 2007, Munich, Germany, PTS, Paper 9, 17 p.

IV Lehto, J., Hiltunen, E., Paulapuro, H. 2010. TMP long fibres as reinforcement pulp. Part 1. Laboratory tests. Nord. Pulp Paper Res. J. 25(3), 328-339.

V Lehto, J., Hiltunen, E., Paulapuro, H. 2010. TMP long fibres as reinforcement pulp. Part 2. Pilot tests. Accepted for publication in Nord. Pulp Paper Res. J. 25(3), 340-350.

Author's contribution

The author's role in each publication has been the following:

I all experiments, all analysis, manuscript
II experiments in part, all analysis, manuscript
III experiments in part, all analysis, first version of the manuscript
IV all experiments, all analysis, first version of the manuscript
V all experiments, all analysis, first version of the manuscript

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1 INTRODUCTION

1.1 Background of the study

The main components of wood containing printing papers are mechanical and chemical pulp, mineral pigments, binders and additives. The share of the fibre components varies roughly from 50% in double coated grades to about 90 - 95% in newsprint grades. Usually the share of mechanical pulp is maximized because it is cheaper than chemical pulp and it gives the desired surface and optical properties to the paper. Mechanical pulp can be manufactured using two different ways: by grinding wood logs in a stone grinder or by refining wood chips in a refiner. Historically, grinding has been the prevailing process but after introducing the modern refiner technology and an effective heat recovery in the late 1970's, the refiner based thermomechanical process (TMP) has gained more and more foothold and is today by far the most important mechanical pulping process. The triumphal march of TMP has been based on the possibility to use cheaper raw material (saw mill chips instead of round wood logs that the grinding process requires), large scale refiners, lower investment costs and pulp with better strength properties. The specific energy consumption of the TMP process is much higher than that of the grinding process, but the heat-recovery enables recovery of a significant part of the spent electric energy as high-pressure steam suitable for paper drying and other purposes.

The good strength properties of TMP have made it possible to reduce the share of the strong but more expensive chemical pulp component in paper furnishes. When the role of chemical pulp is to give strength for the paper web it is called reinforcement pulp. It gives high tensile and tear strength and increases the breaking strain (Räisänen et al. 1997). The difference in the reinforcement pulp content is usually most striking in newsprint grades that can be manufactured from 100% softwood TMP as the fibre component. SC papers which are exposed to higher stresses during the manufacturing process and contain a much higher amount of mineral fillers, typically contain 10 - 15 % of chemical pulp calculated from basis weight of paper. The needed amount of chemical reinforcement pulp depends on the mechanical pulp type but not as much as in the case of newsprint. During the LWC paper manufacture, the demands for the paper web are even bigger than in the SC paper manufacture, because in the coating stage base paper absorbs moisture from the coating colour and the paper loses strength. At the same time, application of the coating colour stresses the paper web. Surprisingly, the difference in chemical pulp content in LWC paper is often reported to be small or even negligible independent of the mechanical pulp used.

TMP contains much more long fibres than GW (groundwood) or PGW (pressure groundwood), but it seems that this does not reflect in the furnish in a desired way. It is well-known that long fibres have a decisive role in the increase of the toughness of a fibrous sheet. Besides the share, also the quality of the fibres is vitally important.

There is no explicit definition for long fibres but writers of scientific papers make the definition case by case. Often they are defined to be the fraction that

retains on the 28-mesh wire of a Bauer-McNett fractionator. Several authors after Forgacs who launched the term in 1963, have used the term 'L-factor' meaning the fibres retaining on the 48-mesh wire. L-factor is not necessarily meaningful when one characterizes pulps with high average fibre length, like softwood chemical pulp or softwood TMP or CTMP since in these pulps the L-factor (weight-%) is so high that the major part of the pulp belongs to it. For characterizing groundwood pulps in the past, L-factor was useful, but later most writers have regarded the 28-mesh fraction (and the fractions longer than that) as long fibres. The arithmetic and length weighted average fibre lengths of different Bauer-McNett fractions for a Black spruce TMP sample are given in Table 1-1. For comparison, the theoretical arithmetic fibre length according to Tasman (1978) is also given.

Table 1-1. Arithmetic average and weighted average fibre length of different Bauer-McNett fractions of a Black spruce TMP sample (Bichard and Scudamore 1988). Analysis made using a Kajaani FS-200 fibre analyzer. Theoretical arithmetic averages are calculated according to Tasman (1978).

Fraction	Arithmetic fibre length, mm	Length-weighted fibre length, mm	Theoretical (arithmetic) fibre length, mm
14	2.87	3.07	3.04
28	2.04	2.22	1.94
48	1.29	1.41	1.28
100	0.63	0.76	0.68
200	0.24	0.34	0.36

The length weighted average fibre length of Norway spruce GW is in the region of 0.5 - 0.8 mm, PGW's average is somewhat higher, 0.8 - 1.2 mm and TMP's 1.4 - 1.8 mm (UPM mill data).

When different fibre fractions are inspected under a microscope, typical features that can be found are that fibres in the long fibre fractions have retained their original shape and structure so that the lumen is left and the cell wall layers are at least partially there. In the longest fractions the fibres are more frequently intact than in the shorter fractions. The 48-mesh fraction contains similar material than the longer fractions, but also broken fibres and ribbons of the cell wall and opened fibres (Forgacs 1963, Honkasalo 1981).

In softwood chemical pulp, the share of the 14-mesh and 28-mesh fractions together represents about 80% of the pulp (Paper IV, Kappel 1999). This reveals that in chemical pulping the fibres are detached from the wood matrix in a much more preserving manner than in mechanical pulping. The average fibre length of softwood chemical pulp is typically in the region of 2.2 - 2.8 mm depending on the wood raw material (UPM mill data, Sixta 2006). The high average fibre length, high tear strength and high tensile strength of softwood chemical pulp are the reasons why it is used as a reinforcement pulp in present mechanical paper grades. Particularly in the case of GW pulp the average fibre length of the furnish rises steeply up by chemical pulp addition, Figure 1-1.

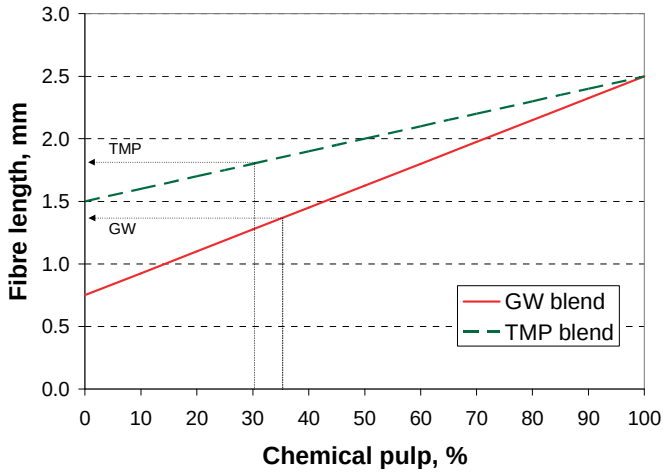


Figure 1-1. Average fibre length of a GW/chemical pulp and TMP/chemical pulp blends as a function of per cent chemical pulp. The length is based on the following assumptions: average fibre length 1.5 mm for TMP, 0.75 mm for GW and 2.5 mm for chemical pulp. The average length of the mixture is proportional to the length weighted average fibre length of the components and their proportions by weight (Paper I).

Besides the increase of the average fibre length with increased chemical pulp share, another interesting observation that can be made from Figure 1-1 is that a GW/chemical pulp mixture reaches the starting point of TMP not until at about 43% of chemical pulp. In practise, in a typical LWC base paper the ratio between mechanical and chemical pulp is about 65/35 when the mechanical pulp component is GW and 70/30 when it is TMP. With these mixing ratios, the average fibre length of the GW and TMP furnishes would be 1.36 mm and 1.8 mm, respectively. It is obvious that the average fibre length cannot be the dictating factor that determines the amount of chemical pulp in the furnish. The paper and furnish recipes differ from production line to production line. Basically, the amount of chemical pulp in the furnish is adjusted to guarantee the runnability of paper in the different stages of the paper manufacture and end-uses (printing house). It has an impact on quality characteristics other than strength, too, but generally speaking these effects are negative. If LWC or SC paper could be produced without the expensive chemical pulp, it would certainly be done.

1.2 Research problem

The observation that the need of chemical reinforcement pulp seems to be less dependent on the strength and average fibre length of the mechanical pulp component of a pulp blend than one might assume, raises the question about the importance of the fibre quality of the mechanical pulp component. Moreover, one can ask how the fibres of mechanical pulp differ from those of chemical pulp and what fibre properties should be developed to improve the reinforcement ability of mechanical pulp, and further, what properties indicating the reinforcement ability of paper are important for the runnability of paper. In

this research, the focus is on the differences between various fibre types and their reinforcement ability.

1.3 Objectives

The objective of this research is to find out the reasons why long-fibred TMP does not give the advantage that it is expected to give - namely a considerably lower chemical pulp content in the paper furnish than groundwood pulp. After the reasons for the 'underperformance' of mechanical pulp fibres have been found out, it is possible to concentrate the efforts to improve pulp properties on the right things and thus manufacture TMP pulps that enable cost savings in LWC paper production. If it becomes apparent that substantial development of the reinforcement ability of mechanical pulp fibres is impossible, further development efforts can be directed to other things, like low energy consumption in mechanical pulping or optical and surface properties of mechanical pulp.

1.4 Hypotheses

There are several well justified potential reasons why mechanical pulp fibres do not give as good reinforcement potential to the paper sheet as chemical pulp fibres:

1. Mechanical pulp fibres are weaker than chemical pulp fibres and break easier under stress.

2. There are less mechanical pulp fibres per unit weight. Consequently, there are less load-bearing elements and a higher percolation threshold consistency.

3. The bonding ability of mechanical pulp fibres is worse and therefore they strengthen the web less than chemical pulp fibres (bond strength, bonded area).

4. Mechanical pulp fibres give disadvantageous rheological (stretch at break, tensile stiffness) properties to the paper web.

1.5 Research methods

The research was divided in two parts, a literature part and an experimental part. In the literature part, fibre properties and strength theories are discussed in more detail than was possible in the publications. The literature part (Chapter 2) supports interpreting the results from the experimental part. The experimental part consisted of three major test series. The contents and objectives of those are described in more detail in Chapter 3.

The research material (pulp samples) was collected from commercial paper mills. In the third test series, pulp was prepared and paper was made on a pilot scale.

Fibres, pulps and papers were analysed mostly using standard test methods widely used in the pulp and paper industry. In addition, some less common test methods were used. In the third series, a special device designed for studying the runnability of running paper webs was used.

1.6 Scope of the research

The wood raw material of the mechanical pulps was Norway spruce (Picea abies) with a few exceptions. The mechanical pulp samples from France were made of a mixture of Norway spruce and other softwood species and the MDF pulp from Ireland was made from an unspecified spruce species.

The mechanical pulp samples collected from commercial mills were manufactured using either grinding (GW, PGW) or refining (TMP, RTS, MDF) techniques. The chemical pulps (spruce/pine) were manufactured in Finnish kraft pulp mills and the studied pulp samples were collected from Finnish paper mills.

This research focuses on the dry paper strength even though the wet web strength is recognized to be of great importance in the paper making process, too. The term ‘runnability’ in this research covers the whole paper manufacturing process from the drying section to converting and printing. In the runnability tests, also rewetted (moisture content of about 10%) paper was studied.

Most of the test results can be utilized in the manufacture of any mechanical printing paper grade. However, in the test series, where paper was made either in the laboratory or in the pilot, the simulated paper grade was LWC.

Different mechanical pulps may require an optimized chemical reinforcement pulp to get the best possible properties for the pulp blend and paper. This point of view was not investigated in this study.

1.7 Structure of the study

Literature review - fibre characterization and structure - strength models	Summary
Existence of the research problem - mechanical pulp fibres have lower reinforcement ability than chemical pulp fibres - first (preliminary) laboratory test series	I
Properties of single fibres and long-fibre fractions - characterization of mechanical and chemical pulp fibres - second laboratory test series	I, II, III, IV
Reinforcement ability of different mechanical pulp fibres - pulps from the second laboratory series - low grammage handsheets using semiautomatic handsheet robot (LWC base paper simulation)	III
Preparing special mechanical and chemimechanical reinforcement pulp	IV
Making pilot paper using the special mechanical and chemimechanical reinforcement pulps - paper tests - runnability tests	Summary, IV, V

2 LITERATURE REVIEW

2.1 Characterization of fibres

Characterization of pulps and fibres is a very essential area of paper making science. Without knowing what kind of features the pulp has and how its properties affect the paper manufacturing process and the end quality, it is very difficult to develop the pulping process to a desired direction. In the beginning of the 20th century, the Schopper-Riegler method was introduced. This method is intended to describe the refining degree of the pulp. Canadian Standard Freeness (CSF) was introduced soon after Schopper-Riegler. Like Schopper-Riegler, CSF analysis is based on the formation of a fibre pad on a screen. The CSF method was supposed to describe water removal on a fourdrinier paper machine. Both analyses are still widely used in the pulp and paper industry. They are considered useful for quality control purposes and undoubtedly they give a general picture of a mechanical pulp - for what end uses one might think to use a pulp. The weakness of these (and similar) methods is that several factors like fibrillation, fines content, flexibility of fibres etc. affect the result. This was soon realized and new methods were developed. One of the methods that still are in use is the fibre fractionation using the Bauer-McNett fibre classifier. Typically four units are assembled to a set which classifies pulp to five fractions mainly based on their fibre length. The Bauer-McNett classifier gives a quite reliable picture of the fibre length and fibre length distribution of pulp. Forcags (1963) studied different mechanical pulp fractions and suggested that pulp properties can be forecasted by determining two factors: the specific surface of the P48/R100 fraction and L-factor, which is the sum (%) of R28 and R48 fractions. Inspired by him, other researchers have proposed different means to characterize pulps (e.g. Mannström 1967, Clark 1968, 1976, Law et al. 1979). A common feature for the suggested methods was that they included at least one parameter that describes fibre length and another one that describes bonding ability. Fibre length, in turn, correlates with tear strength and bonding ability with tensile strength. This kind of thinking is still relevant, but leads only to indicative results.

Much expectation was put on optical fibre analyzers that were introduced in 1980's (Piirainen 1985, Tiikkaja 2007 and references therein). Analyzing fibre dimensions with them became routine but that did not solve the basic problem how to evaluate the usability of pulp for different purposes. Obviously, the problem is a very complicated one and it is unrealistic to wait until a universal model could be created. In spite of this statement, it is fruitful to seek methods to characterize pulp and to try to understand what are the most important fibre properties. Ryti (1971) has presented the general principles for pulp characterization. The usability of two paper pulps can be compared only in the case where the paper grade and the paper manufacturing process are known. The papermaking process should be optimized for each pulp.

2.2 Basic fibre properties

Heikkurinen et al. (1991) discussed the basic fibre properties and concluded that they can be divided in four categories:

- Size distribution
- Shape
- Structure of the cell wall
- Fibre surface

The properties are by definition independent of each other. The basic properties cannot necessarily be determined by a single analysis, but they must be understood as more general titles requiring several analysis methods to be determined. Table 2-1 gives examples of the analysis methods that can be classified under different basic fibre properties.

Table 2-1. Basic fibre properties and examples of methods for measuring them according to Heikkurinen et al. (1991).

Size distribution	Shape	Structure of cell wall	Fiber surface
Fiber length	Specific surface	Flexibility	Chemical composition
Fiber width and cell wall thickness	External fibrillation	Swellability	ESCA
Coarseness	Curl	Pore volume	Fibril angle
		Specific volume	
		Misaligned zones in structure	

The concept of Heikkurinen et al. (1991) is only one approach but it gives a good hint how difficult it may be to characterize fibres or pulp precisely. For instance, one can ask in what way fibres are externally fibrillated. Are there a few long fibrils or a large amount of short fibrils reaching out from the fibre surface? Are fibrils narrow, are they lamellar and so forth? In spite of the possible pitfalls, this approach was used in the experimental part of the present study.

Most of the researchers who have studied fibre characterization have presented or discussed a single analysis method or analyser that describes only some part of the entity. In the following, possible ways to characterize basic fibre properties are described and discussed.

2.2.1 Size distribution

There are plenty of publications about methods that go under the title ‘size distribution. Fibre length analysis can be carried out with several commercially available optical analysers, e.g.: FS-200, PQM, FSA, MorFi, kajaaniFiberLab, Fibermaster (Guay et al. 2005, Tiikkaja 2007). There is an ISO standard on fibre analysis with optical analysers (ISO 16065-1). It differs from the widely used TAPPI method (T 271 om-07) in which the average fibre length is calculated for fibres that are longer than 0.2 mm.

Analysing fibre width and particularly cell wall thickness is more demanding than that of fibre length. Most of the commercial analyzers can measure fibre width and the results with the analyzers correlate reasonably well, although there are differences in the absolute width levels (Guay et al. 2005, Turunen et al. 2005, Heinemann 2006). The only analyzer with cell wall thickness measurement is the kajaaniFiberLab. According to Richardson et al. (2003) the FiberLab cell wall thickness data should be used with caution. In their study, cell wall thickness was highly correlated with the fibre width. The FiberLab cell wall thickness did not correlate at all with the results from two other methods based on different techniques. In contrast, Pulkkinen et al. (2008) have reported that their results did not support the claim that fibre width has a strong influence on the fibre wall thickness index. Fibre wall dimensions are often determined using various microscopy techniques like light microscopy, LM, confocal laser scanning microscopy, CLSM or scanning electron microscopy, SEM. The results can vary depending on the method, on sample preparation and whether the fibres are analyzed wet or dry (Kibblewhite and Bailey 1988, Jang et al. 1996, Ye and Sundström 1997, Lammi and Heikkurinen 1997, Reme et al. 2002, Chinga et al. 2007).

Fibre coarseness and fibre cell wall thickness often correlate with each other. Determination of fibre coarseness can be done based on the fibre length and the number of fibres in a certain amount of pulp (Seth and Chan 1997):

$$C = \frac{m}{n \cdot l_a} \tag{1}$$

where C = coarseness
m = a very small mass of fibres supplied to the analyser
l_a = arithmetic mean length of the fibres
n = total number of fibres in the mass m.

The analysis is more challenging than one might think. A precise analysis of the dry mass of fibres is very critical. It is difficult because only a few milligrams of pulp is analysed. Another error source is the presence of debris (fibrils, fibre fragments, ray cells etc.) in the pulp. It is included in the weight (if not removed before analysis), but not necessarily detected by the analyser, resulting in a higher coarseness value than predicted. Measuring fibre length can be regarded as quite reliable (Guay et al. 2005). For mechanical pulp (Karnis 1994, Seth and Chan 1997), because of the considerable fibre fragments and fines, it is more meaningful to measure and compare the coarseness of various Bauer-McNett fractions than those of whole pulps.

As stated before, fibres having equal coarseness can actually have a very different cross-sectional appearance, as illustrated in Figure 2-1.

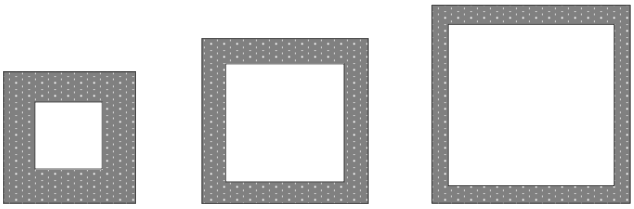


Figure 2-1. Schematic of fibres having same coarseness (cross-sectional area) but different appearance.

It is evident that not only the cross-sectional area or coarseness but also the relationship between fibre width, cell wall thickness and lumen diameter affects the properties of fibre. Moreover, fibre collapse has a drastic impact on how fibres behave in fibre network. To describe the relationship between the cross-directional dimensions and paper properties, several parameters have been developed. Runkel's ratio (= 2*cell wall thickness/lumen width measured in the radial direction) is one of the most common ones (Paavilainen 2002). It has been used extensively in the literature for classification of tracheids. Another similar ratio is Mühlsteph's ratio (cross-sectional cell wall area/cross-sectional area including lumen area). According to Reme et al. (1999) these ratios are hard to use on processed fibres due to large variations in cross-sectional shapes among them. Supposing that fibres are of circular cross-sectional shape, they give modified definitions for the ratios, Equations 2 and 3:

$$RR_{\mathrm{mod}} = \frac{D_i}{D_o} = \frac{P_i}{P_o} \qquad \text{and} \tag{2}$$

$$RM_{\mathrm{mod}} = \frac{A_w}{\pi \cdot r_o^2} = \frac{4\pi A_w}{P_o^2} \tag{3}$$

RR_{mod} denotes modified Runkel's ratio and RM_{mod} modified Mühlsteph's ratio. D_i denotes the lumen diameter and D_o the outer diameter and P_i and P_o are the corresponding perimeters. A_w denotes the fibre wall area and r_o the outer radius. Reme et al. (1999) called the modified Mühlsteph's ratio Z ratio (or Z-parameter) expressed in percent. Fibres having a low Runkel ratio or a low Mühlsteph's ratio are considered less desirable for papermaking, because they have a lower tendency to collapse (Jang and Seth 1998).

Sirviö and Kärenlampi (2001) have used the term cross-sectional compactness, CC, of the same parameter. Z-parameter can achieve a value between 0 and 1 (or 0 and 100 %). A value close to zero indicates an early wood fibre and a value close to one a latewood fibre (or a fully collapsed fibre with no open lumen area). According to them, fibre flexibility depends on the cross-sectional fibre geometry. Law et al. (1999) have used rigidity index as a measure of collapsibility and conformability of fibres. Rigidity index (RI) is defined in the following way (Equation 4):

$$RI = \left(\frac{T}{D}\right)^3 \times 10^{-4} \tag{4}$$

where T is cell wall thickness in µm and D fibre diameter in µm. Fibres are assumed to be thin-walled cylinders under pressure whose collapse depend on the thickness of the cylinder wall and the cylinder diameter. According to Law et al. (1999), a high rigidity index indicates a poor bonding potential. Vesterlind and Höglund (2005) have shown that the compression load needed to collapse a circular cross section (assuming that wall thickness is small compared to the radius) is proportional to the cross section property collapse resistance, CR (Equation 5):

$$CR = \frac{t^2}{2r - t} \tag{5}$$

where t is cell wall thickness and r the radius of the cross section.

Dickson et al. (2006) used collapse resistance index, CRI, when studying decollapse behaviour of Pinus radiata pulp. Their main conclusion was that high-coarseness earlywood fibres with large perimeters and thick walls were identified as having the greatest decollapse potential with wetting. CRI, originally developed by Wakelin et al. (1999), was defined differently (Eq. 6) than the CR (in Eq. 5) by Vesterlind and Höglund.

$$CRI = 1000 \cdot \left(\frac{1}{1 + \frac{P_c^2}{\pi \cdot A_W}} \right)^3 \tag{6}$$

where P_c is centerline perimeter and A_W is fibre wall area.

Reyier (2008) has developed the Bonding Indicator (BIN) which is a linear combination of CR and of external fibrillation. She showed that BIN characterizes well the bonding ability (tensile strength and apparent density of long fibre laboratory sheets) of mechanical pulp. A BIN value can be calculated for each individual fibre and thus generate a BIN distribution of the fibres. In Reyier's study, the kajaaniFiberLab was used to collect the necessary data.

2.2.2 Shape

According to the definition by Heikkurinen et al. (1991), the shape of a fibre means not only the actual shape (whether a fibre is bent, twisted or curled etc.) but also whether a fibre is externally fibrillated. It may be fair to say that the shape means its appearance. External fibrillation is closely related to the specific surface of fibres. In external fibrillation fibrils and lamellae are partially detached from the fibre wall.

The specific surface can be derived hydrodynamically from the water permeability of pulp pad. Examples of this approach have been reported for instance by Forgacs (1963) and Mannström (1967). Forgacs introduced the term shape factor by which he meant the hydrodynamic specific surface of the P48/R100 fraction. A convenient option is to use a freeness tester to determine

specific surface. A change in freeness due to beating is essentially a measure of the change in the pulp's specific surface area. Since mechanical pulps obtain their strength mainly from an interaction between fibre surfaces, and freeness is sensitive to specific surface, freeness has been successfully applied to the strength characterization of mechanical pulps (El-Hosseiny and Yan1980).

External fibrillation is a very polymorphous phenomenon. The nature of fibrillation is different in different fibre layers. According to Fernando and Daniel (2004), the fibrils from the S2 layer of the secondary cell wall are typically ribbon or sheet like whereas those from the S1 layer are flake-like. Fibrillation predominantly follows the orientation of the cellulose microfibrils (i.e. microfibril angle, MFA). Fernando and Daniel identified four types of S2 fibrillation in spruce TMP: macrofibrils, semi-macro ribbons, macro-ribbons and macro-sheets. The average width of those fibril types was 0.12 µm, 0.83 µm, 1.64 µm and 6.5 µm, respectively. The smallestribbons or strings were ca. 0.03 µm in width and these were assumed to be composed of an unknown number of cellulose microfibrils.

The manner of how external fibrillation of spruce kraft pulp and thermomechanical pulps takes place is very similar. In both pulps concentric delamination occurs between lamellae which then split into smaller entities giving rise to fibrillation (Fernando and Daniel 2004).

There is still a lack of convenient methods for an accurate quantification of external fibrillation (Wang et al. 2007). In the laboratory, external fibrillation can be determined using a light microscope, confocal laser scanning microscope or scanning electron microscope (Kang 2007, Sabourin and Hart 2010), often combined with image analysis. The result depends on the software and parameter settings. The same applies obviously also for automatic fibre analysers, like kajaaniFiberLab, Morfi, Fibermaster and others.

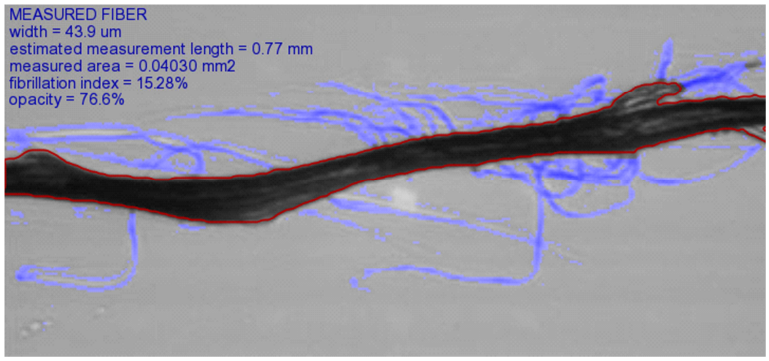


Figure 2-2. A strongly fibrillated softwood TMP fibre (a kajaaniFibreLab image). Fibrils are shown blue in the image and the fibre trunk is cropped with red. Source: Metso Inc. 2008.

One way is to express the degree of fibrillation is to calculate the ratio of the fibril area to the whole fibre area including fibrils like in the kajaaniFiberLab analyzer (Figure 2-2, Equation 7) (Kurhila 2005).

$$Degree\ of\ \ fibrillation = 100 \times A_{fibrils} / A_{total} \quad (7)$$

where $A_{fibrils}$ is the fibrils area and A_{total} total fibre area including fibrils.

Another possibility is to use the fibre perimeter like in the Cybermetrics analyzer (Sandholm 2002), Equation 8:

$$Degree\ of\ \ fibrillation = 100 \times (1 - \frac{P_f}{P}) \quad (8)$$

where P_f is the perimeter including fibrils and P is the perimeter excluding fibrils.

Sandholm (2002) has developed a new method to determine the degree of fibrillation. A fibre image is line-scanned and all crossings are summed up. This sum is then divided with the number of lines where at least one crossing is found. This is called the fibrillation index FI (Eq. 9):

$$FI = \frac{Total\ number\ \ of\ \ crossings}{Total\ number\ of\ \ lines} \quad (9)$$

Fibre curl has been recognized as an important fibre property since early 20th century (Page et al. 1985). Nowadays, the most typical way of describing fibre curl is according to Jordan and Page (Joutsimo 2004). Their definition for the curl index is the relationship between the fibre contour length, L, and the longest dimension (*l*) which is the distance between those points within the fibre which are furthest apart (Eq. 10):

$$Curl\ index = \frac{L}{l} - 1 \quad (10)$$

According to Kibblewhite (1977), curled fibres can be divided in two categories: a) kinked and b) curved and twisted fibres. Fibre kinks are defined as distinct angular bends along the length of pulp fibres. The curl index does not make any difference in which way the fibres are curved. Kibblewhite and Brookes (1975) developed the kink index to quantify the fibre kinks (Eq. 11).

$$Kink\ index = \frac{n_{(10°\text{-}20°)} + 2\,n_{(21°\text{-}45°)} + 3\,n_{(46°\text{-}90°)} + 4\,n_{(91°\text{-}180°)}}{total\ sample\ \ fibre\ length} \quad (11)$$

where $n_{(\alpha°\text{-}\beta°)}$ is the number of sharp bends, i.e. kinks, in the angular range from α to β in the total sample.

According to Seth (2006) curl may be an indicator of fibre deformations, but not a measure. A fibre can contain many deformations along its length, but still remain relatively straight. In addition, the experimental set-up has an effect on the result.

Tozzi and Klingenberg (2008) have shown by simulation that neither the curl index nor the kink index correlates well with the viscosity of a dilute suspension. Instead, they recommend using an invariant of the hydrodynamic resistance tensor to quantify fibre shape and its effect on the suspension properties. The invariant can be computed from 3D images of the fibres. Their results also suggest that experimentally measured intrinsic viscosities could be used to characterize fibre shape.

Fibre shape is often linked to the bonding ability of fibres. A common paper technical test that is used to assess the internal bonding of a paper sheet is the Scott bond test. In the test, a right-angle metal bracket is attached to the sheet with double faced tape. An impact load is applied to one arm of the bracket and the energy needed to pull out the bracket is recorded. The method does not measure the intrinsic fibre-fibre bond strength, because the number and size of bonds in the fracture process cannot be readily determined (Bronkhorst and Bennet 2002). The Scott bond test is not without controversy. It is sensitive to any non-uniformity or layering in the z-direction as delamination will occur at the weakest plane. Fibre failure can take place instead of bond failure. The basis weight of the sheet affects the results. At low basis weights (below 60 g/m2) the penetration of the adhesive increases the strength (Kajanto 2008). Despite these deficiencies the Scott bond test can be regarded as an indicative measure when assessing the bonding potential of different fibre.

2.2.3 Structure of the cell wall

Fibre flexibility has been recognized to be of fundamental importance in paper making. The wet flexibility of the fibres is the controlling factor of the compaction of the sheet (Steadman and Luner 1985). According to Paavilainen (1993), fibre flexibility is the single most important factor that controls the tensile strength of sulphate pulps. Jackson and Williams (1979) have concluded that poor flexibility and conformability of the TMP long fibre fractions is the cause for the poor bonding properties of that pulp. Mohlin (1989) has emphasized the importance of the properties of long fibres of TMP on paper properties. Several methods have been developed for measuring fibre flexibility (e.g. Tam Doo and Kerekes 1982, Steadman and Luner 1985, Fransson et al. 1992 in the patent WO 92/05423, Petit-Conil et al. 1994, Kuhn et al. 1997, Eckhart et al. 2008). According to Paavilainen (1993), the two most promising ways of measuring wet fibre flexibility were the Tam Doo & Kerekes method and the Steadman (and Luner) method. The usability of the former method is limited because only perfect fibres are studied. In the latter one, also non-perfect fibres (fibres with kinks, external fibrillation etc.) can be analysed. Paavilainen claimed that the Steadman method characterizes the role of wet fibre flexibility in the formation of interfibre bonds better than other available methods. Today, probably the methods of Tam Doo and Kerekes, Steadman and the one of Fransson et al. are mostly used. The latter one is applied in the commercial Fibermaster analyzer. The method of (Mohlin-)Steadman is automated by the CyberFlex analyzer (Das et al. 1999). The name of the Steadman methods varies because it is developed by Steadman and Luner (1985) by combining elements of the Mohlin's conformability test and the contact ratio test for fibre bendability (Mohlin 1975, Kuhn et al. 1997).

Fibre flexibility is not a direct measure of the cell wall structure but it is known that changes in the cell wall structure reflect in it. In mechanical pulping, peeling off of the outer wall layers, fibre wall delamination and fibre wall splitting take place. As a result fibre wall elasticity decreases, fibre wall thickness reduces and fibre flexibility and conformability increase (Vehniäinen 2008). The existence of delamination has been under discussion (Bergander and Salmén 1997, Maloney and Paulapuro 2001). However, Vehniäinen (2008) has proposed that this phenomenon does exist in mechanical pulping. When gentle refining was used, she observed that fibre flexibility increased even though fibre wall thickness was unchanged. This was interpreted as evidence of the existence of cell wall delamination. She also reported about increased fibre wall pore volume and local swelling of the fibre wall (S2) at the points where the outer layers had been removed.

Vehniäinen (2008) used water retention value (WRV) and fibre saturation point (FSP) for pore volume determination. The WRV analysis is based on centrifuging a pulp pad which is weighed wet after centrifuging, dried and weighed again. The WRV value is the mass weight of water retained after centrifugation under specified conditions by a wet pulp sample to the oven dry mass weight of the same pulp sample (Heikkurinen and Leskelä 1999, SCAN-C 62:00). Depending on the pulp and the test conditions, the WRV can be higher or lower than the FSP. However, the test is useful as an indicator of relative changes in fibre swelling (Maloney et al. 1999). A solute exclusion technique is used to determine the FSP. Wet fibres are immersed in a dilute aqueous solution of a water-soluble saccharide. It is assumed that all pores larger than the diameter of the saccharide molecule are completely accessible. The amount of water retained in the cell wall can then be determined based on the changes in the concentration of the polymer solution. The FSP is a good estimate of the amount of water held within the cell wall (Stone and Scallan 1967, Maloney and Paulapuro 1999). Other methods that have been used are nitrogen absorption method (Stone and Scallan 1965), nuclear magnetic resonance spectroscopy (NMR) (Li and Henriksson 1993), the inverse size exclusion chromatography (ISEC) (Berthold and Salmén 1997) and mercury porosimetry (Rauvanto et al. 2006). Maloney and Paulapuro (1999) used a differential scanning calorimetry (DSC) technique called thermoporosimetry for pore size analysis. The method is based on the depressed melting temperature of water in small pores. Some of these tests can be made for wet or moist fibres, some only for dry or dehydrated fibres.

Cowan (1970) has suggested that any wet pulp can be characterized with three independent parameters: specific surface, specific volume and compressibility. These properties could be analyzed using the Pulmac permeability tester. From the three parameters, the specific surface is a relevant term even today, but the specific volume and pulp compressibility are seldom referred. The specific volume characterizes the gel state or swollen volume of the pulp on a unit weight basis. It is evident that the structure of single fibres would reflect in the specific volume of the pulp pad formed in the Pulmac tester. According to Cowan, it has an important contribution to drainage resistance and affects the sheet strength. Beating of chemical pulp increases the specific volume markedly. Compressibility characterizes the manner in which pulp particles can

be compressed together to form a sheet. It would likely correlate with fibre flexibility.

A misaligned zone is one of the terms that have been used to describe dislocations in pulp fibres. Dislocations most likely develop already in the wood of standing trees. They are also produced by mechanical action during various process stages like chipping, pulping and pulp processing like refining and wet pressing. It is obvious that dislocations affect the pulp quality in many ways. Fibre kinks are typically at dislocations or at nodes as some researchers call them. Fibres tend to swell, bend and rupture preferentially at sites of dislocations. A large number of dislocations might reduce the elastic modulus of fibres and lower thereby the fibre strength (Nyholm et al. 2001).

The number of deformations has been shown to affect paper strength properties. Song and Duffy (2002) made intentional deformations to kraft pulp fibres using a continuous laboratory fibre processor (CLFP). The device simulated a MC pump. They observed that an increased amount of deformations decreased particularly the wet zero-span tensile strength. They kept this result as evidence that the CLPF device damages fibres and reduces intrinsic fibre strength.

Fibre strength can be kept as an indirect indicator of the fibre wall structure. The measured value for fibre strength depends not only on the intrinsic strength of a fibre but also on the changes in the fibre wall that the process has caused.

Many researchers have investigated the strength of single fibres by tensile testing as overviewed by Wathén (2006). However the method is very tedious and thus it is not suitable for routine analysis. Quite recently, the single fibre fragmentation technique, SFF, has been used to study the influences of different treatments on pulp fibres. The advantage of the method is that fibres are constrained during the test and thus the testing situation resembles better the actual stress situation in real paper (Ljungqvist et al. 2005). In the SFF analysis, the breaking strength of single fibres is calculated with the assumption that pulp fibres are linear elastic and characterized by Young's modulus (Thuvander et al. 2001). The method gives information of the strain-at-failure distribution of pulp fibres which can then be used in paper strength models.

The zero-span strength differs from the other two as it is measured from a paper strip and thus represents the average of the fibres in the fracture zone (Wathén 2006). He defended the use of the zero-span test by stating that it is commonly available and easy to use and that it gives an indication of the average strength of pulp fibres. The strength of individual fibres can be estimated from the zero-span test if the coarseness and the average fibre length of the pulp are known (Somboon and Paulapuro 2009).

Several factors can have an impact on the measured fibre strength value. Some researchers (Mohlin et al. 1996, Seth 2001, Clark and Ellis 1997) have emphasized that fibres should be straightened before the zero-span tensile strength analysis since fibre deformations will influence the results. Contrary to those studies, Wathén and his co-authors (Wathén 2006, Joutsimo et al. 2005) suggested that fibre curl and kinks may not affect the zero-span results. They hypothesized that the result depends on the load distribution uniformity of the 3-

dimensional fibre wall structure. The undamaged fibre wall distribute load evenly, which leads to high fibre strength. Instead, the damaged fibre wall distributes load non-uniformly, which generates points in the fibre wall that carry most of the load leading to lower fibre strength. Beating increases uniformity of fibrils and fibril aggregates, which explains why fibre strength seems to increase due to gentle beating.

Batchelor et al. (2006) regard the zero-span test as an important test of fibre quality. In order to get reliable results, they emphasized that the sample grammage should as low as possible and that zero-span strength comparisons should be made at equal grammage, since it has a clear effect on the result.

Joutsimo (2004) studied the effect of mechanical treatment of softwood kraft pulp. When fibres were damaged by mixing during cooking, the zero-span tensile strength was markedly lower for the mixed pulp at a given tensile strength even though the curl index and the number of kinks were lower after gentle PFI refining. He deduced that the curl and kinks are not the only reasons for the lower tensile and zero-span tensile strength of kraft pulp. The damage width and the pull-out width at a given tensile strength were also significantly reduced. The results were interpreted to indicate that the single fibre strength was reduced.

Kärenlampi and Yu (1997) observed that zero-span strength of fibres is drastically reduced by acid-vapour treatment. Earlier, Seth (1996) had used the acid-vapour treatment to weaken the fibres in the sheet when investigating the effect of fibre strength on the fracture toughness. The treatment allows weakening the fibres without affecting other fibre properties.

Batchelor (2006) has listed the pros and cons of the zero-span measurement in the following way:

Pros
- rapid measurement
- related to average fibre strength
- thousands of fibres broken per test
- affected by fibre defects

Cons
- measures stress transfer from the jaw
- measures breaking strength only
- average only
- affected by fibre defects

It can be deduced from the references above that the zero-span test is suitable for describing fibre strength in general. It is not necessarily good for the evaluation of single fibre strength, but it can be used for example for the evaluation of fibre defects, which actually is of great interest in this work. In case one wants to determine the strength of intact fibres, the zero-span analysis is not good, since the fibres that are broken in the test strip are randomly chosen.

Fibre damage

The terminology that describes the structure of the cell wall, discontinuities and divergences in it and the changes that processing has caused to it is not well-established (Nyholm et al. 2001, Rauvanto 2010). The term misaligned zone shortly discussed above is only one of the many terms used. Terms like dislocations, deformations and fibre damage can be regarded as more general terms in nature. Rauvanto (2010) has investigated fibre damage in chemical pulping. She divided the term in three categories:

- Loosening and breakage of fibre wall structure
    - Seen as changes in the ability of the fibre wall to retain water, delamellation and changes in porosity profile
- Changes in the three dimensional fibre form
    - Fibre deformations characterized as fibre curl, kink, dislocations and alterations in fibre crimping, and broken fibres
- Changes in the fibre surface
    - Surface fibrillation and crack formation.

In the current research, the term fibre damage is used in a similar way as Rauvanto. It is good to notice that the fibre damage as defined above covers two basic fibre properties, namely fibre shape and cell wall structure (cf. Table 2). Fibre damages are generated in all stages of pulp manufacture: in harvesting, wood handling, chipping and above all in the actual process during cooking and bleaching, due to pumping, screening and pulp processing (Allison et al. 1998, Joutsimo 2004, Nyholm et al. 2001, Rauvanto 2010). Mechanical pulping is very violent and it can be said that actually the whole process is based on damaging fibres.

The grinding process has been shown to cause much more fibre splitting (longitudinal cracks) than mechanical pulping by refining. In the study of Reme et al. (1998) 40 - 46% of GW long fibres were split whereas only less than 10% of TMP long fibres were split. Split fibres are typically thin walled early wood fibres. In GW pulp, the cracks locate more frequently in the ends of the fibres than in TMP. The advantage of fibre splitting is a reduced tendency of roughening upon moistening. The fibre split, the average split length of the fibre population as a percent of the total fibre length, was determined using a light microscope.

Simons' staining can be used to analyze local damages in the cell wall structure. The stain is a two-colour differential stain that is sensitive to variations in the accessibility of the interior structure of fibres. It is independent of the kind of fibres. Thus, it can be used for analysis of chemical and mechanical pulps. The orange dye has a much larger molecular size than the blue dye. Therefore, it has much less capability to penetrate the fibre interior. Untreated wood stains deep blue and fibrillated parts of fibres stain yellow-orange (Blanchette et al. 1992, Yu et al. 1995). Vehniäinen (2008) used Simons' staining to provide information of the degree of internal fibrillation of TMP and GW pulps.

2.2.4 Fibre surface

Differentiating between the basic fibre properties (see Table 2) is not always easy since e.g. pronounced external fibrillation is hardly possible without affecting the cell wall structure. Similarly, the physical and chemical nature of the fibre surface is almost inevitably affected by the fibre treatment. In spite of these considerations, it is useful to try to distinguish the basic fibre properties when characterizing fibres.

The chemical composition of the fibre surface has a decisive effect on how fibres behave. The ability to create bonds without any additive or glue is an essential feature of paper making fibres. Therefore, it is surprising that there is no direct characterizing method of fibre surface that would be used on a daily basis. Modern chemical and physical analyses offer almost limitless possibilities to analyse fibre surface from different points of view. It may not be possible to find a single factor that alone or combined with some other factor could determine the chemical state and physical performance of the fibre surface. Therefore, in this overview, only a few examples are given.

Chang et al. (1979) analysed TMP and RMP pulps and pulp fractions for Klason lignin and carbohydrate contents. Carbohydrate analyses were performed using a gas chromatographic method. They observed that the fines fraction (-100-mesh) were lignin-rich relative to the long fibre fraction (+48-mesh). The lignin/carbohydrate ratio for the fines generated in TMP was higher for the fines from RMP. Conversely, TMP long fibres were characterized by lower lignin content than RMP long fibres.

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), has been used in numerous fibre studies after it was first applied to pulp studies in the 1970's. It yields information on the elemental and chemical composition of the surface (Koljonen et al. 2003).

The sample is irradiated with monoenergetic x-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity are determined (anon. 2010). The intensity of escaping electrons decreases rapidly as the penetration depth increases. The penetration depth is typically of the order of 1-3 nm (Holmbom and Stenius 2000, Koljonen 2004).

Kangas (2007) and her co-authors (Kleen et al. 2003, Kangas and Kleen 2004) have made a comprehensive study of the fibre surface of various mechanical pulps and their fractions. In addition to gross chemical analysis, ESCA, ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and AFM (Atomic Force Microscopy), were used for surface characterization. ESCA gives information about the coverage of lignin and extractives on the fibre surface down to depth of 5-10 nm. ToF-SIMS is very surface-specific and particularly useful for investigating the elements and organic compounds present on the outermost surface (1 nm) of the sample. AFM was used to study the surface morphology. By employing phase imaging in AFM different surface components such as lignin and cellulose can be identified. The lateral resolution

of AFM is of the order of Ångströms (1 Å = 0.1 nm). Several interesting observations of the chemistry of the pulp components were made. E.g. it was reported that almost 80% of the surfaces of fibrillar fines were covered by lignin and extractives and 20% was covered by polysaccharides. Flake like fines also had a high surface content of lignin, but the extractives content was lower than for fibrillar fines (Kangas and Kleen 2004).

Wood resin, isolated from TMP, on the fibre surface has been shown to decrease the tensile strength of kraft pulp considerably (Sundberg et al. 2000).

Fibril angle was given as an example of a physical surface characteristic by Heikkurinen et al. (1991). However, one can argue if the fibril angle as such is important for instance for the bonding ability of a fibre. Instead, it is common knowledge that microfibril angle (MFA) of the dominating S2 layer has a very important contribution to the physical properties of a fibre.

2.3 Cell wall ultrastructure

The ultrastructure of wood fibre cell walls has been studied for decades but still the final consensus on the details is missing. However, the idea that a fibre wall consists of different layers, called primary wall (P) and secondary wall (S) is generally accepted. Secondary wall is divided in three distinctive layers S1, S2 and S3. Between the fibres there is middle lamella. Figure 2-3 depicts the suggestion for the cell wall ultrastructure of Brändström (2002).

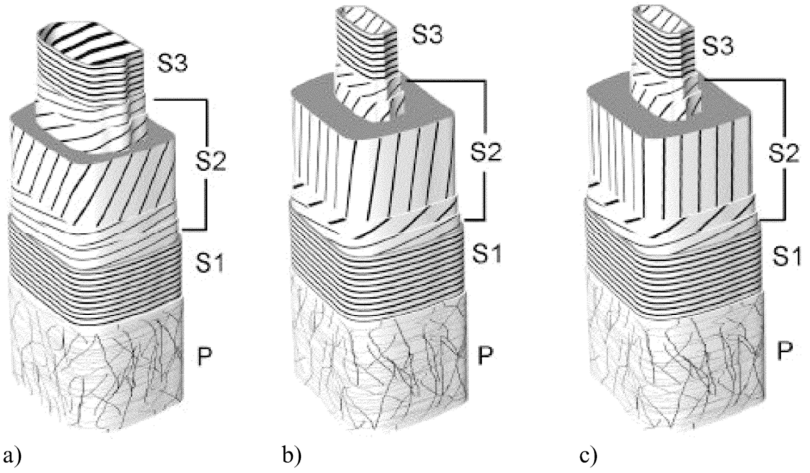


Figure 2-3. Cell wall models of Norway spruce tracheids. a) earlywood tracheid, b) latewood tracheid, c) latewood tracheid from the mature wood (Brändström 2002).

The detailed structure of the cell wall is still under discussion. The S2 layer has been proposed to be a concentric lamella structure consisting of up to several

hundred lamellae. The S2 layer is easily separated from both S1 and S3 (Forgacs 1963, Stone and Scallan 1965). Stone and Scallan suggested that the microfibril lamellae in a water swollen cell wall of spruce pulp are less than 10 nm thick and the median spacing between them is about 3.5 nm. The cell wall model(s) by Brändström (2002) deviates in some respects from the older models. In the S1 layer, the microfibrillar angle (ca. 70 - 90°) is homogeneous and not crossed as usually presented. The transition lamella, where the microfibrillar angle gradually changes, should be designated to S2. Brändström does not indicate any lamellation of the S2 because of the disagreement in the literature.

Stone and Scallan (1965) proposed that a lamellar structure would have an important effect on the fibre flexibility. They calculated that if the lamellae can freely glide over one another, the flexibility is 10^5 times higher than in the case where no sliding takes place. This would offer an explanation for the marked difference in the wet fibre flexibility of chemical and mechanical pulps fibres. In the former ones, the cell wall is largely split in to lamellae since lignin is dissolved between them but in the latter ones, the split is based on mechanical treatment which is essentially less effective. It is clear that in reality the separation of the cell wall to lamellae is far from complete. Even if the S2 were not a lamellar structure but rather a network of oriented microfibrils, dissolving material, mostly lignin, between them would undoubtedly have a marked effect on the strength of the water swollen fibre wall. The elastic modulus of the water-swollen cell wall has been found to drop from about 10 MPa to 2 MPa as the yield was lowered from 100% to 65% (Scallan and Tigerström 1992). This difference corresponds roughly to differences in the flexibility which Karnis (1994) has reported for the long fibre fractions of RMP, TMP and kraft pulp.

Different pulping and bleaching processes affect differently the structure of the secondary cell wall. A dominant peak in the cellulose microfibril width at 18-20 nm has been reported by Bargade et al. (2004). This refers to the existence of an inherent aggregation pattern of 4 cellulose fibrils in width. Larger aggregates are most probably a consequence of the pulping process. Removal of hemicellulose was found to induce aggregation of cellulose fibrils.

The fibril terminology in literature varies. The smallest fibrillar building element in the cell wall has been often called an elementary fibril consisting of 36 parallel cellulose molecules (Sjöström 1992). However, in this research the terminology used by Brändström (2002) and Wathén (2006) is adopted. The smallest cellulose molecule aggregate unit is called microfibril and the next larger unit fibril or fibril aggregate. The width of the microfibrils is 3-4 nm (Mark 2002 and Wathén 2006).

Kangas (2007) has presented SEM micrographs of a fibril fraction isolated from the first mainline TMP refiner and from second stage reject refiner. The first refiner stage fibrils are roughly 100-1000 nm in width, i.e. approximately of the same size as the fibrils called macrofibrils by Fernando and Daniel (2004). Interestingly, reject fibrils seem 20-30 nm in width by visual estimation, or of the same size than the fibril aggregates observed by Bargade et al. (2004).

2.4 Strength models

In the 1960's much effort was made on explaining the factors that contribute to static hand sheet properties like tensile strength and tear strength, burst factor and light scattering coefficient.

Alexander and Marton (1968) studied the effect of beating and wet pressing on fibre and sheet properties. They tried to find the limits for the strength development. They observed that tensile strength increased with increasing apparent density but reached maximum at the point where fibre walls begin to disintegrate and single fibres begin to lose their strength. According to them density is an important but alone not a sufficient criterion for characterizing paper properties since the strength-density relationship depends on how the density is achieved (by refining or wet pressing). Sheet density was regarded as a more reliable measure of interfibre bonding than scattering coefficient because it behaved more logically than light scattering even at extreme values. Tear factor reached its maximum at a much lower density than the tensile strength. The maximum of the single fibre tensile strength was at a higher density than the maximum tear factor. According to the authors, this result made the classical explanation for the shape of tear-tensile curve questionable. One interesting conclusion from their study with spruce kraft pulps was that the bonded area between the fibres is more important for the sheet tensile strength than the number of fibres or individual fibre strength.

Page presented his famous equation (12) for tensile strength in 1969 (Page 1969):

$$\frac{1}{T} = \frac{9}{8ZS} + \frac{12A\rho g}{bPl(RBA)} \qquad (12)$$

where T = tensile strength
ZS = zero-span tensile strength
A = fibre cross sectional area
ρ = density of fibre wall
g = acceleration due to gravity
b = bond shear strength per unit bonded area
P = perimeter of the fibre cross section
l = fibre length
RBA = relative bonded area of the sheet

Page's theory has certain limitations. It is assumed that fibres are straight and free from crimps and kinks, have a uniform elastic modulus along their lengths and the sheets have good formation (Seth and Page 1996). In fact, Page himself reminded about the limitations and drawbacks in the original publication. In any case, numerous researchers have referred and utilized Page's equation in its original or modified form. The beauty of the theory is in its simplicity: tensile strength is determined by the strength of single fibres, fibre dimensions and the bonding degree of the sheet. The equation is based on the assumption that all the fibre-fibre bonds down the length of the fibre contribute equally to the axial load. According to Page, this assumption is valid at failure, but before it, the shear-lag model holds (Page 2009). By this way, he gives an explanation to the

contradiction between the Page equation and the equation that he together with Seth had developed for the elastic modulus of paper (Page and Seth 1980).

As an example of the use of Page's equation, Gurnagul et al. (2001) used it to show that the tensile strength reduction upon drying of softwood kraft pulp is primarily due to the loss of shear bond strength.

Quite recently, the Page equation was used when studying the effect of CMC on bond strength (Duker and Lindström 2008). In fact, this is a typical way to use the Page equation; there is no need to evaluate tensile strength using a theoretical equation because tensile strength is easy to measure. Instead, shear bond strength that is difficult to measure directly can be solved from the formula.

The light scattering method by Ingmanson and Thode (1959) is one possibility to determine the RBA of chemical pulps. Another possibility is to base the determination of the RBA on the BET analysis, like Duker and Lindström (2008) did. Applying the light scattering method to mechanical pulps is problematic since refining creates a significant amount of additional specific surface area altering the dry total unbonded area. This prevents the use of refining as a bonding inducer. It has also been shown that bonding in mechanical pulps cannot be significantly increased with the wet pressing procedure that is applicable for chemical pulps (Lehtonen 2004).

Kallmes, Bernier and Perez presented a theory of the load-elongation of paper a few years before Page. Later, the theory was improved and evaluated using data from Seth and Page with reasonably good results (Kallmes et al. 1977).

Shallhorn and Karnis presented semi-quantitative models for tensile and tear strength of paper in 1979. Their theory considers paper as a continuum. According to the derived equations based on the science of composite structure, tensile strength first increases linearly with increasing fibre length (l) and bond shear strength (τ). When bonding of fibres to the fibre matrix becomes so strong that some fibres rather break than are withdrawn intact, the behaviour turns nonlinear. Shallhorn and Karnis claimed that the Page equation (Eq. 12) is adequate for chemical pulps but not for mechanical pulps because it does not include the concept of the critical shear strength which defines the transition from the linear regime to the nonlinear one. According to them, the majority of mechanical pulps fail in shear linearly, that is, the tensile strength is limited by fibre bonds rather than fibre strength. Tear strength is initially proportional to the square of fibre length but above the critical value of the shear strength τ_c fibres begin to break rather than be withdrawn intact and tear strength starts to decrease inversely proportional to fibre length and τ^2. The sharp turn after exceeding the critical τ, is based on the assumption that breaking a fibre in tension consumes negligible work compared to withdrawing a fibre.

When the tensile and tear equations of Shallhorn and Karnis are combined, tear strength can be expressed in the following way (for $\tau<\tau_c$)

$$W = \frac{l \cdot T}{6} \tag{13}$$

where W is tear strength, l is fibre length and T is tensile strength.

For $\tau > \tau_c$, it becomes

$$W = \frac{l \cdot T}{3} \cdot (1 - \frac{T}{T_0})^2 \qquad (14)$$

where W, l and T are as above and $T_0 = N\pi r^2\sigma$ (N is number of fibres per unit sectional area of the crack, r is fibre radius and σ is fibre tensile strength) (Shallhorn 1994).

Retulainen (1996) modified the models so that the basic fibre properties (different term than used in Chapter 2.2) could be used (fibre strength, fibre length, fibre coarseness, fibre width, specific bond strength and relative bonded area). Generally, there are more parameters available to affect tensile strength than tear strength (or fracture toughness). Increasing fibre length, fibre width, specific bond strength and relative bonded area improve tensile strength and increasing coarseness decrease it. Fibre strength begins to increase tensile strength only at a high RBA. Only fibre strength and fibre length can affect the tear strength at a given tensile strength (Retulainen 1996).

Seth and Page (1988) have emphasized the importance of fibre strength for tear strength. Using a method where fibres were weakened with vapour of concentrated hydrochloric acid they showed that the tear strength of well-bonded long fibre chemical pulp sheets is proportional to the square of fibre strength. In a poorly bonded sheet tear strength depends more strongly on fibre length. They made tests also with TMP and observed a nearly proportional dependence of the tear index on the fibre strength determined with zero-span. Later, Page and MacLeod (1992) reported that at a given tensile strength, the tear strength of well-bonded softwood kraft handsheets is proportional to the fibre strength raised to a power between 2.5 and 3.0. This would mean that a 10 % loss in fibre strength could lead to a 25-30% loss in tear strength. This result agrees well with the Shallhorn-Karnis for tear strength of well-bonded sheets. The four-ply Elmendorf tear test may be more sensitive to the fibre strength than other tests with different loading modes. If the tearing mode in practise is not the out-of-plane one, as in the Elmendorf tear test, it may overemphasize the importance of the fibre strength.

Carlsson and Lindström (2005) have derived equations for tensile index based on the shear-lag theory (Cox 1952). A central concept in the shear-lag theory is the transfer of load into the fibre from the surrounding matrix in a composite material. Axial stress is transferred to fibre by shear stresses, as illustrated in Fig. 2-4. Because shear stress is assumed to be constant along the fibre length, axial stress builds up linearly, Figure 2-5.

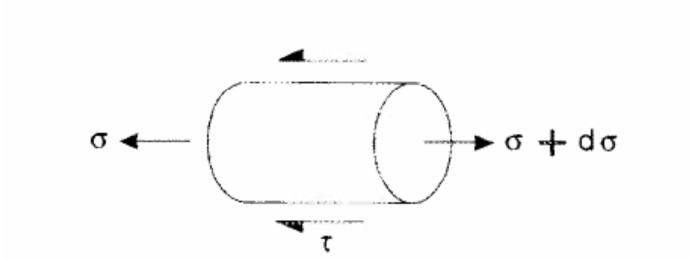


Figure 2-4. Element of a circular cross-section fibre showing axial stress build up through shear at the fibre/matrix interface. (Carlsson and Lindström 2005).

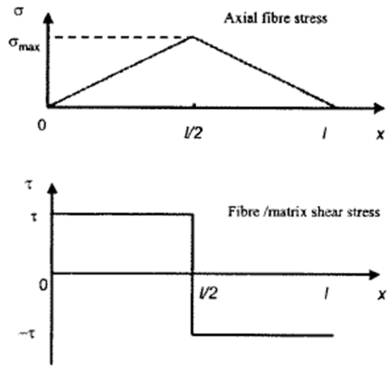


Figure 2-5. Axial and shear stress diagrams for short fibre (Westerlind et al. 2007).

What happens to a fibre under tension, whether it is extracted intact from the matrix or whether it breaks, depends on the fibre length, fibre strength and how it is bonded to the matrix. The model of Carlsson and Lindström fits relatively well to the experimental material of other researchers. The prediction using the developed model requires seven parameters: the fibre strength (σ_b), shear strength of the fibre-fibre bonds (τ_b), density of cellulose (ρ_c), fibre cross-sectional area (A_c), fibre length (l), perimeter (p) and RBA.

According to de Ruvo et al. (1986) the theories of Page and Kallmes-Perez and the shear-lag theory have many similarities. The differences between the three tensile models are small and generally unimportant and arise from slightly different views on how fibre strength and bond strength balance each other in a sheet during straining. The equations can be used for a qualitative evaluation of the importance of some intrinsic fibre and sheet properties on the tensile strength of paper.

The use of the Kallmes-Perez (sometimes called Kallmes-Bernier-Perez) and Page equations and the equations derived from the shear-lag theory require analyses that are not made routinely or are other ways difficult to make. Therefore, Westerlind et al. (2007) made an attempt to replace some of the needed information (like RBA, bond strength) with information that can be retrieved from standard tests (fibre dimensions from a commercial optical fibre analyzer, Z-strength, zero-span tensile strength, water retention value). Both models predicted the tensile strength of various chemical and mechanical pulps fairly well when proper fitting parameters were used.

The theories discussed above are based on the assumption that the fibres are similar. It is clear that that assumption is not valid when normal paper raw materials are in question. Kärenlampi (1995a, 1995b) has developed a strength theory that takes the distributions of fibre properties into consideration. Based on simulated results, an increasing variation of fibre properties considerably decreases tensile strength.

Fracture toughness was introduced to the paper industry from other industries in 1970's (Seth and Page 1975) with the hope that it would become a more useful and fundamental pulp and paper strength characteristic than e.g. the Elmendorf tear strength. The terminology is diverse: the term fracture resistance was used by Seth and Page (1975) and Shallhor (1994), 'tenacity' was introduced by Swinehart and Broek (1995), 'fracture toughness' was used by Seth (1996) and 'fracture energy' by Tryding and Gustafsson (2000) just to mention a few examples. The listed terms do not mean exactly the same thing. However, in all cases, the question is about the sheet's ability to resist propagation of a pre-existing flaw or crack, or like Mäkelä (2002) puts it, the capability of the material to sustain locally high stresses, usually referred to as the fracture toughness. Several different fracture mechanics (a discipline that studies the strength of structures containing defects) approaches to determine the fracture toughness have been applied to paper (Mäkelä 2002).

In the experimental part of this research, the terminology is adopted from Hiltunen (2003) and Niskanen et al. (2005). Fracture toughness, a material property, is denoted by K_c. According to the linear elastic fracture mechanics

$$K_C = \sqrt{G_C \cdot E} \tag{15}$$

where G_C is fracture energy and E elastic modulus (tensile stiffness index). In the experimental part, G_C is determined with the Lorentzen-Wettre device for fracture toughness following the SCAN standard for fracture toughness (SCAN-P 77:95). Actually, the device and the standard give the fracture energy based on the J-integral approach.

Naturally, researchers tried to clarify the fibre characteristics that contribute to the fracture toughness. Shallhorn (1994) proposed that the Shallhorn-Karnis model for tear can be applied also for the fracture toughness. For the determination of the fracture toughness (fracture resistance) he used the method presented by Seth and Page (1975). Retulainen (1996), who slightly modified the Shallhorn-Karnis models, stated that at a given tensile strength only fibre strength and fibre length can affect the tear strength or the fracture toughness. The fracture toughness maximum occurs at high tensile strength values.

Niskanen et al. (2005) modified the basic equation of the linear elastic mechanics to the following form:

$$T = \frac{1}{\beta}\sqrt{\frac{GE}{2\pi w_d}} \tag{16}$$

where T = tensile index
G = fracture energy index
E = tensile stiffness index
w_d= damage width
β = a geometry factor of defect and sample dimensions

According to Eq. 16, tensile strength is favoured by a narrow damage width w_d and through that affected by fibre length. However, since damage width is often in a linear relationship with fracture energy, the effect is counteracted. By making several assumptions on the elasticity and sheet structure, Niskanen et al. (2005) transformed Eq. 16 to the following form:

$$T = \sqrt{\frac{2 \cdot E \cdot W_z \cdot w_{fibre}}{\pi^2 \cdot t_{sheet} \cdot t_{fibre}} \cdot (\frac{1}{\rho_{sheet}} - \frac{1}{\rho_{fibre}})} \quad (17)$$

where E = tensile stiffness index
W_z= Scott bond
w_{fibre}= fibre width
t_{sheet} = sheet thickness
t_{fibre} = fibre thickness
ρ_{sheet}=sheet density
ρ_{fibre}=fibre density (=1500 kg/m³).

The fibre parameters in Eq. 17 should be determined from the dry paper because the papermaking process influences them. Eq. 17 suggests that increasing bonding (Scott bond) increases the tensile strength, just like the Page equation does. Wide and flat fibres increase strength but a thick sheet has an inverse effect. Fibre length does not have a role in the suggested model. The model agreed well with many, but not all data sets that were available for the authors. They stated that the z-directional strength obviously does not capture all the aspects of interfibre bonding that have a contribution to in-plane tensile strength.

An interesting point is that by rearranging Eq. 16, replacing w_d by fibre length l_l (Kettunen et al. 2000) and combining constants, the fracture energy can be expressed in the following way:

$$G = \alpha \cdot \frac{T^2}{E} \cdot l_l \quad (18)$$

where α is a geometry factor and l_l is length weighted average fibre length and the rest of the symbols are as in Eq. 16. Thus, strongly simplified, the fracture energy depends on two terms, bonding and fibre length. If one goes even further with the interpretation and assumes fibre length to represent tear strength, fracture energy depends on the product of tensile and tear strength, which in fact is often used by papermakers to characterize the overall strength of pulp. It is clear that the applicability of Eq. 18 is limited. When the bonding degree of the sheet is decreased, the critical fibre length of fibres is exceeded and the fibre strength begins to restrict the development of fracture energy as shown by Shallhorn and Karnis (1979). Above the critical fibre length, a fibre is anchored to the matrix so strongly that it rather breaks than pulls out intact. The fracture

energy increases with increasing fibre strength. On the other hand, fracture energy decreases greatly with only a small increase in fibre failure probability caused by decreased fibre strength (Kärenlampi and Yu 1997).

Seth (1996) has reported based on two experimental data sets of kraft pulps that the in-plane fracture toughness F (measured using the essential work of ductile fracture method) of chemical pulp depends on tensile strength and extensibility (stretch at break):

$$F = a \cdot T^{b} \cdot S^{c} \tag{19}$$

where T is tensile strength, S is stretch at break and a, b and c are parameters. Parameter a had values 1.07 and 0.60, parameter b 0.63 and 0.74 and parameter c 0.52 and 0.58 depending on the data set. Both the fracture toughness and tear strength were shown to be linearly dependent on the zero-span tensile strength. This result was achieved with sheets where the fibre strength was decreased by exposing the sheets to vapours of concentrated hydrochloric acid. Kärenlampi and Yu (1997) used to same method with similar results like referred above.

Kettunen (2000) studied the fracture process of paper using a combination of an in-plane tear test and a silicon impregnation technique for damage analysis. Fracture energy increased linearly with damage width and fibre length. However, when the damage width was increased with badly bonding fibres, the fracture energy decreased in spite of the larger fracture process zone. He observed also that increased number of fibre failures decreased the fracture energy.

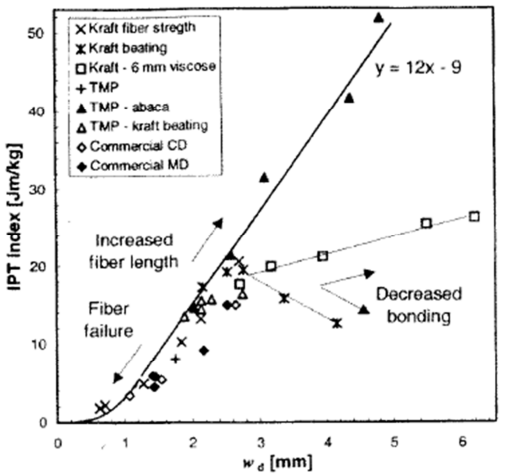


Figure 2-6. In-plane tear index vs. damage width. (Kettunen 2000).

The test points in Fig. 2-6 represent papers (handsheets) that are reasonably well bonded. An interesting point in Kettunen's work is that he can show a connection between fibre length and fibre strength, and fracture energy.

2.5 Stress strain behaviour of paper sheet

The fundamental mechanical properties of material are its elastic modulus, tensile strength, extensibility and fracture toughness (Seth 1996). Thus, it is natural that the tensile test of paper has a central role when characterizing it. The stress-strain curve gives a lot of information about paper. Its interpretation is one of the basic challenges when studying the strength of paper.

Based on the shear-lag model presented by Cox (1952), Page and Seth (1980) derived an equation (Eq.20) for the elastic modulus of paper. The authors discussed the matter in more detail in (Seth and Page 1983).

$$E_p = \frac{1}{3} E_f \left(1 - \frac{w}{l_a \cdot RBA} \sqrt{\frac{E_f}{2G_f}} \right) \tag{20}$$

where E_p = elastic modulus of paper
E_f = axial elastic modulus of the component fibres
w = mean fibre width
l_a = the arithmetic mean fibre length
RBA= the relative bonded area of the sheet
G_f = the shear modulus of the component fibres for shear in the (l_a,w) plane.

The factor in brackets in Eq. 20 describes the stress distribution between the fibres. When fibres are long, flexible and well-bonded, the factor approaches 1, i.e. in an extreme case, the elastic modulus of paper is dependent on the elastic modulus of fibres only. Alava and Niskanen (2008) advised caution with the microscopic interpretation of Eq. 20 as the elastic modulus of ordinary handsheets has been shown to be almost independent of fibre length referring to Kimura and Uchimura (1995). These researchers cut a pulp mat of bleached softwood kraft pulp into different lengths such that they got pulps with fibre lengths of 0.95 to 2.55 mm. The fibre length did not have any effect on the Young's modulus (elastic modulus) when the handsheet density was varied between 400 and 900 kg/m³. Instead, fibre length had a considerable effect on the tensile index.

There are a few theories about what happens in the plastic region. Earlier authors claimed that a disruption of fibre bonds takes place. Later, the opinion that the non-linearity and visco-elasticity arises largely from fibres has gained general acceptance. Bond breakage has only a modest impact on the stress-strain curve by reducing the value of the efficiency factor during straining (Seth and Page 1983, Kärenlampi and Niskanen 1998). I'Anson et al. (2008) suggested that bond failure has little influence in higher density (around 1000 kg/m³) sheets, but is significant at lower densities (700 kg/m³). They also confirmed the results of previous researchers that the tensile index and the specific elastic modulus increase with increasing grammage. According to them, tensile index depends upon two competing effects. On one hand, strength increases at low grammages due to increased efficiency of stress transfer as the fraction of the fibre length in the sheet surface decreases with grammage (fibres in the surface contribute less to the network strength than fibres that are below the surface).

On the other hand, strength decreases as the likelihood of weak spots increases with grammage. However, in well bonded sheets the dependence disappears.

2.6 Pulp mixtures

2.6.1 Network theories

Most of the strength models that have been described in Chapter 2.4 are created for ideal fibres that are from the same origin and have similar physical properties. In practice, paper is most often made of pulp mixtures and even if not so, single pulps consist of very heterogeneous fibres. Therefore, it is no wonder that many researchers have studied the interactions between different fibres and fibre types. The question is about the roles of different fibre types. As mentioned in the introduction of the present study, often in pulp mixtures consisting of mechanical and chemical pulps, the former form the bulk of the paper and gives the desired surface and optical properties to the paper and the latter ones give strength.

Mechanical and chemical pulp fibres behave differently in a fibre network. Mohlin and Wennberg (1983) got results based on which they stated that mechanical and chemical pulps in the furnish act as though they formed two almost independent networks due to imperfect fibre bonding between the two types of fibres. They observed that adding chemical pulp with different mechanical pulps resulted in lower bonding related strength properties than could be assumed based on linear additive mixing rules. Instead, wet web tensile strength and tear strength were better in pulp mixtures than assumed. It was assumed that the reason for poor bonding between mechanical and chemical pulp fibres is because of their different behaviours during drying. Chemical pulp fibres have a bigger tendency to shrink and twist during drying which leads to high stress at the contact points between the two fibre types, and consequently weaker bonding.

The theory of Mohlin and Wennberg has been criticized by other researchers so that it cannot be regarded as a consistent theory today (e.g. Alava and Niskanen 1997, Retulainen 1997, Honkasalo 2004). Retulainen (1997) came to the conclusion that the question is about different activation of the fibres. During the sheet consolidation mechanical pulp fibres do not shrink enough to activate chemical pulp fibres. Mechanical pulp fibres are relatively stiff and straight and are immediately loaded when paper is stretched. Retulainen (1997) suggested that the activity of the chemical pulp fibres could be increased by using a pulp which has a smaller fracture elongation and fewer microcompressions and kinks in the fibres. He also suggested that the swelling ability and extensional behaviour of mechanical pulp fibres should be made more like those of the chemical pulp. This would make the different fibre types more compatible. The uniform distribution of fines in all bonds tends to smear out the bonding differences that pure pulps would have (Alava and Niskanen 1997).

Percolation theory was used by Ritala (1987) and Ritala and Huiku (1989) to explain the role of chemical reinforcement pulp in pulp mixtures. Ritala (1987)

suggested that length-to-coarseness ratio should be considered as a pricing basis for reinforcement pulp. This is because slender fibres percolate at a lower grammage, i.e. less pulp is needed to reach the percolation threshold. It can be expressed as a critical grammage m_c (Alava and Niskanen 1997):

$$m_c = 5.71 \cdot C / l \tag{21}$$

where C is fibre coarseness and l is average fibre length. At the percolation threshold where a continuous network starts to form, on the average, there are 2.7 bonds per fibre. Application of elastic modulus simulations suggests that a change in the mechanical properties of paper happens at 2-4 times the percolation threshold. Based on this, the cross-over in mechanical properties should occur at about 10 bonds per a reinforcement fibre. Using Equation 21 it can be calculated that the changes in mechanical properties should be detected at a reinforcement pulp grammage of about 3 g/m². The actual importance of the percolation threshold is not clear. Evidently the bonding properties of the reinforcement fibres have a major role. It may be that the mass fraction of reinforcement pulp necessary for the percolation effect is 30 % or even higher. Long, ductile and flexible fibres with many ductile bonds should enhance the fracture toughness of paper at all concentrations. The mechanical compatibility of the reinforcement pulp can be evaluated from the mechanical properties of paper measured at low reinforcement pulp contents (Alava and Niskanen 1997).

The existence of the percolation threshold would require that reinforcement fibres should bond essentially better to each other than to the bulk of fibres (mechanical pulp). If the bonding between reinforcement fibres and mechanical fibres is good, the remaining question is how well the mechanical pulp fibres transfer load, how strong and conformable are they, or briefly, how similar they are compared to reinforcement pulp fibres.

2.6.2 Reinforcing with chemical pulps

The question about an optimal reinforcement pulp has been a subject for many scientific papers. It is generally accepted that the fibres must be long, since increasing fibre length improves in-plane strength properties (tensile and tear). All the created models (Page, Niskanen, and many others) support this.

Also the number of fibres has been suggested to improve strength properties. It can be justified by the geometrical fact that two cylinders of equal size and a given length have 1.414 times larger mantle area than one cylinder with the same cross-sectional area and length. Thus, the higher number of fibres the larger available bonding area, and the higher paper strength. The maximum in theory then depends on the fibre strength. This thinking is in a good accordance with that of Page and of Shallhorn and Karnis. In practise, only few of the fibres that cross the crack path actually fail. In the majority of paper grades, macroscopic failure occurs when bonds between the fibres on the crack path break. Paper fracture is therefore a network process that is not governed by the fracture properties of individual fibres (Alava and Niskanen 2006). Fig. 2-7 (Retulainen 1997) illustrates that the percentage of broken fibres is very low (2 % for TMP fibres, 7% for chemical pulp fibres) in a slightly bonded network

consisting of TMP and kraft pulps (fines removed). When the bonding degree is increased with cationic starch and different fibre fines the percentage increases markedly. An interesting observation is that kraft pulp fibres tend to break more frequently than TMP fibres that are supposed to be much weaker. Probably, TMP fibres were not bonded to the network as tightly as the kraft pulp fibres and therefore their breakage was less frequent. The higher fibre length of the kraft fibres (which is likely although not reported by Retulainen) may have contributed to the bonding and to the result observed.

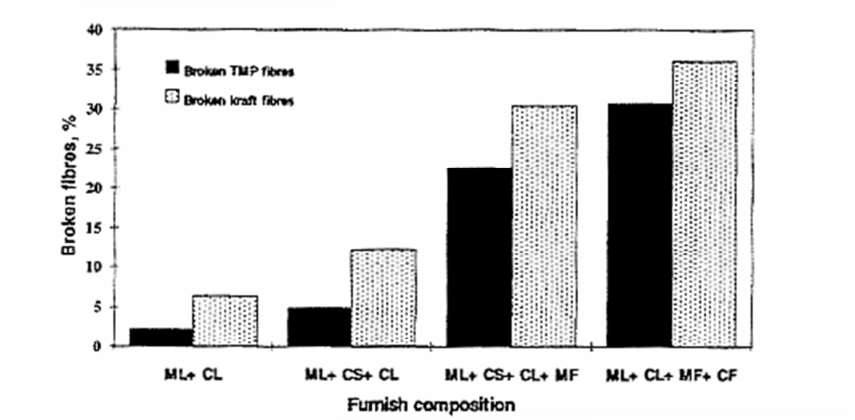


Figure 2-7. The percentage of kraft and TMP fibres broken in tensile rupture of handsheet. The fibre composition is in all cases 55% TMP fibres and 45% bleached kraft fibres. ML = TMP fibres, CL = kraft fibres, CS 1.2% cationic potato starch, MF 30% TMP fines, MF+CF = mixture of 20% TMP fines and 10% fines of bleached kraft pulp. (Retulainen 1997).

The percentage of broken fibres depends very much on the fibre type and the degree of the bonding of the paper in question. Based on Helle's results (Helle 1963) virtually all sulphate fibres are pulled out intact when the tensile test is made for a handsheet from unbeaten kraft pulp. When the pulp is refined to 24°SR, two thirds of fibres are intact. In the case of acid sulphite pulp, 62% of fibres are intact when the pulp is unrefined. At 24°SR, only 8% of fibres are intact anymore. Out-of-plane tear rupture is more violent to single fibres than tensile rupture, and as a result, the number of intact fibres is lower. Helle did not analyse the pulps for their single fibre strength but is clear that the sulphite pulp had much weaker fibres than the sulphate pulp.

Page (1994) has suggested that the energy of tear failure derives principally from the energy release when fibres fail, rather than when fibres pull out. This suggestion contradicts the idea that the tear index decreases with increased bonding because fibre failure requires much less energy than fibre pull-out. Page explains that energy is stored in the failing fibre and the zone surrounding it. In a well-bonded sheet the tear strength is proportional to the square of fibre strength. The drop in tear strength with increasing bonding arises from the smaller fibre span and smaller rupture zone. The increase of tear strength with increasing fibre length is explained to arise from the increasing rupture zone. This observation is analogous with the results of Kettunen (2000) in which

fracture toughness was found to be dependent on the damage width, that is, the size of the fracture process zone.

Levlin (1990) has suggested that the ratio between fibre length and fibre coarseness is a good indicator of the reinforcement ability of softwood chemical pulp in a SC paper furnish where the share of chemical pulp is relatively low. The suggestion was based on the idea that the number of fibres is essential for the reinforcement ability. When the share of the chemical pulp is higher like in a LWC paper furnish, the fibre strength becomes also important and the reinforcement is expected to correlate with the tear strength at a given tensile strength times the ratio between fibre length and fibre coarseness.

According to Ebeling (1997) the tear index of a weakly bonded chemical pulp sheet is proportional to the fibre length to the power of 1.5 - 2. The reinforcement potential (which is a combination of tear strength at a given tensile strength, fibre coarseness and fibre length) of chemical pulp is related to the power 2.5 - 3 of the average fibre length. Ebeling's suggestion is based on an empirical equation of the reinforcing potential and the results of Page and McLeod (1992) and Seth and Page (1988).

2.6.3 Reinforcing ability of mechanical pulp fibres

The term 'reinforcement ability' is usually, if not always, connected to chemical pulps in the literature. Very few researchers have actually considered the possibility to utilize mechanical pulp fibres as reinforcement pulp. However, mechanical pulp can be thought as a two-compound pulp that contains both the compound that gives the desired printing quality to the paper and another compound that gives the required strength.

In the early 1980's after the modern CTMP process was launched, one of the ideas to utilize the potential of new pulp was to use it as a replacement for chemical pulp (Atack et al. 1980). Strong chemimechanical pulp made with a modification of the CTMP process, the OPCO process, was tested in Finland as reinforcement pulp for supercalendered paper. It was possible to replace all low yield chemical pulp with the OPCO pulp. In spite of a relatively high amount of OPCO pulp in the furnish, the CD tear strength was some 15% lower than reference. However, the runnability at the paper machine (speed 800-838 m/min) and in pressroom was good (Barnet and Vihmari 1983). Later, OPCO pulp was produced and used in Canada (Evans 1985). The OPCO process never became a real success probably because it did not offer any real advantage in newsprint production where the need of reinforcement pulp disappeared when TMP quality rapidly improved, the use of GW in newsprint stopped and the relatively strong RCF gained more and more foothold.

Winberg et al. (1990) made a practically oriented study on the sulphonation of TMP screen rejects. Sulphonation improved fibre flexibility, increased density and the tensile index of rejects considerably. This would basically enable a 10 units reduction of chemical reinforcement pulp in the furnish, if tensile strength was the criteria. However, since sulphonation decreased the tear strength somewhat, the authors did not give any clear answer about the savings potential.

The conclusions were similar to those of Nurminen and Sundholm (1995), who reported that the improved tensile strength induced by the sulphonation of TMP rejects would indicate 10 - 20 % savings of reinforcement pulp if the lower tear strength is accepted.

Mixing long fibre TMP into a furnish containing short fibre groundwood pulp can be regarded as an attempt to reinforce it. Honkasalo (2004) carried out an extensive study of the possible synergistic effects of TMP in SC and LWC furnishes. He observed that the different pulp mixtures showed synergy in tear strength if the pulp component had their bonding degrees on the opposite sides of their tear strength maximum (cf. the tear strength models in Shallhorn and Karnis 1979). The synergy in strength properties is particularly sensitive to the bonding degree and fibre length in paper. To achieve synergy in SC paper containing a mixture of GW and TMP, TMP should have well-bonding and flexible fibres with a high WRV. In LWC paper furnishes with low filler content no synergistic effects were found.

The long fibres of TMP are known to be relatively poor bonding (Jackson and Williams 1979). Law et al. (2009) made an attempt to improve bonding by oxidising TMP long fibres using a reaction system that converts the primary alcohol on cellulose into carboxylic acid. The treatment did increase tensile strength of the long fibres but almost halved tear strength. The unsurprising result was that the best tear strength for a pulp mixture was achieved with untreated long fibres and the best tensile strength with the oxidized fibres.

Since long fibres of TMP can be harmful for the surface smoothness of paper, Reme et al. (1998) suggested that one should make longitudinal splits into coarse fibres so as to improve the smoothness and simultaneously maintain the length.

2.6.4 Activation

The term (fibre segment) activation is used to describe the phenomenon of modification of originally kinky, curly or otherwise deformed fibre segments into active, load-bearing components of the network. When a fibre network dries, lateral shrinkage of the fibres is transformed into axial shrinkage of the neighbouring fibres in the bonded areas. By restraining the shrinkage the slackness of the segments is removed and both the segments and bonded areas are capable of bearing load (Vainio et al. 2006). In Fig. 2-8, activation is illustrated schematically.

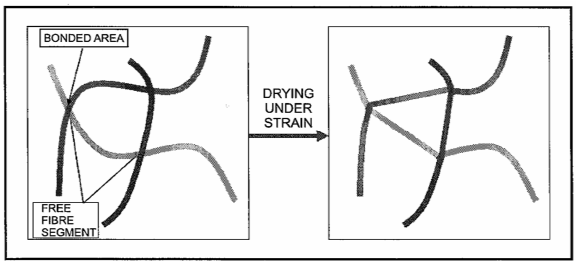


Fig. 2-8. Schematic illustration of activation (Vainio et al. 2006)

Tensile stiffness can be used as an indicator of the level of activation. Elastic breaking strain (tensile index divided by tensile stiffness index) is considered to depend on inter-fibre bonding. Fracture energy divided by damage width can also be used as a bonding indicator (an indicator of the shear strength of inter-fibre bonds) (Hiltunen 2003, Vainio 2007). Tensile stiffness (elastic modulus) has an important practical meaning because it controls the behaviour of paper. For example, it determines how web tension depends on the speed difference in open draws in printing presses and other web-fed end-use processes (Alava and Niskanen 2008).

Although the drying strategy has a significant effect on activation, fibre properties are also important. In TMP sheets, the overall extent of activation is rather small, and in kraft pulp and TMP mixture sheets, the properties of kraft fibres seem to govern activation. In TMP fibres the slackness of free segments is probably much less pronounced, since they are generally stiff and have low conformability and poor swelling ability. Due to the high activation potential of kraft pulp containing sheets, their tensile stiffness can be significantly improved by restrained drying (Vainio 2007).

Vainio (2007) proposed that TMP fines have a significant effect on the activation of mechanical pulp fibre network. She hypothesizes that fines are situated near the corners of the bonded areas rather than inside the bonding between two fibres. In this way, the effective length of the free, unbonded fibre segments shortens making them easier to activate. Because fines also have a greater shrinkage potential, they increase the stress caused by shrinking bonded areas which is then transmitted to the axis of fibres, pulling the free segments straight.

Pulkkinen et al. (2010) have developed an activation parameter based on the fibre wall thickness distribution, fibre curl distribution, and WRV of the unrefined fibres. Their results with eucalyptus kraft are in agreement with Vainio's results with TMP in that fines are a major contributor to fibre network activation.

2.6.5 Coarseness of different fibres

The coarseness of mechanical pulp fibres is sometimes erroneously thought to be double compared to chemical pulp fibres due to the much higher yield of mechanical pulp. However, as Karnis (1994) has shown, refining decreases the coarseness of mechanical pulp fibres drastically so that at high energy inputs the level of chemical pulp is reached, Fig. 2-9. Vehniäinen (2008) has reported about similar results. In her study, the coarseness of the TMP long fibre fraction after the 2nd stage was 0.259 mg/m. After two-stage rejects refining the coarseness was 0.218 mg/m. The drop in coarseness of mechanical pulp is due to peeling off of the outer fibre layers.

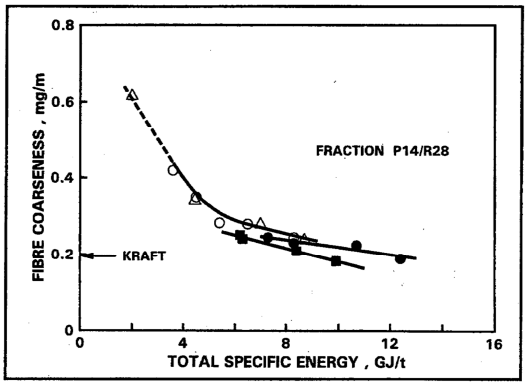


Figure 2-9. The coarseness of the long fibre fraction of different RMP's (open circles and triangles) and TMP's (closed circles and triangles) as a function of refining energy. The coarseness of a low-yield kraft pulp shown by the arrow (Karnis 1994).

Varying opinions about the importance and impact of coarseness on the sheet strength exist. According to Ebeling (1997), low coarseness is advantageous for the reinforcement potential of kraft pulp fibres partially due to the high number of low-coarseness fibres. The tear strength of moderately refined kraft pulps with coarseness varying from ca. 0.2 mg/m to 0.3 mg/m was reported to be about constant. Clark (1985) has presented an empirical formula according to which tear strength is proportional to the zero-span tensile strength and to fibre length to the power of 1.5, and that it is inversely proportional to the square root of fibre coarseness. This result agrees somewhat with the results that Seth and Page (1988) gained for weakly bonded sheets with respect to dependence on fibre length and strength but contradicts with the effect of coarseness. According to Seth and Page, coarser fibres give higher tear strength at a similar fibre length and strength at any given degree of bonding. Probably these conditions are so strict that they are not always prevailing and consequently, the results and conclusions on the effect of coarseness vary.

Based on the strength models presented in Chapter 2.4, high coarseness has a negative impact on tensile strength (Page 1969 and Retulainen 1996). According to the modified Shallhorn-Karnis -model derived by Retulainen (1996), increasing coarseness decreases tear strength when the sheet is not well bonded but increases that of well-bonded sheets. This result gives another explanation why the conceptions of the effect of coarseness are vague.

2.6.6 Bonding of fibres

Analyzing fibre bond strength has been the object of many scientific papers. Retulainen and Ebeling (1993) evaluated different indirect ways to evaluate bonding strength. They got contradictory results with different methods. The main error source was the measurement of the bonded area of fibres. Other sources were the measurement principle of the strength measurement and the mode of loading. They reminded that the fibre bond is a three dimensional anisotropic structure and that its strength cannot be measured unambiguously. The bond strength should be measured only in relation to a definite loading

mode. One of the methods that Retulainen and Ebeling tested was the utilization of the Page equation (Eq. 12), which is a popular manner to do it. Görres et al. (1995) calculated the shear bond strength of various pulps using a modified Page equation where the bonded area was calculated from the fibre dimensions. They reported that the shear bond strength of TMP and CTMP fibres was lower than kraft, whereas that of CMP was clearly higher than that of kraft pulp, Table 2-2. Differing wood raw materials do not allow a conclusive comparison. However, it seems that the bond strength of kraft pulp is of the same magnitude than that of mechanical or chemimechanical pulps.

Table 2-2. Comparison of shear bond strength of TMP and kraft pulp. Data from Görres et al. (1995).

Pulp	Wood species	Shear bond strength, dynes/cm^2*10^7
TMP	Spruce, balsam fir	3.1
TMP	Southern pine	2.3
CTMP	Hembal	1.5
CMP	Spruce, balsam fir	6.2
Kraft	Black spruce	3.8

Bonding of papermaking fibres is often explained to be due to hydrogen bonds that are created between fibre surfaces when the paper sheet is dried. However, this explanation probably gives a too simplified picture of the matter. Given that fibre surfaces are not smooth and the length of the hydrogen bonds is small (0.27 nm, Ojala 1999) compared to the roughness and to the dimensions of a pulp fibre and surface microfibrils, it is not self-evident that fibres can bond to each other immediately through hydrogen bonds.

According to Linhart (2006), the strength of paper is principally the result of the physical entanglement of fibres and that the formation of hydrogen bonds between individual fibres does not play a substantial role. Hydrogen bonds have a very important role in determining paper strength, but it is the hydrogen bonds between the cellulose molecules, in the crystalline and amorphous regions in the interior of the fibres and fibrils, that are mainly responsible for the effect. When fibres and fibrils are swollen in a wet stage, they loosen and become flexible and the paper loses its strength.

Retulainen (1997) listed prevailing theories of adhesion between polymeric materials:

1. Mechanical interlock theory
2. Adsorption theory
3. Chemical bonding theory
4. Electric theory
5. Acid-base theory
6. Diffusion theory
7. Weak boundary layer theory.

Thus, Linhart's opinion and the opposite opinion that hydrogen bonds are in charge of fibre bonding, represent only two possible options from a variety of options. It is likely that in reality fibre bonding is contributed simultaneously by

several factors and the importance of different factors varies depending on the pulp type and even from bond to bond. Consequently, it is evident that bonding of chemical and mechanical pulp fibres is different in many respects due to the different nature of the pulps. Chemical pulp fibres are more flexible and more conformable and can wrap and conform around each other and also around mechanical pulp fibres better than mechanical pulp fibres. The particle size distribution of different pulp types is very much different. Mechanical pulps contain less intact fibres but much more fibre fragments and fines than chemical pulps and there are also differences in chemical and physical properties of those two pulp types. All these factors are likely to have an impact on the mechanisms that dominate in the bonds.

Moss and Retulainen (1995) have shown that the tensile index and Z-directional tensile strength of handsheets made of TMP long fibres (+30-mesh) are vastly improved when either TMP or kraft pulp fines are added to long fibres. Without fines, a long fibre handsheet is very weak (tensile index 9.2 Nm/g). With TMP fines it increased to 35.5 Nm/g and with kraft fines to 66.1 Nm/g. Contrary to the TMP long fibres, the tensile strength of handsheets made of kraft pulp long fibres is relatively high even without fines. Retulainen et al. (1993) reported that the tensile index of the +20-mesh fraction of a slightly beaten bleached pine kraft pulp was about 46 Nm/g. Adding 15% of kraft fines almost doubled the strength. With mechanical pulp fines fractionated from a low-freeness TMP the increase was less dramatic. Based on these examples, the relative importance of fines is bigger for the strength of TMP than that of kraft pulp.

The ability of chemical pulp fines to enhance bonding is assumed to be due their fibrillar nature. Mechanical pulp fines contain lots of flake like fines that improve light scattering but not strength (Luukko and Paulapuro 1999). Görres et al. (1996) proposed that mechanical pulp fines can have three different effects on the thickness of a sheet: bridging, blocking and filling. In the case of bridging, fines particles facilitate bond formation between fibres by forming a bridge between two fibres that would not come into contact without the fine particle. Bridge forming increases the density of the structure. Blocking does not mean that fines would reduce bond formation. Instead, a fibre bond is formed like in bridging. The difference lies in that in blocking the bond would have formed even without the fines particle. The result is that the sheet remains less dense. In the third case, filling, fines just fill the voids without affecting bonding or sheet thickness.

Chemical pulp fines are suggested predominantly to strengthen by covering fibre surfaces and filling the peripherical regions at fibre crossing points, whereas mechanical pulp fines strengthen by forming discrete interfibre bridges. Chemical pulp fines have a very strong tendency to enhance Campbell's forces and form tight and dense structures. Mechanical pulp fines do not enhance Campbell's forces as much as chemical pulp fines and favour looser structures (Retulainen 1997, Moss and Retulainen 1995). Toven et al. (2008) have reported that MFC (microfibrillar cellulose) made from bleached kraft pulp enhanced fracture properties of SC paper (MFC was used to simulate kraft pulp fines). They concluded similarly to Moss and Retulainen that MFC increases the bonded area between the fibre components and thus makes reinforcement more capable to prevent crack growth.

Vainio (2007) observed that TMP fines have a significant effect on the activation (evaluated by tensile stiffness) of mechanical pulp fibre network. Based on experimental work, she suggested that fines are located near the corners of the bonded areas rather than inside the bonding zone between two fibres. The suggestion is analogous with the one presented for chemical pulp above. Vainio's suggestion differs somewhat from the bridging idea of Görres et al. (1996), but is not necessarily in contradiction with it, because one can say that fines facilitate bridge forming even though they were not located in the actual fibre contact area. Probably, fibrillar fines of mechanical pulp strengthen bonds as described by Vainio and the flake-like fines contribute more to bridge forming.

The appearance and physical and chemical structure of the fibre surface have a key role in fibre bonding. The nature of the fibrillation of chemical pulp is probably different than often thought. In beaten pulp fibres, the S1 layer is typically a loose, fibrillated sheath that covers the S2 layer and acts to enlarge the contact surface between fibres (Uesaka et al. 2002). At lower levels of beating, the P and S1 layers of the cell wall are fibrillated. With prolonged beating, fibrillation of the S2 layer will commence (Bergander 2001). Chhabra et al. (2005) have reported that there is a compliant fibrillar layer at the surface of chemical pulp. The layer comes thicker and softer with the degree of beating; beating partially peels off fibrils that extend up to 1 µm from the fibre surface. The importance of small scale external fibrillation is in agreement with the observations reported earlier by Nanko et al. (1989). Using TEM microscopy, they found a thick colloid layer at the contact zone of two beech BKP fibres. It is obvious that commercial fibre analyzers cannot detect fibrillation on this scale (cf. Fig. 2-2 in Chapter 2.2.2).

In mechanical pulping, when the target is to produce pulp with good bonding ability, exposing the S2 layer is one of the manners to enhance it. This is because S2 can swell more when exposed. In addition, fines formed from the S2 layer with the well oriented fibril structure are longer and better bonding than fines from the outer layers (Karnis 1994, Luukko 1999, Vehniäinen 2008).

Whether mechanical pulp fibres have a similar sheath as chemical pulp fibres is an interesting question. Tan and Li (2008) studied the adhesion forces on the fibre surfaces using an AFM probe covered with HPC (hydroxypropyl cellulose). They found that the adhesion force between HPC and unbeaten spruce BKP fibres was 33% higher than that of aspen CTMP fibres. The wide variation in the adhesion between single points was striking. In CTMP, a significant portion of the adhesion force values felled below 400 nN, whereas in kraft pulp virtually all points were above that limit. The scattering results were explained to be due to the uniformity of the fibre surface in terms of physical structure or topography that is quite heterogeneous in natural fibres, and the varying surface chemistry along the fibres. Some areas of the fibre surface are rich in lignin and some are relatively rich in carbohydrates. This is particularly true for the CTMP. In lignin rich areas adhesion is much weaker than in carbohydrate rich areas. Tan and Li concluded that interfibre bonding is mainly due to hydrogen bonding between fibre surfaces. Lignin, having much less hydroxyl groups than cellulose disturbs interfibre bonding. They also observed

that the adhesion force of the BKP extended much longer than that of the CTMP. From this they deduced that the compliant layer around the BKP fibres is thicker than around the CTMP fibres, that is, CTMP fibres have a thinner fibrillar sheath than BKP fibres.

The observation of Wågberg et al. (2002) that the interfibre bond strength can be increased by layering polymer-layers on the fibre surface is in accordance with the idea of the importance of a compliant layer on the fibre surface. The same statement applies to the results of Torgnysdotter and Wågberg (2004). They studied fibre bonding using regenerated cellulose fibres as model fibres. Fibre properties were altered by bulk and surface charge. They showed that the fibre surface softness is very important for the joint strength between fibres while the bulk-charge properties affect the wet fibre flexibility and through that, the possibility for fibres to form contact points in the sheets. Together these factors influence both the tensile strength and sheet density of the paper. One can speculate that the mechanical pulp fibre surface is harder than that of chemical pulps and therefore bonding is less effective.

The results that Thomson et al. (2008) achieved using FRET techniques (Fluorescence Resonance Transfer) confirm that interdiffusion of surface polymers have a marked role in inter-fibre bonding of lignocellulosic fibres. This result does not inevitably mean that hydrogen bonds would have no role. Probably, interdiffusion may be a necessary precondition for a strong bond.

In a literature review, Luukko (1998) summarized the differences and roles of chemical and mechanical pulp fines by stating that rough fibre fragments and pieces of fibres, appearing largely in mechanical pulp fines, fill voids and cavities and promote the structural integrity of the sheet, improving its smoothness and light scattering coefficient. Fibrillar and ribbon-like material, which are the main components in chemical pulp fines, improve sheet strength but reduce the light scattering coefficient. In his own research Luukko (1999) showed that mechanical pulp fines contain basically two different types of fines, namely fibrillar fines and non-fibrillar, flake-like fines, which behave in different ways in the network. Fibrillar fines behave similarly to chemical pulp fines by increasing bonding and decreasing light scattering, whereas non-fibrillar fines increase light scattering but give poor sheet strength.

The intrinsic ability of mechanical and chemical pulps to form fibre bonds is so good that the role of bonding chemicals is only complementary as far as normal printing and writing papers are concerned. The most commonly used strength additive in paper making is cationic starch (Linhart 2006). Recently, the use of CMC has been promoted (Duker and Lindström 2008).

Based on the discussion above, on a rough microscopic level (seen with standard light microscopy, SEM or comparable techniques), different bonding types may be classified in the following way:

1. Direct bonding between fibre surfaces
2. Bonding assisted by fibrils and lamella
3. Bonding assisted by fines material

Bonding types 1 and 3 are prevailing or more pronounced in the case of chemical pulp fibres and the types 2 and 3 are more typical to mechanical pulp fibres. When the question is about bonding between mechanical and chemical pulp fibres, all types of bonding come to question and it is hard to say, what type dominates.

Table 2-3. Comparison of bonding mechanisms of chemical and mechanical pulp fibres.

	Chemical pulp	**Mechanical pulp**
1. Direct bonding between fibre surfaces	Effective due to • a thick compliant layer • advantageous chemical structure (lignin removed) • homogeneous surface • flexible and conformable fibres	Less effective because of • a thin and patchy compliant layer • lignin rich areas (middle lamella, lignin not removed from any layer) • stiff and non-conformable fibres
2. Bonding assisted by fibrils and lamella (external fibrillation)	Effective • but important only in case beaten long enough	Effective • and important • long fibrils and lamellae bond well to adjacent fibres
3. Bonding assisted by fines	Effective due to • fibrillar fines that strengthen bonds and enlarge bond area	Effective • when there are fibrillar fines available that strengthen bonds and enlarge bond area • high fines content facilitates bonding by bridge forming and blocking

2.7 Runnability of paper

The nominal tension applied in pressrooms is typically much lower (0.2 - 0.6 kN/m) than the tensions applied in the pilot scale straining tests or the tensile strength of paper (Uesaka 2005). The tension on a paper machine is also low compared to the paper strength (Parola and Beletski 1999). Thus, a paper web should actually never break due to low average strength. Yet the runnability of paper during production and converting is still a topical question. Gregersen (2005) reminded that many causes of web breaks are quite trivial like paper rolls damaged during transport or handling, poor tape gluing etc. Even if all the possible were done to avoid such causes, web breaks would take place since there are always some damage and weaker spots in the paper webs.

Seth and Page (1975) described a method for the measurement of resistance of paper to failure in the tensile mode by propagation of a pre-existing flaw, that is, the fracture resistance. According to them, fracture resistance of paper is a unique material property which is well defined both experimentally and theoretically. They regarded it likely that the mode they used occurs during certain converting operations and particularly during the printing of a running paper web. They encouraged other researchers to examine whether the method was suitable for analyzing runnability problems.

The reason why researchers have been interested in launching new methods to describe the runnability of paper web is in that the ability of the traditional strength analyses to forecast runnability is not necessarily satisfactory. For example, Adams and Westlund (1982) found no direct correlation between commonly used strength properties (tensile, burst and tear strength) and the break frequency of newsprint rolls when testing with a runnability winder. According to Fellers et al. (2001), the information necessary to assess the influence of reinforcing pulps on the fracture properties of paper in a printing press application cannot be obtained from standard strength tests (tensile and tear strength). Instead, fracture mechanics must be applied.

Swinehart and Broek (1996) showed that fracture toughness can be used to predict coater runnability. They derived a web break model that included fracture toughness which was determined using a simple test procedure (Tenacity©). They observed that flaws in the web were more important than the web strength as such. Tensile strength and tenacity correlated well for paper grades made with the same paper machine.

Moilanen and Lindquist (1996) received indicative results showing that the fracture toughness index was a more plausible predictor of breaks in a rotogravure press than the hole index. The heterogeneous research material did not allow making a proper statistical analysis.

Not only average strength properties of web but the distribution of the properties is of interest for the pressroom runnability. Uesaka et al. (2001) made a wide survey covering 30 000 to 50 000 rolls run in different pressrooms. They observed that the tensile strength uniformity, as represented by the Weibull exponent, had the highest impact on the break frequency. Among the conventional paper properties, tensile strength and elastic stretch consistently predicted the break frequency. CD tear strength that is often used as a runnability indicator was shown not to be a controlling parameter of web breaks. The findings of Deng et al. (2007) were very similar to the ones of Uesaka et al. The strength uniformity of MD tensile was shown to be very important for the press-room runnability. The MD tensile strength was the strength property that was most consistently associated with the press-room runnability of newsprint. The CD tear strength predicted runnability only in few cases. Interestingly, the break statistics of the pressrooms showed that macroscopic defects were minor causes for web breaks. The majority of the breaks were press-related or unknown.

Realising that the conventional tests can only vaguely reflect the behaviour of the running web, the Finnish KCL developed a new pilot scale device, KCL AHMA (Niskanen et al. 2003). The tension of the web is increased by increasing the speed difference between the brake nip and the pulling nip, until the web breaks. The breaking tension and breaking strain are recorded. The KCL AHMA recovers automatically from web breaks within a few seconds and the break sequence immediately starts again. The sequence is typically repeated for 30 - 100 times which enables the collection of reliable probability distributions of the dynamic breaking strain and breaking tensions. The KCL AHMA is equipped with a device for making notches to the running paper web.

It makes it possible to study the effect of defects of different shapes, sizes and positions on the runnability of paper.

From above it is clear that all the web breaks cannot be avoided by increasing the strength of the web. However, high strength helps to keep the break frequency low. A question of its own is how to evaluate the web strength and relevant pulp strength properties.

2.8 Conclusions based on the literature

When thinking of the quality and applicability of a wood pulp for different end uses, the first question is how to characterize the pulp. The number of parameters should be as low as possible. A quantum-leap in pulp characterization was taken by Forgacs (1963) who suggested that pulp can characterized basically by two factors, one describing the particle size distribution and another one, specific surface, that indicates its bonding potential. Heikkurinen et al. (1991) discussed the basic fibre properties that should be independent of each other by definition. They proposed that the basic fibre properties are four: size distribution, shape, structure of cell wall and fibre surface. This division may not be perfectly sound. However, it offers a useful tool or check-list when considering how to characterize pulps comprehensively. Therefore it was taken for a basis also in this research.

The size distribution is probably best covered by various commercial analyzers (fibre length and fibre width and their distributions and some other fibre dimensions). The fibre shape is conceptually not as clear as the fibre size. However, some of its features, like fibrillation and curl can be analyzed using commercial analyzers. The structure of the cell wall cannot be analyzed unambiguously with any analyzer which is understandable since describing a complex microscopic structure with one or few parameters is not possible. In practice, the structure of the cell wall is described using indirect parameters, like fibre flexibility and water retention value (WRV). Fibre strength can be thought to be a parameter that is affected by the cell wall structure. The direct determination of the single fibre strength is tricky and therefore using the zero-span strength of a paper strip has gained popularity (Wathén 2006). Fibre damage as a term is not well-established. Since the fibre shape and the cell wall structure are included in it, it partly overlaps the basic fibre properties defined by Heikkurinen et al. (1991). Fibre damage is a very relevant term in this research because in mechanical pulping, fibres are treated very harshly and as a result they are more or less damaged.

The basic fibre properties are thought to be independent of each other, but it can be difficult to decide what matters belong under the term fibre surface and what to other properties like the cell wall structure or fibre shape. There are numerous analysis methods or techniques that can be used for the investigation of the fibre surface. Probably the most used techniques are SEM, XPS/ESCA and AFM. With these techniques it is possible to get a comprehensive picture of the appearance, topography and certain chemical characteristics of the fibre surface.

The ultrastructure of the cell wall has a decisive impact on the fibre and pulp properties. When manufacturing pulp using either chemical or mechanical processes the starting point is the same, a native wood fibre. However, these processes treat fibres very differently so that processed pulp fibres are different in many respects. Almost all the lignin is removed from chemical pulp fibres by cooking and the remaining is mostly cellulose. Mechanical pulp fibres contain virtually all the lignin of the native wood fibres. In addition, the lignin rich middle lamella is in the pulp in the form of fines or still attached to the fibres. The ultrastructure of chemical pulp fibres enables good bonding between fibres without major external fibrillation.

The relationship between fibre properties and paper properties has always been an interesting question to papermakers and several researchers have tried to build models or theories that would explain the connection between those properties. Page's equation for tensile strength (Page 1969) is undoubtedly the mostly frequently used and referred strength theory probably because it is understandable and because it has proved to be useful in many investigations. The models of Shallhorn and Karnis (1979) and those of Kallmes, Perez and Bernier (1977) are frequently referred in literature. From the newer models, the model for tensile strength of Niskanen et al. (2005) is interesting, since it connects fracture energy, tensile strength and the damage width. The latter one is related to fibre length and strength, and bonding.

The stress-strain curve is an important tool when investigating the properties of paper. When paper is stretched gradual bond breakage takes place. However, the contribution of single fibre properties becomes more important with increasing sheet density. High stretch at break has been reported to enhance fracture toughness. High elastic modulus (tensile stiffness index) is advantageous for the control of the paper web.

High fibre length and fibre strength are two very important properties for reinforcement fibres. It has been reported that the tear strength is proportional to the fibre length up to the power of 1.5 – 2 in the case of weakly bonded sheets. In well bonded sheets the dependence is lower. Similarly, the tear strength is found to be proportional to the fibre strength (zero-span tensile strength). With highly bonded sheets the dependence can be up to the power of 2.5 - 3. There are varying opinions about the effect of fibre coarseness. According to some researchers low coarseness is advantageous for the reinforcement ability since the number of reinforcing fibres is high, but there are also results in which coarser fibres give higher tear strength at a similar fibre length if the degree of bonding is comparable. Investigating the effect of fibre coarseness is difficult because it is often interrelated with fibre length and likely also with fibre strength. Obviously, the importance of the fibre coarseness depends on the paper grade, the level of bonding and the share of the reinforcement pulp in question.

The share of reinforcement fibres is usually minimized for economic reasons. This raises questions like what is the least possible share of reinforcement fibres and whether a percolation threshold, below which the reinforcement fibres do not contribute to the strength anymore, exists. It can be calculated that the mass fraction necessary for the percolation effect is 30% or higher. In practise wood

containing printing papers (SC, LWC) are manufactured below that value without problems. It is likely that good reinforcement fibres are useful at any concentrations. If there were a clear percolation effect at a certain concentration, the bonds between reinforcement fibres should be essentially stronger than those between reinforcement fibres and mechanical pulp fibres or the bonds between the mechanical pulp fibres. This seems not to be the case. Mechanical and chemical fibres can bond to each other and form a common network. Also mechanical pulp fibres are integrated to the matrix with the help of fines and fibrils. Consequently, the onset of direct contacts between the reinforcement fibres does not cause any sudden change in the network properties.

In the literature the term reinforcement pulp is always connected to chemical pulp. However, it has been long assumed that also the long fibre fraction of mechanical pulp has considerable reinforcement potential. In fact, refiner mechanical pulps are regarded as better than groundwood pulps because their long fibre content is much higher and they have better strength properties. Thus, the idea of mechanical reinforcement pulp is in a way built-in to the refiner mechanical pulps. There have been attempts to improve the properties of the mechanical pulp long fibre fraction by chemical means, mostly sulphonation. However, no such process has gained a wide acceptance.

The coarseness of mechanical pulp long fibres is typically higher than that of chemical pulp. This is often explained by the high yield of the mechanical pulp which means that only a little material is dissolved during their manufacture contrary to chemical pulping where roughly 50% of the wood is dissolved. This explanation is not fully consistent, since peeling off outer layers of mechanical pulp fibres is an essential feature of mechanical pulping and it is quite possible to reduce the coarseness of mechanical pulp fibres near the level of chemical pulp fibres by refining.

The fact that natural fibres that are used for papermaking are able to bond to each other without any additives or glue, is the basis of the whole papermaking, and bonding as such has a central role in the paper structure. The macroscopic bonding mechanisms of mechanical and chemical pulp fibres are somewhat different. The long fibre fraction of mechanical pulp separated from a normal mechanical pulp is not strongly bonded which shows as a low strength and high bulk whereas the long fibre fraction of chemical pulp can be relatively well-bonded. To form a strong network, mechanical pulp fibres need support and mediation from finer pulp fractions. In addition, extensive external fibrillation is needed. The fibre surface of chemical pulp fibres is more prone to direct fibre bonding due to its different chemistry and physical structure (low lignin content, loose surface structure).

The runnability of paper at different manufacturing and end-use stages depends on several factors. In addition to the average strength and other properties of the paper, many other factors like flaws (holes, cuts, creases, shives), bad profile, rolls being out-of-round, bad splices etc. have a major impact on the runnability. Moreover, variations in tension either induced by the paper or the manufacturing process can have a big influence on the runnability. Dry paper is so strong that it should never break due to the average tensions prevailing in the process chain. However, for the reasons listed above there are rare situations where the

endurance of the web is exceeded and it breaks. A logical conclusion is that to reduce web breaks, all kinds of variations and faults in the paper should be minimized. This does not mean that the average strength of paper would not be important at all. From the traditional strength measurements, the MD tensile strength is likely to be the most important one. During the last few decades, high hopes have been put on the fracture toughness and its usability in predicting paper runnability. Evidently, it is an important and useful measure of paper strength, but not an all-embracing solution for the runnability prediction. From other than strength properties, the importance of stretch has been brought out in the literature.

Runnability is naturally closely linked to the requirements for the reinforcement pulp; the main reason for the use of reinforcement pulp is to give strength to the paper web and ensure its runnability (low frequency of web breaks). Based on the literature, the important properties of reinforcement pulps are the following:

- high tensile strength
- high tensile stiffness
- high stretch at break
- high tear strength
- high fracture toughness
- high fibre length
- high fibre strength
- suitable coarseness

Z-strength is an important paper property in many applications, but it is not a primary target for the use of reinforcement pulp.

The four fundamental mechanical properties of a material are its elastic modulus, tensile strength, extensibility (stretch at break) and fracture toughness. The important properties of reinforcement pulp most often mentioned in the literature go well under those properties. Obviously, the relative importance of the different material properties of paper is different in different unit processes and loading situations. Instead of going for a detailed analysis, a more general approach was chosen in this research.

The importance of the tensile strength can be regarded more or less self-evident, but the importance of fracture toughness that describes the flaw carrying ability, is worth commenting. It is understandable that that type of property is important for any material. The difficult question is, however, how that property should be measured from paper in practise. In the literature, several ways to test it has been reported. In this research, fracture toughness (energy) has been tested using the SCAN method based on the J-integral. It is good to realize that the normal Elmendorf tear strength is also a measure of fracture energy. Thus, it belongs to the group of the basic material properties and thus, there is no principal reason to not use it.

3 EXPERIMENTAL

3.1 Experimental approach

The experiments were carried out in a traditional order; starting from the preliminary trials where the existence of the problem was demonstrated, then going on to sort out any possible fibre level reasons for the different performance, then moving on towards practical paper making by studying the problem with handsheets by simulating LWC paper and finally making LWC base paper on a pilot scale.

The basic idea was that the research environment should be relatively practical such that the results could be easily understood and that implementing them would be feasible. In spite of this, a certain amount of freedom was taken to avoid a too limited research view.

The experimental part consisted of three major trial series. Series I was a test series with laboratory handsheets applying standard pulp and paper tests, Series II contained a detailed study of fibre properties as well as their behaviour in pulp blends. The handsheets were made using a semiautomatic handsheet mould. Series III was a pilot scale study with four different pulp furnishes.

The results of the studies are reported in Papers I to V. In addition, some results, not published in those Papers, are reported in this summary.

3.2 Laboratory studies

The first laboratory series (Series I) confirmed doubts that the reinforcement ability of mechanical pulps fibres are not as good as that of chemical pulp, are well justified. Based on this, the decision to continue the research was made. (Paper I)

In Series II, the characterization and testing was done for single fibres and handsheets. The pulps were collected from full-scale processes. The results were used when choosing pulps and processes for the pilot studies (Series III).
(Papers II and III)

3.3 Pilot studies

It is widely realized that predicting paper runnability based on laboratory results is difficult. Therefore, research was done also on a pilot scale. In the first part, the aim was to produce mechanical reinforcement pulp (with or without chemicals) that would be as strong as possible and at the minimum, stronger than normal TMP rejects. In the second part, pilot paper was made from two different mechanical reinforcement pulps (in which one was sulphonated) which were compared with a reference paper with chemical pulp (NBSK) as a reinforcement pulp and with a paper with no reinforcement pulp at all. The

dynamic strength properties and runnability of the papers were tested using the KCL AHMA device. Since pilot studies are expensive and time consuming, it was not possible to test several different pulp or furnish options.
(Papers IV and V)

4 RESULTS

4.1 Laboratory studies

4.1.1 Appearance of the research problem (Paper I)

Chemical long fibre pulp, typically bleached softwood kraft pulp is used to increase pulp strength. Increasing the average fibre length of a pulp is known to increase tear strength and fracture toughness (e.g. Seth 1996). As shown by Page (1969), increasing the fibre length is beneficial for the tensile strength as well. Because the fibre properties are not necessarily independent of each other, the positive effect of the increased fibre length on the tensile strength may disappear if the fibre coarseness increases and bonding ability decreases simultaneously. Due to different manufacturing processes and fibre morphology, it is probable that it is not possible to achieve similar fibre characteristics for mechanical and chemical pulps. This means also that they have a different impact on the strength properties of a pulp furnish.

The effect of fibre length achieved with different fibres was demonstrated by adding different long fibres to a commercial TMP. The long fibres were extracted from a commercial softwood kraft pulp and the commercial TMP. Naturally, the longest fractions increased the fibre length most effectively (Fig. 4-1). The most important observation, however, was that mechanical pulp fibres had only a slight effect on the fracture energy. The 16-mesh fraction of TMP increased the average fibre length as effectively as kraft pulp, but its effect on the fracture energy was minimal. The effect on the tear index was quite similar with the fracture energy. The kraft pulp and its long fibre fractions increased the tear index whereas the mechanical pulp fractions only maintained it.

The different pulps and their long fibre fractions had a very different impact on internal bonding of the handsheets, Fig. 4-2. Adding well-bonding kraft pulp to the TMP increased the Scott bond of the sheets. The 30-mesh fraction of the kraft pulp increased also the Scott bond of the blend even though its Scott bond was somewhat lower than the original TMP. This was probably due to the increased density of the sheet. The effect of the 16-mesh fraction of the kraft pulp was not consistent but roughly speaking it did not affect the Scott bond of the blend. The mechanical pulp fractions had a very detrimental effect on internal bonding.

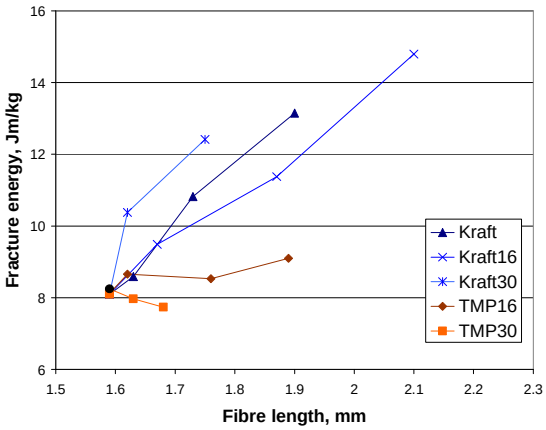


Figure 4-1. Fracture energy vs. weighted average fibre length of the TMP/fibre fraction blends. The added proportions were 5, 20 and 50 parts (the 30-mesh fraction of the kraft pulp at 20 parts is not included). Starting point: original TMP. Redrawn from Paper I.

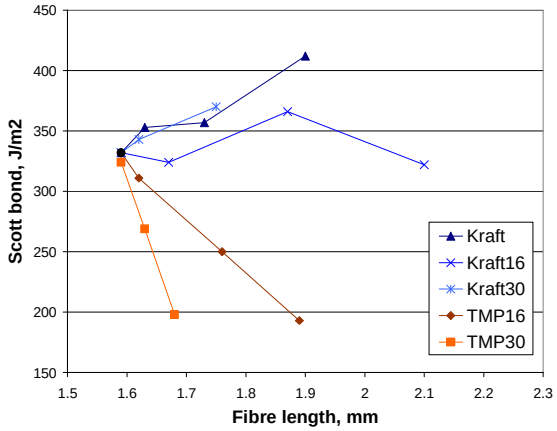


Figure 4-2. Scott bond vs. length weighted average fiber length of the TMP/fibre fraction blends. The added proportions were 5, 20 and 50 parts (the 30-mesh fraction of the kraft pulp at 20 parts is not included). Starting point: original TMP. Drawn from data presented in Paper I.

The effect of the long fibre addition on the tensile strength was fairly similar with the Scott bond. The kraft pulp and its fibre fractions increased it and mechanical fibres decreased it. The same applied for the sheet density. The kraft pulp and its long fibre fractions had a much higher breaking strain (3.2 - 3.9%) than the mechanical long fibre fractions (1.1 - 1.2%). This difference reflected also in the properties of the pulp blends. The blends with kraft pulp fibres had higher breaking strain than the blends containing mechanical long fibres.

The observations listed above revealed that adding mechanical pulp fibres to TMP did not improve any strength properties of the blend and that kraft pulp fibres were superior as reinforcement pulp in comparison to mechanical pulp fibres even at a given fibre length of the blend.

The finding that the long fibre fractions of kraft pulp had a breaking strain and tensile index several times higher than mechanical pulp and that they were able to simultaneously increase all strength properties, elongation and tensile stiffness were the most essential findings of this study, since they clearly lighten the target when trying to make long mechanical pulp fibres better than they are today.

4.1.2 Properties of long fibre fractions (Paper II)

The study reported in the previous chapter demonstrated that the long fibers of mechanical and chemical pulp do have different reinforcement abilities. However, individual fibre properties were not studied in detail. In the following stage of this research, the focus was on the properties of single fibres. Knowing the fibre properties was seen critical since otherwise the modification of mechanical fibres in a desired direction would be difficult.

The approach chosen was to study pulps sampled from existing mechanical pulp processes and ascertain whether better mechanical reinforcement fibres than those studied in the first part could be found and in which way mechanical pulp and chemical pulp fibres differ from each other.

The pulp selection contained two different groundwood pulps (GW and PGW) and five different TMP pulps from two European countries. One of the TMP's was so called RTS-TMP ('TMP5'). The pulps were tested following the idea of the basic fibre properties proposed by Heikkurinen et al. (1991). By definition, the basic fibre properties are independent of each other. They are not specific, measurable fibre properties as such. Instead, they can be characterized using a set of various test methods. E.g. 'size distribution' means the physical dimensions of fibres which can be described with several ways, e.g. with the average fibre length, fibre width, cell wall thickness and their distributions.

The average fibre length was analyzed using three different optical fibre analyzers. The comparison of the analyzers was not the main purpose of the study and therefore differences between them are commented only very briefly in this context. The long fibre fractions in Figures 4-3 - 4-7 are Bauer-McNett 30-mesh fractions from which shives have been removed using a Somerville apparatus (see Paper II).

The fibre length results obtained using the Fibermaster and MorFi correlated well (r=0.89) with each other whereas the correlation between the FS-200 and the other two was clearly lower (r=0.69 and r=0.66, respectively). Generally speaking, the kraft pulp fibres were longer than the mechanical pulp fibres and the groundwood fibres were shorter than the refiner pulps. It was expected that the MDF fibres would be long. However, only FS-200 confirmed this expectation but both Fibermaster and MorFi suggested that those fibres are short. The repeatability figures were not available, but based on the results using the kajaaniFiberLab analyzer by Metso (see Paper IV), the coefficient of variation is in the region of 1 to 2%. This translates to a 95% confidence interval of ±0.04 mm to 0.07 mm at the 2.5 mm average fibre length (n=2).

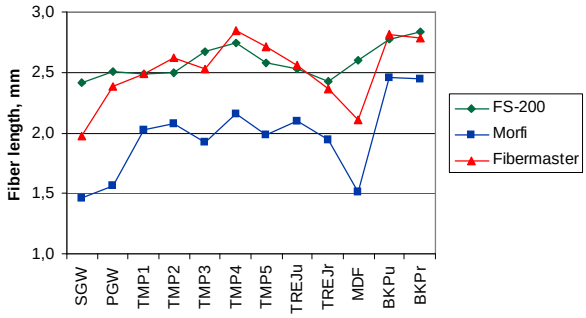


Figure 4-3. The length weighted average fibre length of the pulp fractions. SGW = Stone Groundwood, PGW = pressure groundwood, TMP1 - TMP5 = thermomechanical pulps from various production lines, TREu = unrefined TMP rejects, TREr = refined TMP rejects, MDF = medium density fibreboard, BKPu = unrefined bleached kraft pulp, BKPr = refined bleached kraft pulp. FS-200 = fibre analyzer by Metso, MorFi = fibre analyzer by Techpap, Fibermaster = fibre analyzer by L&W.

The pulps were analyzed also for the fibre width, cell wall thickness and fibre coarseness. Some differences between the pulps were found, but generally speaking, one can state that the chemical pulp long fibre fractions did not deviate strikingly from the mechanical pulps. The cell wall thickness results are illustrated in Fig. 4-4. For other properties, see Appendix A or Paper II.

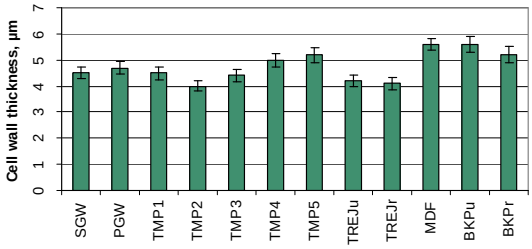


Figure 4-4. The cell wall thickness analyzed using light microscopy. Error bars indicate 95% confidence limits.

The kraft pulp fibres had somewhat thicker cell walls than the mechanical fibres on an average. This can be due to different raw material or due to swollen cell walls. The TMP rejects originated from the TMP2 line. Thus, their low cell wall thickness is well in line with the main line pulp.

The shape of the fibres was characterized by measuring the external fibrillation and curl and kinks. The chemical pulp fibre fractions were less fibrillated than the mechanical pulp fibres. The same result was achieved independently with two methods (light microscopy and the CyberSize analyzer by CyberMetrics).

When wetted, the flexible chemical pulp fibres took a more curled configuration than the stiff mechanical pulp fibres. When the analysis was done dry using the CyberSize, the result was opposite.

The structure of the wall was characterized using several methods, some of which were direct (like the WRV) and some indirect (like fibre stiffness). The

stiffness analysis using the Tam Doo & Kerekes method (Tam Doo and Kerekes 1982) showed that the MDF fibres are stiffer than normal mechanical pulp fibres. The chemical pulp fibres were not analyzed for stiffness with the TD&K method but the analyses done later (Paper IV) revealed that the stiffness of chemical pulp fibres is essentially lower than that of mechanical pulps. The flexibility analysis with the CyberFlex analyzer by CyberMetrics told the same story.

The analysis results of the fibre saturation point (FSP), freezing bound water (FBW) and the water retention value (WRV) correlated with each other. All these three gave higher values for the kraft pulp long fibres than for the mechanical ones indicating that the former ones are much more porous. The WRV of the mechanical pulp fibres was mostly 1.2 - 1.4 g/g whereas that of the kraft pulp was ca. 1.6 g/g.

The Simons' staining method was used for studying cell wall deformations, i.e. internal fibrillation. It correlated well with the three methods mentioned above and gave very consistent results, as Fig. 4-5 depicts.

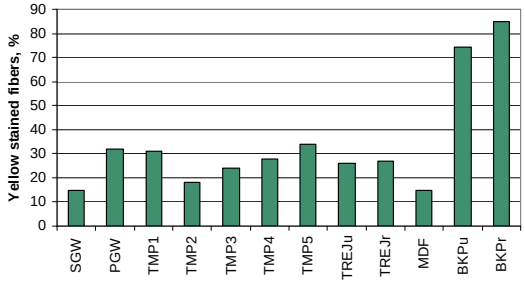


Figure 4-5. Internal fibrillation as indicated by Simons' staining.

Staining yellow means that relatively small molecules yellow in color have been able to intrude into the outer surface of fibres, that is, the fibre surface is porous. The kraft pulp fibres distinguish clearly from the rest. PGW fibres seemed to be more damaged than SGW fibres which is in agreement with the results of Tuovinen and Liimatainen (1993) who reported that the filtration resistance of PGW fibres is higher than SGW. The RTS fibres (TMP5) were stained yellow to a greater extent than the TMP4 manufactured from the same raw material. The MDF fibres had a closed surface just like the SGW. Mill beating of kraft pulp seemed to increase the share of the yellow stained fibres somewhat.

The relative bonded area (RBA) can be regarded as an indirect, non-specific measure of the cell wall structure, since it is influenced by several factors like internal fibrillation, swellability and flexibility together with the cross-dimensional area of the fibre. The RBA results were quite consistent with the yellow stained fibres and other properties correlating with it. The RBA of the kraft pulp long fibres was 45 - 50% whereas that of the mechanical pulp fibres was ca. 20%. However, PGW fibres had a RBA of almost 30% and refined TMP rejects 25%. The MDF was at 10% which shows its extremely limited conformability.

The zero-span tensile strength is another indirect measure of the cell wall structure. The mechanical pulp fibres were surprisingly similar excluding the MDF that had a markedly lower strength than the others. The chemical pulp fibres were roughly 50% stronger than the mechanical pulp fibres, Fig. 4-6

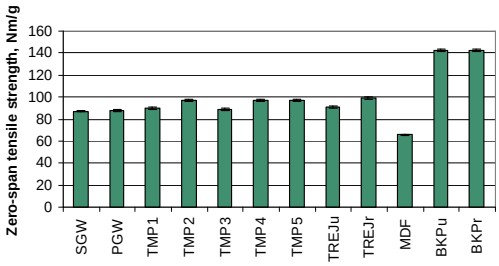


Figure 4-6. Zero-span tensile index for dry sheets. Error bars show 1.0% coefficient of variation (from ISO 15361).

The fibre surface was characterized using the ESCA (Electron Spectroscopy for Chemical Analysis). The ESCA results were translated into extractives and the lignin coverage of fibres. The lignin coverage results were very distinctive. The normal mechanical pulp fibres located at ca. 35% level, the MDF at 60% and the chemical pulp fibres at 10-13% level. The extractives coverage was not as clearly dependent on the pulp type as the lignin coverage, Fig. 4-7.

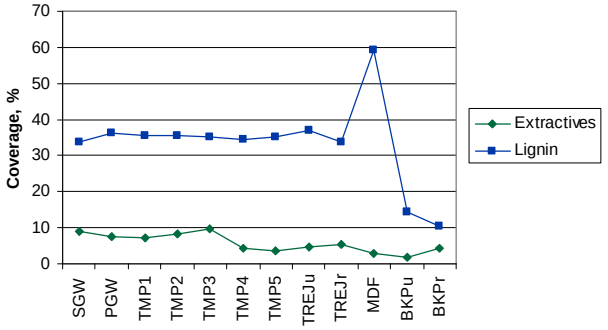


Figure 4-7. The extractives and lignin coverage of fibres as indicated by the ESCA analysis of handsheets.

This research implied that the essential differences between chemical and mechanical pulp fibres are not in their dimensions (size distribution) but in other basic properties (shape, cell wall structure and fibre surface).

4.1.3 Performance of different fibres in pulp blends (Paper III)

It is well known that many properties of pulp blends exhibit a non-linear behavior, in other words, they cannot be predicted based on linear mixing rules. Therefore, making pulp blends from a base TMP pulp and long fibres of different TMP and kraft pulps was seen as a sensible approach when studying the performance of the separated long fibre fractions. Simulating a LWC furnish

was chosen because LWC is the paper grade where the need to reduce the amount of chemical pulp is very topical. The same fibres (except the long fibre fraction of the refined kraft pulp) that were studied in detail in the previous part (Chapter 4.1.2) were mixed with a base TMP.

Figure 4-8 illustrates how reducing the amount of kraft pulp from 35% (basic reference level) gradually reduces the tensile index in a two-component blend (reference line REF). The change is not very big because the other component is a relatively strong TMP. When different long fibre fractions are used to compensate the decreasing share of kraft pulp, the tensile strength drops drastically, particularly when the component is poorly bonding, like MDF or SGW. The unrefined kraft fibres also deteriorated the bonding level of the sheet. The best long fibre component was the refined TMP rejects. However, even it reduced the tensile strength of the blend clearly.

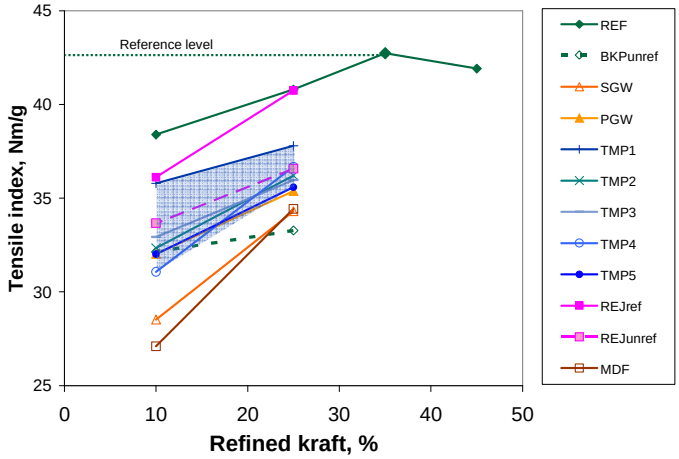


Figure 4-8. Tensile index as a function of refined kraft pulp percentage when kraft pulp is partially replaced with different long fibre fractions in a TMP/long fibre/kraft pulp blend. The dotted line represents the reference level with 35/65 kraft/TMP blend. The blue shaded area is cropped by different TMP long fibres. Redrawn from Paper III.

The mechanical long fibre fractions had a big effect on the sheet structure, as Fig. 4-9 illustrates. With them, the sheet density decreased drastically combined with decreasing Scott bond. Those fractions can be classified to the poorly bonding category B in Fig. 4-9. As for the tensile index, the biggest reduction took place with the GW and MDF fibres. The behavior of the refined TMP rejects differed from the other mechanical fibres, since it stayed quite close to the basic reference point at the 10% replacement ratio and it decreased the density and Scott bond less than the rest. This was a promising result because it indicated that by an adequate treatment the behavior of mechanical pulp could be brought to resemble chemical pulp. In this case, the rejects were just normal TMP rejects collected from a mill process. Plausibly, by a more careful treatment, the behavior could be brought even closer to chemical pulp. The behavior of the unrefined kraft pulp long fibre fraction resembled the refined TMP rejects. In Fig. 4-9, it is classified to category C (poorly bonding but flexible fibres) although its fibre characteristics are evidently quite different from the TMP rejects. When the percent chemical pulp in the furnish was

reduced (category A), the Scott bond increased even though the density decreased. Increasing the share of chemical pulp resulted in an opposite impact (category D). Because only one point represented the category D, the real direction could be somewhat different. It is likely that the real path should be more horizontal and heading to South East.

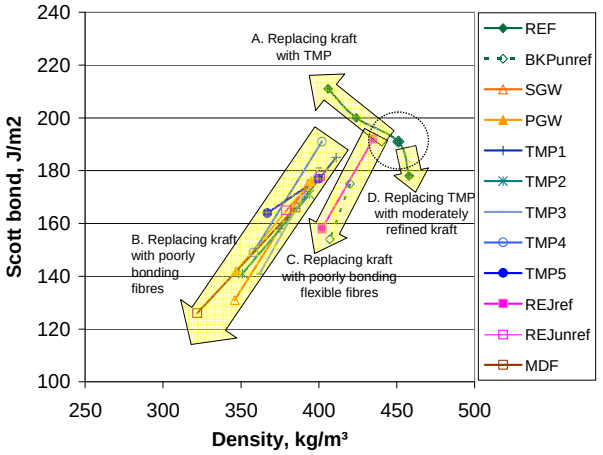


Figure 4-9. Scott bond vs. density with different pulp furnishes.

The added fractions had longer fibres than the TMP which was replaced with them. This explains why in most cases the long-fibre fractions gave a higher tear index than the reference series (Figure 4-10). However, this result is not satisfactory because the tear indices remained lower than the basic reference point with the equal total amount (35%) of reinforcing fibres. As an exception, the refined rejects gave a higher tear index for the pulp blend than the reference when only 10% of kraft pulp was replaced with it. However, at the 25% replacement rate, its performance was only mediocre; it was among the TMP long fibres. Instead, the unrefined kraft pulp long fibre fraction gave a very high tear index for the pulp blend. At the 25% replacement rate (=10/25/65 refined kraft/unrefined kraft/TMP; total chemical pulp 35%) it gave the same tear index as the refined kraft pulp at 10 points higher total kraft pulp share (45/55 refined kraft/TMP; total chemical pulp 45%). A noteworthy observation is that the tear index decreased with the mechanical long fibres in spite of the slightly increased fibre length of the blend (the average fibre length of the blends increased because all the long fibre fractions had somewhat higher fibre length than the refined kraft that they replaced). Thus, the average fibre length alone did not explain the tear strength of the pulp blend.

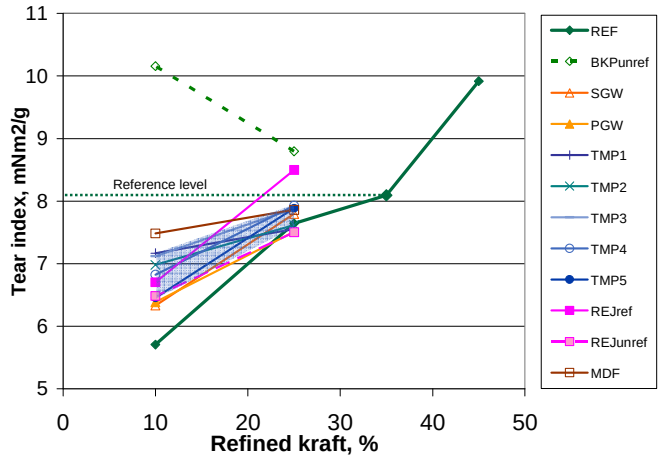


Figure 4-10. Tear index as a function of refined kraft pulp percentage when kraft pulp is replaced with different long fibre fractions. Uncalendered robot sheets, grammage ca. 38 g/m². The blue shaded area is cropped by different TMP long fibres. Redrawn from Paper III.

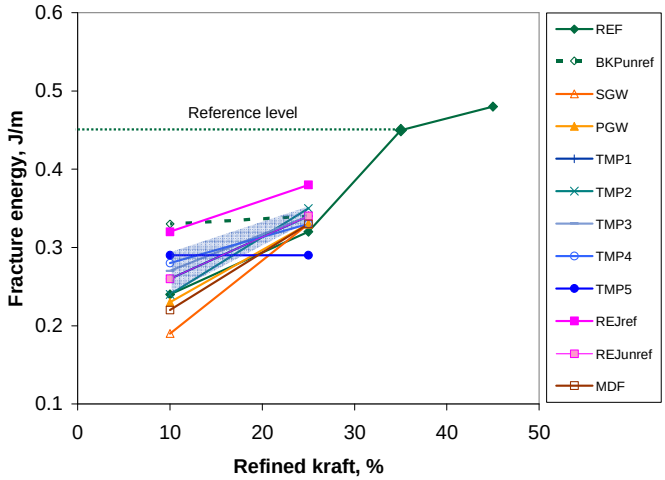


Figure 4-11. Fracture energy as a function of refined kraft pulp percentage when kraft pulp is replaced with different long fibre fractions. Uncalendered robot sheets, grammage ca. 38 g/m².The blue shaded area is cropped by different TMP long fibres. Redrawn from Paper III.

When the reinforcement ability was evaluated based on the fracture energy, the long fibre fractions performed even worse than for the tear, Fig. 4-11. The SGW, PGW and MDF fractions were below the reference curve with much lower average fibre length. The refined TMP reject performed quite well but the unrefined kraft long fibre fraction was surprisingly bad.

The graphs shown above clearly reveal how none of the mechanical pulp long fibre fractions actually reached the performance level of the chemical pulp in terms of reinforcement ability judged by the most common paper technical properties. The impact on the tensile strength was very detrimental so that if it

was the decisive criteria, it would be better not to use them at all. They gave a slightly better tear strength and fracture energy than TMP but compared to chemical pulp, they were inferior. The best from the mechanical pulps was the refined TMP rejects. From these results it was concluded that by developing mechanical fibres further by refining, and perhaps combining with chemical treatments, the reinforcement ability of mechanical long fibres could be brought to a reasonable level.

4.2 Pilot study (Papers IV and V)

The purpose of the pilot study was to test if the findings of the laboratory scale tests could be confirmed on a pilot scale. In addition, the tests with the AHMA device were thought to give conclusive results of the effect of mechanical pulp fibres on the runnability of LWC base paper.

4.2.1 Making test pulps and their properties

The reject pulp that was further processed in order to improve its reinforcement ability was unrefined spruce (Picea abies) TMP rejects from a Finnish paper mill with freeness of ca. 420 ml. The pulp was first refined in three stages at high consistency using a Sunds RG 32/36 atmospheric refiner. After refining, it was fractionated using a pressure screen in order to minimize the fines content and increase the average fibre length. After fractionation, it was processed in two alternative ways: a) by refining and b) by sulphonation followed by refining. The pulp from case 'a' was called MRP, Mechanical Reinforcement Pulp and the pulp from case 'b' CMRP, Chemimechanical Reinforcement Pulp. Sulphonation was carried out by spraying a sulphite solution on the pulp and then cooking it for 30 minutes at 150°C. The sulphite charge was 150 kg/t pulp. More details from the experiments are given in (Paper IV). The test procedure is depicted in Fig. 4-12.

The energy consumption for the MRP was a combined 2274 kWh/t pulp of which 1840 kWh/t was spent in the three-stage refining in the Metso pilot. The energy consumption for the CMRP was somewhat less, 1989 kWh/t pulp, since the energy consumption in the final refining stage was lower than in the case of the MRP. Normally, the energy consumption in the TMP rejects refining is 800 - 1000 kWh/t pulp. Thus, both trial pulps were manufactured very energy intensively. The properties of the trial pulps are shown in Appendix B and more detailed in Paper IV.

Although the MRP and CMRP were long-fibred, they did not reach the fibre length of the chemical pulp. However, in comparison with TMP, they had a much higher average fibre length and contained much more long fibre fractions. The sulphonation made the CMRP sheets denser than those of the MRP. This indicates enhanced fibre conformability for the CMRP fibres. The chemical pulp had much higher elongation (stretch at break) and strength properties than the rest of the pulps. The fibre strength evaluated with the zero-span tensile strength was also markedly higher than for the rest. The MRP and CMRP were better than the TMP in all other respects excluding the internal bond strength (Scott

bond). The sulphonation gave certain advantages for the CMRP in comparison with the MRP. It had a higher tensile strength, TEA and fracture energy index and also a higher zero-span tensile strength. The optical properties, the air permeance and the roughness were well in line with other properties and with the manufacturing processes of the pulps.

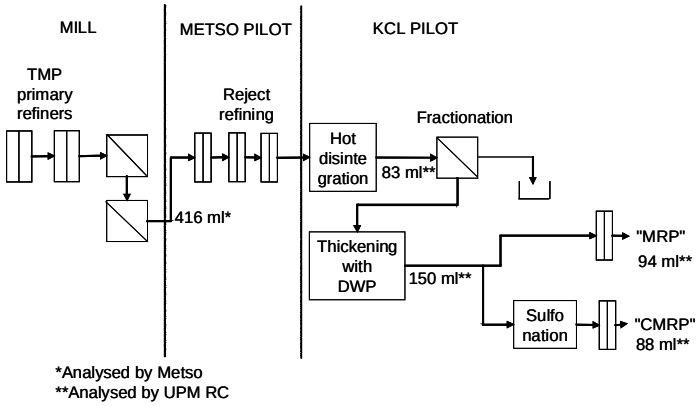


Figure 4-12. Flow sheet of the pilot test run.

The stress-strain curve of the different pulps revealed how the chemical pulp differed from the other pulps particularly in terms of the relative strain.

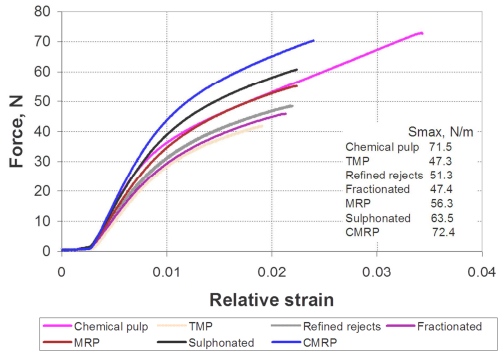


Figure 4-13. Force as a function of relative strain for various pulps. Paper strips were 100 mm in length, 15 mm in width and rate of elongation was 10 mm/min. Curves represent averages of 10 strips, end point is where the first strip breaks. Tensile stiffness (S_{max}) values are given in insert. Chemical pulp, TMP, MRP and CMRP are explained in the text. Refined rejects = rejects after the 3-stage refining, fractionated = rejects after fines removal and sulphonated = sulphonated rejects before final refining (cf. Fig. 4-12).

Additional refining alone increased the force needed to break the strip and the tensile stiffness. It also increased the relative strain somewhat. Sulphonation had a clear boosting effect on all properties. The breaking force of the CMRP was relatively near to that of the chemical pulp and it had a slightly higher tensile stiffness than the chemical pulp. Even though sulphonation improved the relative strain, the chemical pulp was far better in this respect.

The properties of the long fibre fractions were studied in more detail to find reasons for the different behaviour of the pulps. The pulps were fractionated with a Bauer-McNett classifier and the longest fractions; 16-mesh and 28-mesh fractions were combined to represent the long fibre fraction, Table 4-1.

Table 4-1. Properties of the long fibre fractions (16 and 28-mesh fractions combined) of the trial pulps. Handsheets were made without white water recirculation.

		Chemical pulp	LWC TMP	MRP	CMRP
Zero-span tensile strength					
Zero span, dry	Nm/g	157	98.0	95.0	96.7
Zero span, wet	Nm/g	143	85.9	84.3	90.2
WRV, stiffness and flexibility					
WRV	g/g	1.92	1.54	1.57	1.62
Stiffness TDK average	*10^-12 Nm²	1.28	30.4	60.1	22.2
Stiffness TDK median	*10^-12 Nm²	1.0	18.1	37.9	13.3
Flexibility TDK average	*10^12 1/Nm²	1.37	0.08	0.05	0.13
Flexibility TDK median	*10^12 1/Nm²	1.0	0.06	0.03	0.08
Handsheet properties					
Apparent density	kg/m³	654	322	311	474
Tensile index	Nm/g	56.8	15.0	17.7	37.5
Tear index	mNm²/g	21.4	7.0	8.5	9.5
Light scattering coefficient	m² /kg	20.7	29.1	26.5	21.8

The chemical pulp had a much higher fibre strength than the other pulps based on the zero-span tensile strength analysis. The differences between TMP, MRP and CMRP were relatively small. The ability to retain water was markedly higher for the chemical pulp than for the other pulps. The sulphonated CMRP could retain water somewhat more than the MRP or the TMP. The chemical pulp fibres were much more flexible, or less stiff, than the mechanical fibres. Sulphonation enhanced the flexibility effectively, however, CMRP was still more than 10 times stiffer than the chemical pulp. The fibre properties reflected in the apparent density of the handsheets as the chemical pulp with flexible fibres gave significantly denser sheets than the other pulps. Again, the flexibility enhanced by sulphonation contributed to the high density of the CMRP. The tensile index is directly proportional to the density. The tensile strength of the MRP long fibre fraction was slightly lower than what was reported for refined TMP rejects in Paper III. Thus, the MRP process was not quite able to develop long fibres to the desired extent.

The tear index of the chemical pulp was more than two times higher than that of the mechanical and chemimechanical reinforcement pulps. This can be explained by the lesser bonding and lower fibre length (not analyzed) but also with the fibre strength of the latter ones.

Although the tensile strength of the MRP long fibres was not as good as one might expect based on the refining energy used, the properties of the whole pulp (Appendix B) met the targets. It had a good tensile strength in spite of the low fines content, the average fibre length was much higher than normally in TMP rejects and it had a good tear index. The high tensile strength of it as a whole pulp must arise from the well-bonding medium and fines fraction rather than well-developed long fibres. The properties of the CMRP deviated even more

from normal TMP rejects. All in all, it was of interest to study whether these extraordinary mechanical pulps were able to replace chemical pulp as a reinforcement pulp. Because pilot tests are expensive and the amount of trial points must be kept at minimum, it was decided to replace chemical pulp totally with the MRP and CMRP without any intermediate points. This allowed seeing the maximum effect of these pulps.

4.2.2 Pilot papers

The pilot paper was manufactured with a slow, Fourdrinier type paper machine. The machine has been considered suitable for paper raw material comparisons. The reference point contained TMP as mechanical pulp and softwood kraft pulp as the reinforcement pulp, Table 4-2. This kind of furnish is typically used for a LWC base paper. In the proper trial points, the softwood kraft pulp was totally replaced with MRP or CMRP. In addition to these points, a fourth trial point, where reinforcement pulp was totally left out, was run.

The differences which were apparent for the single pulps (see Appendix B) were largely levelled off. This was simply because the main component in the paper was the same TMP and the reinforcement pulps were minor components. In addition, the mineral filler as a non-bonding component tends to smooth differences between the pulps. The CMRP gave an equal MD tensile strength to the paper as the chemical pulp even though its tensile index was 8% lower than the chemical pulp. The differences in the tear strength were significantly reduced. The same statement applied also for the TEA index. For the fracture energy, the chemical pulp was clearly the best. The TMP was fully comparable with the MRP and CMRP in the machine direction but in the cross direction it was weaker than the other two. The CMRP gave a slightly better tensile stiffness than the chemical pulp. The TMP paper had the lowest tensile stiffness which is in good agreement with its low tensile index. In brief, the paper properties were logical taking the properties of the pulp components into consideration. The only exception was the high tensile index of the CMRP paper as discussed above.

Table 4-2. Furnish composition (% of paper) of pilot papers. Filler: Intramax JR by Imerys. Kraft pulp: Mill refined NBSK from a Finnish pulp mill.

Test point	TMP	Kraft	MRP	CMRP	Filler
1 Reference	63	27	0	0	10
2 MRP	63	0	27	0	10
3 CMRP	63	0	0	27	10
4 TMP	90	0	0	0	10

The papers were tested using mostly ISO standard testing methods, see Paper V. The important paper technical properties are given in Table 4-3.

Table 4-3. Properties of pilot papers (laboratory analysis).

	Reference	MRP	CMRP	TMP
Grammage, g/m²	47.4	46.0	45.8	45.0
Bulk, cm^3/g	1.54	1.57	1.58	1.57
Tensile index MD, Nm/g	67.9	63.2	68.1	58.1
Tear index CD, mNm^2/g	7.8	5.9	5.4	5.2
Stretch at break MD, %	2.0	1.8	1.6	1.8
Stretch at break CD, %	2.4	2.2	2.1	2.0
TEA index MD, J/kg	922	724	697	664
TEA index CD, J/kg	399	345	364	304
Fracture energy MD, J/m	0.56	0.44	0.45	0.44
Fracture energy CD, J/m	0.39	0.31	0.32	0.26
Tensile stiffness index MD, kNm/g	7.5	7.1	7.8	6.5
Tensile stiffness index CD, kNm/g	2.6	2.4	2.7	2.3
Light scattering coeff. avg of TS and WS, m²/kg	49.5	49.8	46.2	53.9

In addition to the routine tests, the pilot papers were tested for the damage width and pull-out length using the siliconizing techniques presented by Kettunen and Niskanen (2000), Table 4-4. The damage width characterizes the extent of the fibre debonding from the crack line, i.e. the area where plastic deformation during the paper fracture occurs.

Table 4-4. Results of damage analysis of pilot papers.

	Reference	MRP	CMRP	TMP
Damage width MD, mm	2.27	1.94	2.00	1.73
Damage width CD, mm	2.00	1.54	1.63	1.39
Damage width (geom. mean), mm	2.13	1.73	1.81	1.55
Pull-out length MD, mm	1.23	1.03	1.02	0.96
Pull-out length CD, mm	1.07	0.88	0.86	0.80
Pull-out length (geom. mean), mm	1.15	0.95	0.94	0.88

The reference paper with the longest fibres had the highest values both for the damage width and the pull-out width. Correspondingly, the TMP paper with no added long fibres showed the lowest values.

4.2.3 Runnability with KCL AHMA

The strength of evidence of the standard strength tests to predict the paper runnability has often been questioned as discussed in Chapter 2.7. Therefore, a special testing environment, KCL AHMA, developed for the studying the runnability of running paper web (Niskanen et al. 2003), was used for the runnability evaluation.

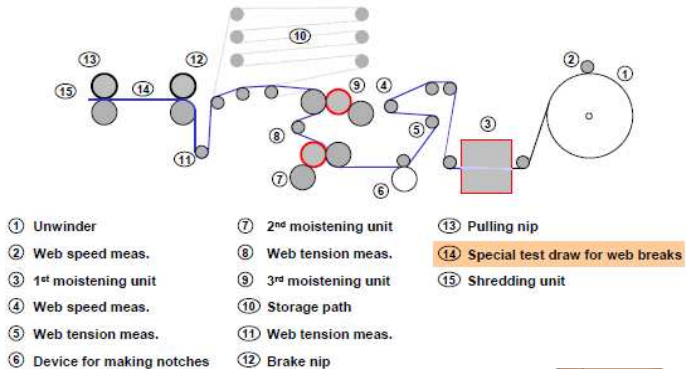


Figure 4-14. Main components of KCL AHMA. Unwinding tension T1 is measured at point 5, tension between moistening units T2 at point 8 and pre-tension T3 at point 11. Web speed refers to brake nip (12).

The most important part of the KCL AHMA device is the one-meter long test draw section from the break nip (part 12 in Fig. 4-14) to the pulling nip (13). When analyzing the paper strength, the tension of the web is increased by increasing the speed difference between the brake nip and the pulling nip, until the web breaks. The breaking tension and the breaking strain are recorded using a tension sensor integrated into the brake nip (12). The device recovers automatically and the break sequence immediately starts again. The sequence is typically repeated for 30 - 100 times. This enables the collection of reliable probability distributions of the dynamic breaking strain and breaking tensions. The web can be moistened by a water spray in a moistening unit (3) or by the roll application of water. In this study, the moistening was done by the roll application in the lower moistening unit (7). The amount of water applied was 3 g/m^2. After moistening, the moisture content of the paper web was approximately 10% which roughly corresponds to the moisture level in a 4-colour offset printing. Another interesting feature of the KCL AHMA is the possibility to make controlled defects to the web. In this study, cross-directional cuts 2 cm in length were made to the middle of the 25 cm wide web.

The straining speed on the KCL AHMA is much faster than in the standard tensile test. With the settings of this trial it was 252 mm/min versus the laboratory test's 20 mm/min. Another, even a more important one, dynamic feature is that the paper is drawn between nips instead of clamps. In an open draw, the major part of the strain occurs within a short distance immediately at the beginning of the open draw, i.e. the web speed increases very rapidly to the speed level of the drawing nip.

Wathén and Niskanen (2006) have applied Weibull statistics to the KCL AHMA results. A 2-parameter Weibull distribution is fitted to the break frequency distribution. By extrapolating the web tension (or strain) to a level where one break per 100 10 km-rolls can be expected, gives the threshold value. A 2-parameter Weibull distribution for the failure probability $W_2(\sigma)$ of a paper web at a given tension σ is expressed in the following way:

$$W_2(\sigma) = 1 - \exp - \left(\frac{\sigma}{\sigma_0} \right)^m \quad (22)$$

where m is the Weibull modulus and σ_0 is the scale parameter for the measurement geometry. The Weibull m modulus is a parameter that measures variability; high m means low variation and a narrow distribution and vice versa.

The results for the intact webs (the webs without intentionally made defects) were somewhat surprising (Tables 4-5 and 4-6). As could be assumed from the properties of the furnish components, the reference paper was the best paper in almost all respects both dry and wet. Instead, particularly the MRP showed surprising features. It had the lowest mean breaking strain and mean breaking tension values and very low threshold values for those properties. The results with the CMRP were also worse than expected.

Table 4-5. KCL AHMA test results of dry, intact webs.

	Breaking strain, %	95% conf. for strain	$\varepsilon_{1/100}$, %	Weibull m (for strain), %	Breaking tension mean, kN/m	95% conf. for tens.	$\sigma_{1/100}$, kN/m	Weibull m (for tension), kN/m	Elastic modulus, kN/m	No of breaks
Reference	1.30	0.01	0.77	23.59	3.31	0.02	2.41	44.03	331	84
MRP	0.99	0.03	0.28	7.47	2.59	0.05	0.85	12.25	305	103
CMRP	1.01	0.03	0.48	11.03	3.08	0.06	1.61	20.70	338	100
TMP	1.21	0.02	0.75	21.74	2.85	0.03	2.11	46.16	289	89

Table 4-6. KCL AHMA test results of wet, intact webs.

	Breaking strain, %	95% conf. for strain	$\varepsilon_{1/100}$,%	Weibull m (for strain), %	Breaking tension mean, kN/m	95% conf. for tens.	$\sigma_{1/100}$, kN/m	Weibull m (for tension), kN/m	Elastic modulus, kN/m	No of breaks
Reference	1.66	0.03	0.92	17.77	2.27	0.03	1.45	30.20	165	45
MRP	1.47	0.06	0.60	10.45	1.78	0.05	0.82	16.75	137	80
CMRP	1.39	0.05	0.64	16.18	2.10	0.04	1.12	21.03	176	79
TMP	1.57	0.02	0.86	18.57	1.80	0.02	1.09	26.63	128	64

$\varepsilon_{1/100}$ =threshold strain; one roll out of 100 rolls (10 km each) is predicted to break at this strain level

$\sigma_{1/100}$ =threshold tension; one roll out of 100 rolls (10 km each) is predicted to break at this tension level

It was striking that the Weibull m values for the breaking strain and tension were very low for the MRP paper and also for the CMRP paper. The low Weibull m values were caused by the wide distributions in the afore-mentioned properties. The possible causes for this observation will be discussed in Chapter 5.

The results for the defected webs were more logical than for the intact webs, Tables 4-7 and 4-8.

Table 4-7. Defect resistance, dry web.

	Breaking strain, %	95 % conf.	Breaking tension mean, kN/m	95 % conf.	No of breaks
Reference	0.46	0.01	1.38	0.03	32
MRP	0.40	0.01	1.22	0.02	33
CMRP	0.38	0.01	1.22	0.03	32
TMP	0.39	0.01	1.13	0.02	31

Table 4-8. Defect resistance, wet web.

	Breaking strain, %	95 % conf.	Breaking tension mean, kN/m	95 % conf.	No of breaks
Reference	0.85	0.01	1.13	0.03	34
MRP	0.84	0.07	1.05	0.05	23
CMRP	0.65	0.02	1.09	0.04	23
TMP	0.56	0.07	0.94	0.02	22

The reference paper with chemical pulp as reinforcement pulp performed best both dry and wet. The TMP paper that was better than the MRP and CMRP papers when the webs were intact was the worst when the webs were defected. It is evident that the defect, in this case a 2 cm CD cut, causes the break to initiate from the cut and not from a random weak spot in the paper web. This decreases markedly the effect of the obvious variability of the sheet structure and the effect of pulp and furnish properties become more pronounced.

Figures 4-15 and 4-16 summarize how the pulp properties reflected in the paper properties and how the pilot papers behaved in different papers.

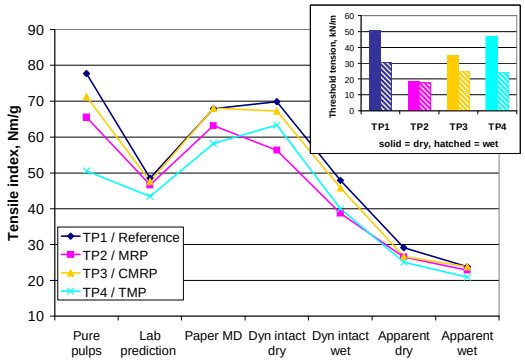


Figure 4-15. Tensile index in different stages. Lab prediction is based on nonlinear dependence of pulp components properties as shown by Mohlin and Ölander (1985). 'Paper MD' refers to laboratory analysis of pilot papers in machine direction. 'Dyn intact' and 'Apparent' refer to AHMA tests on intact and defected webs, respectively (Tables 4-5 – 4-8). Tension values from AHMA tests are converted to indexes. Threshold tension values for dry (solid bars) and wet (hatched bars) are shown in the inserted bar diagram. A typical mean web tension on a printing machine is up to 450 N/m which translates to 10 Nm/g if the basis weight is 45 g/m².

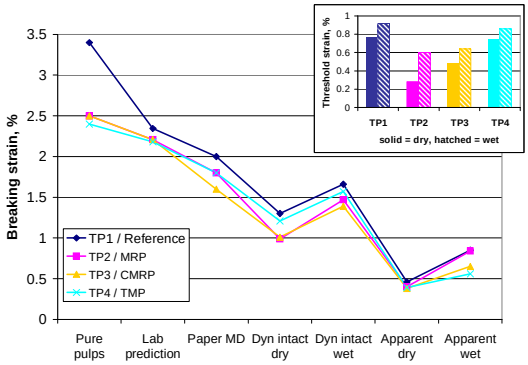


Figure 4-16. Breaking strain in different stages. Lab prediction based on a linear mixing rule of pulp components. Threshold strain values are shown in the inserted bar diagram for dry (solid bars) and wet (hatched bars) sheets. Abbreviations as in Fig. 4-15.

The predicted strength values for paper (Fig. 4-15) were much lower than the actual paper strength, since the prediction was for an isotropic sheet and the paper is measured in the MD direction in which case the anisotropy increases the tensile strength significantly. The dynamic tensile strength measured with the KCL AHMA was on average at the same level as the strength values measured from laboratory analysis. If the MRP paper had behaved like other papers, the situation would have been quite clear: the reference paper would have been best in all stages, the TMP paper the worst and the MRP and CMRP papers in between. It is worth noting how much the paper strength decreased due to wetting and defects. E.g. the wet apparent (=defected) strength (23.8 Nm/g) of the reference was only 21% of that of the dry, intact web (69.8 Nm/g). The results for the wet web with defects were very interesting since the MRP and CMRP papers reached the level of the reference paper. This indicates that the relative weakness of the MRP and CMRP fibres did not have such a role in the wet paper as in the dry, strongly bonded paper.

The breaking strain of the chemical pulp was much higher than that of the other pulps (Fig. 4-16). It gave the highest breaking strain also for the paper. However, the difference to the other options was not that great as for pure pulp.

5 DISCUSSION

5.1 Mechanical and chemical pulp fibres

The fact that chemical and mechanical pulps differ from each other in many ways is a well-known fact that can be regarded even as self-evident. The difference is partly explained by the different fibre distribution: chemical pulps have a much higher long fibre fraction than mechanical pulps made from the same raw material. The interesting question is how the long fibres of chemical and mechanical pulps differ. It is easy to find comments from literature saying that mechanical pulp fibres are rigid, stiff and coarse etc. but there is little comparable analysis data from those fibres. In Paper II, a variety of mechanical pulps and their long fibre fractions were compared with a normal chemical reinforcement pulp. Although the pulp samples were single, random ones and there was basically only one kraft pulp representing soft wood chemical pulps in the study, certain generalizations can be made. Naturally, this requires great care in the interpretations. The mechanical pulps originated from three European countries, six mill sites and 10 different production lines or processes. Thus, it can be expected that the results give a good picture of what kind properties a printing grade pulp can have. In addition, the MDF pulp gave an interesting additional spice to the investigation. The chemical pulp was maybe the weakest link in this part of the present study. This was indicated by the sometimes illogical results with the beaten and unbeaten pulps. Nevertheless, in Table 5-1 the mechanical and chemical pulp fibres are compared following the system by Heikkurinen et al. (1991).

The question of external fibrillation is interesting. The statement in Table 5-1 is based on two methods (light microscopy and the CyberSize analyzer). It is quite possible that other methods would give a different result. It is evident that the nature of fibrillation is different for different pulps. The fibrillation of chemical pulp is more fine-featured than that of mechanical pulp and therefore not so easily detected as the fibrillation of mechanical pulp fibres. The beating degree of reinforcement fibres for LWC paper is usually low, as it was also in this study, which explains the low fibrillation degree. Even though chemical pulp fibres were not externally heavily fibrillated, a much larger share (more than 75%) of them stained yellow with Simons' stain. This can be interpreted as an indication of an open and porous surface. It is a question of definition, if this kind of surface porosity is called either internal or external fibrillation (in this research Simons' staining was used as an indicator of internal fibrillation). Independent of the term, the structure and state of the outer fibre surface is known to be extremely important for fibre bonding.

Table 5-1. Comparison of mechanical and chemical pulp long fibres based on four basic fibre properties of the studied pulps.

Size distribution (dimensions)	• Chemical pulp fibres are somewhat longer. However, mechanical pulp fibres can in some cases reach the length of chemical pulp fibres. • Coarseness of mechanical pulp fibres can be lowered by refining so that it reaches the level of chemical pulp fibres. • The cell wall thickness (wet fibres) of chemical pulp fibres is equal or somewhat higher than that of mechanical pulps. This is probably due to swelling. => Mechanical and chemical pulp fibres can be surprisingly similar and cannot be distinguished based on size distribution properties unambiguously
Shape of fibres	• Chemical pulp fibres are externally less fibrillated • Chemical pulp fibres are more curly => Visual appearance of mechanical and chemical pulp fibres is different
Structure of cell wall	• Chemical pulp fibres are markedly more flexible • Chemical pulp fibres are more porous in wet state • There are more deformations in the outer layer of chemical pulp fibres • Chemical pulp fibres conform better (higher RBA) • Chemical pulp fibres are much stronger => Very essential differences
Fibre surface	• Lower lignin coverage for chemical pulp fibres • Extractives coverage is somewhat lower for chemical pulp fibres => Fibre surface (chemistry) is clearly different

Since the raw material was not the same for mechanical and chemical pulps, some uncertainty is involved in the properties where the difference is small.

The low zero-span tensile strength of the mechanical pulps was one of the key findings of this study. Conventional mechanical pulps were surprisingly similar. The dry zero-span tensile strength of their long-fibre fractions varied from 87 to 99 Nm/g. Chemical pulp fibres had a zero-span strength 40 - 60% higher than mechanical pulps. The MDF pulp was clearly weaker than other pulps. One can speculate whether the weakness arises only from the weak fibres or does the very low bonding have an impact on the result. According to Seth (2001), bonding has only a little effect on the zero-span tensile strength. However, MDF's bonding was so low that one cannot exclude the possibility that it had an effect on the result taking into consideration that MDF fibres were relatively straight and had fewer kinks than the rest. On the other hand, refining almost

doubled the tensile index of TMP rejects but increased the zero-span tensile only modestly. Similarly, refining increased the tensile strength of chemical pulp fibres by ca. 60% with almost no effect on the zero-span tensile. Based on these observations, the role of bonding is usually not big and its plausible positive effect does not change the overall picture.

The zero-span tensile strength is not a direct measure of the single fibre strength because it is measured from a paper strip 15 - 25 mm in width. The number of fibres bearing the load in the gap can in principal be calculated from the dimensions and grammage of the test piece, and on the average fibre length and coarseness of the fibres. Knowing the zero-span strength of the test strip, the strength of individual fibres can be calculated (Somboon and Paulapuro 2009, Perez and Kallmes 1965). The calculation of single fibre strengths from the data reported in Paper II revealed varying results depending on what fibre analyzer was used. E.g. using the coarseness values from the Fibermaster analyzer gave a very high strength value for the GW fibres whereas Morfi gave high values for the chemical pulp fibres. The latter result is obviously a more orthodox one and supported by the findings of Somboon and Paulapuro (2009). A successful application of the zero-span strength and fibre dimensions for calculating single fibre strength would require a big certainty of the constituent parameters. Otherwise, cumulating errors could lead to misleading results. Confirmation of any of the doubtful results was not possible in this research and therefore it was not seen fruitful to present and discuss the single fibre strength results in detail. Theoretically, the real single fibre strength would have been interesting. However, in practise, the zero-span tensile strength is also valuable, because it in a way combines both the quality and quantity and in the end, the collective strength of the fibres per unit weight, not the strength of single fibres, is decisive for the sheet strength.

5.2 TMP fibres' ability to reinforce

The high average fibre length is regarded as one of the biggest quality advantages of TMP. It is fascinating to speculate what if the fibre length was even higher. Would the advantages, mostly strength and runnability related, be even more pronounced? If so, would it be possible to develop the present TMP process to produce such a long fibre mechanical pulp that would enable a drastic reduction in the usage of chemical reinforcement pulp? In the first part of the present study (Paper I) this kind of situation was simulated by artificially increasing the average fibre length of TMP by adding long fibres that were fractionated from the same TMP to it. The test was analogous with so called blood doping where erythrocytes are transfused into an athlete's circulation in order to enhance his/her performance. For comparison, equal amounts of softwood chemical pulp (kraft pulp) or its long fibre fractions were added to TMP. This test gave interesting and clear results (see Fig. 4-1). The kraft pulp and its long fibre fractions increased both the average fibre length and the fracture energy of the handsheets. Instead, increasing the average fibre length of the TMP with its own fibres proved to be more or less useless in terms of the fracture energy. This simple comparison demonstrated that the quality of long fibres have a tremendous effect on the handsheet strength.

5.3 Effect of bonding

Kettunen (2000) has reported that adding long but poorly bonding viscose fibres to kraft pulp improves the IPT index of handsheets only slightly even though it increases the damage width (w_d) which is proportional to the average fibre length. Analogically, it can be hypothesized that maybe the poor performance of mechanical pulp fibres is due to their poor bonding ability. The bonding ability of the mechanical pulp fibres studied in the current research was essentially lower than that of the chemical pulp. The low bonding ability caused an immediate drop in the Scott bond when mechanical pulp fibres were added to the base TMP. The impact of mechanical pulp fibres was quite similar with the impact of the Kevlar fibre addition reported in Paper III. Fig. 5-1, which is compiled from data presented in Papers I and III, illustrates this observation.

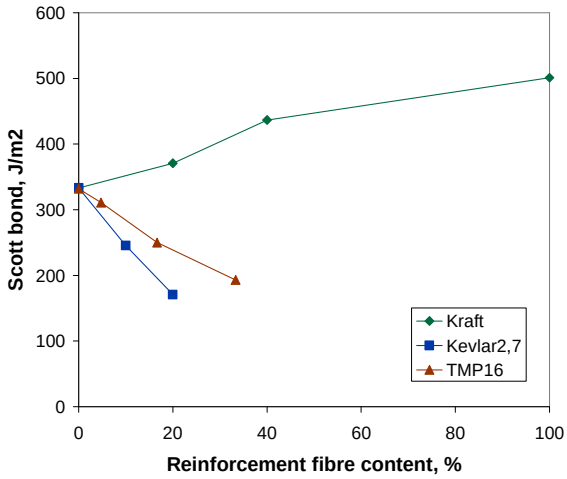


Figure 5-1. Scott bond vs. reinforcement fibre content of a TMP/reinforcement fibre blend. Kraft = beaten NBSK from a Finnish pulp mill, Kevlar2.7 = 2.7 mm long Kevlar fibres, TMP16 = 16-mesh fraction of TMP (average fibre length 2.54 mm). The base TMP (starting point) is the same for the Kraft series and the Kevlar series but different for the TMP16 series (the Scott bond of the base TMP's happened to be almost identical).

Kevlar fibres decreased the fracture energy (Fig. 12 in Paper III) presumably because they bond so poorly to a natural fibre network. It can be deduced that also in the case of the TMP long fibres, poor bonding must be at least one reason for their adverse effect on the fracture toughness. The importance of bonding was confirmed by the tests carried out for Paper III. The replacement of refined kraft pulp with the long fibres fractionated from unrefined kraft pulp had a very detrimental effect on the fracture energy (see Fig. 4-11). In fact, even refined TMP rejects gave a higher fracture energy than unrefined kraft pulp fibres. It is worth noticing that the ability of kraft pulp to increase Scott bond depends on one hand on the beating degree of it and on the other hand on the quality of TMP. The weak synergy phenomenon seen for kraft pulp in Fig. 5-1 is in agreement with the results reported by Honkasalo (2004).

In Fig. 5-2 the fracture energy is plotted against the average fibre length scaled with the zero-span tensile strength which can be kept as an estimate for the

damage width (the scaling procedure is given on page 87 - 88, see Equations 23 and 24). Thus, the format of the graph is basically similar with the one of Kettunen (2000) and Hiltunen (2003). Kettunen showed that damage width-fracture energy points form a straight line when the sheet is reasonably well bonded. Somewhat surprisingly, the pulp blends of the current study also formed a rough trend line that resembled the one presented by Kettunen (2000). Thus, the handsheets were "reasonably well bonded". That would mean that the fracture energy depended solely on the fibre length and strength. The pulp containing unrefined kraft pulp fibres seems to be an exception. According to Hiltunen et al. (2002), the points that fall clearly to the right from the trend line are considered poorly bonded. In their study, highly refined TMP provided sufficient amount of bonding to the mixture sheets of TMP and unrefined softwood kraft pulp. In the current study, the long fibre fraction of the unrefined kraft was used instead of whole pulp. Thus, it did not contain any of the well-bonding finer fractions the lack of which likely caused the reduced bonding in the blend.

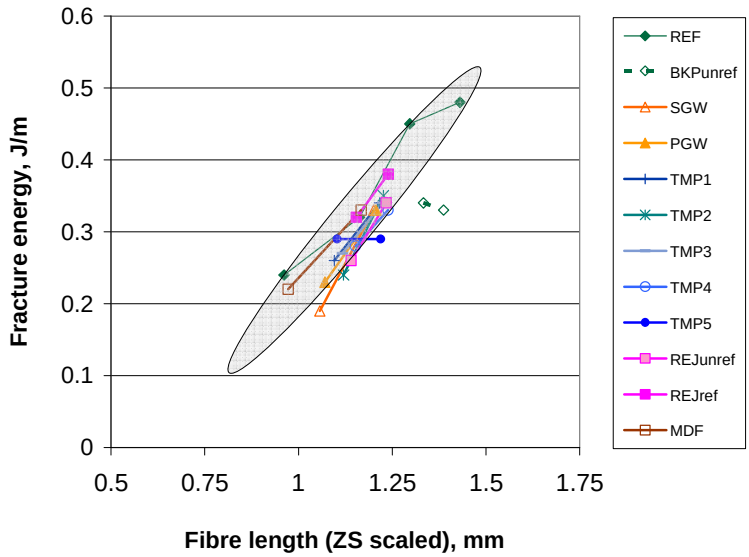


Fig. 5-2. Fracture energy of zero-span scaled fibre length. Points represent pulps blends of LWC TMP and long fibres separated from different pulps (Papers II and III). Scaling of fibre length with the zero-span strength is explained in Paper IV. Points containing same pulps in different ratios are connected with a line. The share of TMP in the furnish was 55% excluding the reference series were it varied from 45% to 80%. The share of the various long-fibre fractions was 10% to 25%. The grey oval serves as a guide for the eye showing the trend line from which the unrefined kraft pulp fibres deviate.

The blends with mechanical pulp long fibres located somewhat below the reference line with kraft pulp. However, it was surprising that even the blends of TMP and mechanical pulp fractions with a very low bonding ability were located so near to the reference line. It is particularly hard to explain why the MDF performed so well. One explanation is the rather small share of the long fibre fractions. It is a well-known fact among paper makers that mixing a small amount of different fibres to a pulp does not have big impact on the properties.

TMP rejects (unrefined and refined) formed a pair where increased bonding seemed to increase the fracture energy.

What is the role of bonding actually in mechanical pulp mixtures? Fig. 5-2 suggests that the average fibre length and fibre strength - or damage width - play the main roles. The ability of TMP to integrate the mechanical long fibres into the matrix may explain why the role of the bonding ability seems to be smaller than expected.

5.4 Testing some strength models

The strength models or equations offer one way to investigate the factors that contribute to the fracture toughness. In the following, data from Series II are fitted to three different strength models.

5.4.1 Seth's model

According to Seth (1996) fracture toughness depends on the tensile index and stretch at break (extensibility), Eq. 19. Applying it to the data resulted in fairly good results, Fig. 5-3.

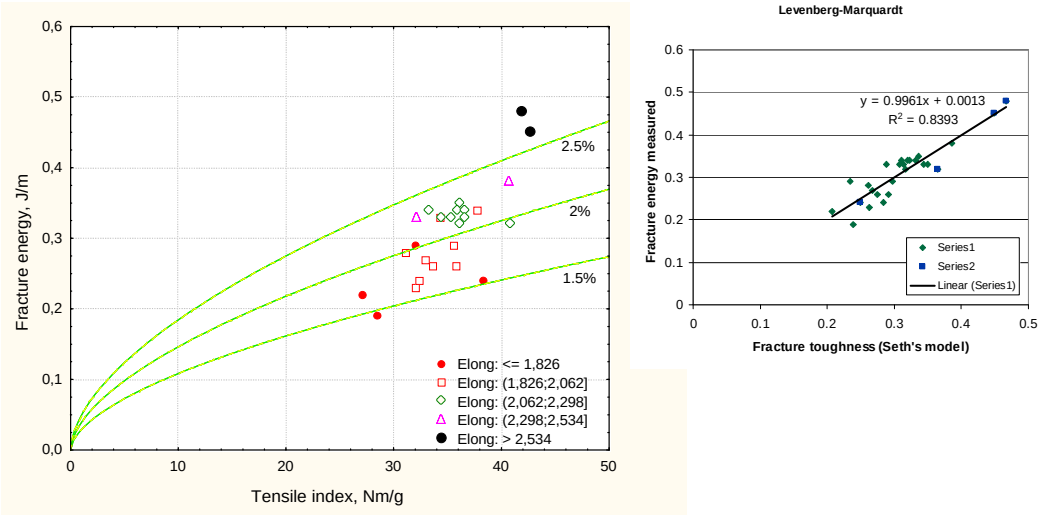


Figure 5-3. Fracture energy vs. tensile index. Stretch at break as a parameter (1.5%, 2% and 2.5%). The parameters of Seth's equation were fitted using the Levenberg-Marquardt algorithm with STATISTICA software. Measured vs. predicted values are plotted in the small graph. r^2=0.839 (n=26). Drawn from the data presented in Paper III.

The two trial points of the reference series with the highest chemical pulp share stand out from the rest. Those pulps had both a high tensile index and a high stretch at break. A special feature of this data set was that the average fibre length of the pulp blends varied within a relatively narrow range, 1.47 - 1.73 mm. The average fibre length did not have any correlation with the fracture energy. With the parameters in the current study, the importance of stretch at

break (extensibility) is pronounced, see Table 5-2. This will be discussed later in more detail.

Table 5-2. Correlation coefficients of the variables in Seth's model and the goodness of the model. Parameters in the model: a = 0.0188, b = 0.576 and c= 1.04. Data from Paper III, n=26.

Independent variable(s)	r	r^2
Tensile index (T)	0.763	0.583
Stretch at break (S)	0.888	0.789
$a*T^b*S^c$	0.916	0.839

Although the parameters of Seth's model were somewhat different in this research than what he reported in 1996, the results are similar to the extent that it can be said that similar phenomena were present. The effect of the parameters is demonstrated with the following example. At the tensile strength of 60 Nm/g, doubling the stretch from 1% to 2% would increase the fracture energy by 44% when the parameters given by Seth are used, whereas the present parameters give a rise of 65%, see Figure 5-4.

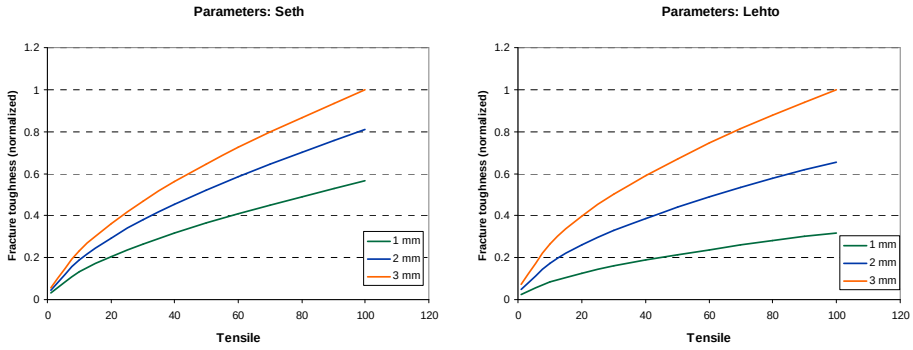


Figure 5-4. Normalized fracture energy as a function of tensile index at varying stretch at break (1, 2 and 3%). The parameters of the model according to Seth (left) (a=1.08, b=0.63 and c=0.52) and Lehto (right) (a=0.0188, b= 0.576 and c=1.04).

5.4.2 Niskanen's model

Seth and Page (1988, 1996) showed that the fracture toughness and Elmendorf tear for well-bonded sheets depend strongly on fibre strength. They found a linear correlation between the zero-span tensile strength and those strength properties on a logarithm scale. In the second laboratory series of the current research (Paper III), the handsheets made from pulp blends were not tested for the zero-span tensile strength. Neither the handsheets were tested for the damage width. That would have allowed testing the model (Eq. 16) presented by Niskanen et al. (2005) using the original parameters. However, analysing the component pulps and fibre fractions for the zero-span tensile strength (ZS) enabled testing the approach introduced in Paper IV. Instead of the damage width used in the original model, the average fibre length scaled (corrected) with the ZS of the pulp components is used. In that way, the fibre strength is taken into consideration when calculating the fracture energy, Eq. 23.

$$G = \chi \cdot \frac{T^2 \cdot l_s}{E} \qquad (23)$$

where T is tensile index , E tensile stiffness index, l_s scaled fibre length and χ geometry factor. The scaled fibre length l_s is defined in the following way, Eq. 24:

$$l_s = l_i \cdot \frac{zsd_i}{zsd_c} \qquad (24)$$

where l_s = scaled average fibre length of pulp i
l_i = average fibre length of pulp i
zsd_i = dry zero span strength of pulp i
zsd_c = dry zero span strength of chemical pulp.

Fitting the modified Niskanen's model to the data presented in Paper III is illustrated in Fig. 5-5.

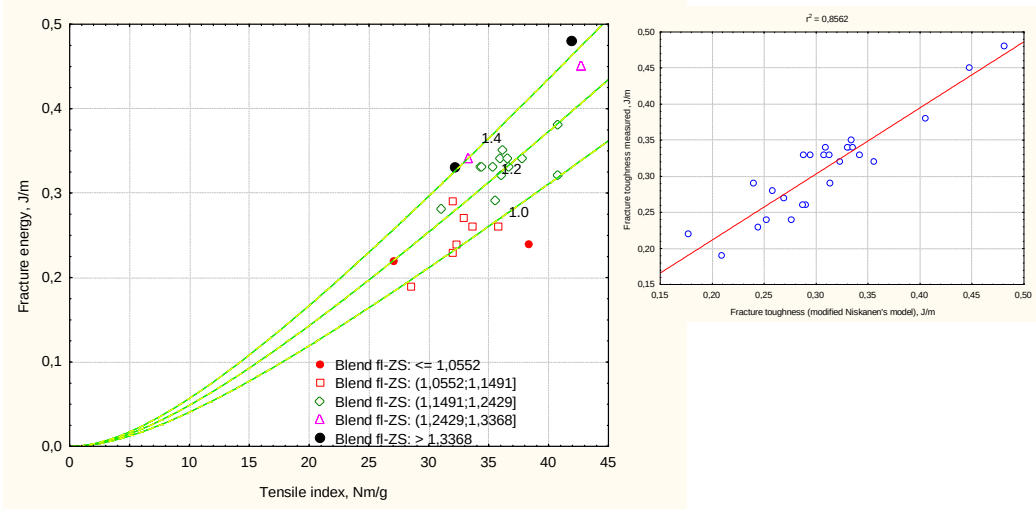


Figure 5-5. Predicted fracture energy vs. tensile index using Eq. 23. Drawn from the data presented in Paper III. The C parameter was chosen so that the measured and predicted values are equal for the basic reference point with 35% of chemical pulp (fracture energy = 0.45 J/m). r^2=0.856 (n=26). The level curves are for scaled fibre lengths of 1 mm, 1.2 mm and 1.4 mm. Points are categorized based on the zero-span scaled fibre length. E in the model is replaced with an expression for the linear relationship between tensile strength and tensile index. Measured vs. predicted fracture toughness values are plotted in the small graph.

The correlation coefficient r between the predicted and measured fracture energy was 0.925. Without the fibre length scaling the correlation was 0.833. Thus, introducing a kind of effective fibre length to the model improved the model considerably. In Paper V it was observed that the zero-span scaled fibre length of the furnish correlated well with the damage width of the pilot papers. On the grounds of those results, the scaled fibre length can be used as an estimate for the damage width. An inconvenience in its usage is the need of setting the reference level for the zero-span strength. Here, the zero-span tensile strength of the refined kraft pulp that was used as the reinforcement pulp in the

reference series was taken as the reference level. It is hard to say what the right value should be since the maximum achievable value for the chemical pulp varies depending on the wood species, process, refining techniques etc. Evidently, a theoretically correct, universal value cannot be given. Therefore, the modified model (Eq. 23) is not suggested to be a universal model for the fracture energy but rather a model that facilitates thinking for the problem.

Although the two models used in Figures 5-3 and 5-5 are different and the contribution of tensile strength differs, there is no big difference in the goodness of fit. The data available did not cover the whole range from zero to high tensile strength which causes uncertainty to the models. However, it seems obvious that the modified Niskanen's model would give a better prediction for pulps with a low tensile strength, since below a tensile index of 10 Nm/g a paper sheet is virtually unbonded and consequently its fracture toughness approaches zero. The second variables (stretch at break and zero-span scaled fibre length) of the models have a strong mutual correlation (r= 0.879) which explains why the goodness of fit is so similar. The blends with a high stretch at break and a high ZS-scaled fibre length were mostly those that contained unrefined or refined chemical pulp. It is reasonable to deduce that fibres that are long and strong, can also give stretch to paper.

Table 5-3. Fracture energy as a function of selected independent variables and variables of modified Niskanen's model. Data from Paper III (n=26).

Independent variables	**r**	**r^2**
Tensile index squared (T^2)	0.768	0.590
Tensile stiffness index (E)	0.593	0.352
Average fibre length (l)	-0.042	0.002
Average fibre length with zero-span scaling (l_s)	0.837	0.701
T^2/E	0.791	0.625
$T^2/E*l$	0.833	0.694
$T^2/E*l_s$	0.925	0.856

The average fibre length of the furnish had no correlation with the fracture energy whereas with the ZS-scaling a significant correlation occurred between them. It is apparent from Table 5-3 that both the tensile index and the ZS-scaled average fibre length have a strong correlation with the fracture energy. The squaring of the tensile index did not increase the correlation (cf. Table 5-2).

5.4.3 Shallhorn's model

According to Shallhorn (1994), the fracture resistance (R) - tensile strength (T) curve for a pulp is determined by the following equation:

$$R=l*T/6 \qquad (25)$$

when only fibre pull-out occurs, i.e. the fibres are strong in relation to the bonding degree of the paper sheet (l in the equation is the average fibre length). The form of the equation is the same as the one for tear strength by Shallhorn and Karnis (1979). The equation is also very similar to that of Niskanen taking into consideration that in Niskanen's equation the effect of squaring tensile is

largely compensated by the increasing tensile stiffness. When bonding (shear force τ) is sufficiently large, the fracture resistance begins to drop due to increased fibres breakage. The maximum fracture resistance is given by R_{max}=l*ZS/12 and it occurs at T=ZS/2. It can be estimated from the properties of the furnish components that in the data of Series II the tensile strength of all trial points was below the R_{max}. Thus, Eq. 25 is applicable. Fig. 5-6 illustrates how Shallhorn's model fits to the data from Paper III.

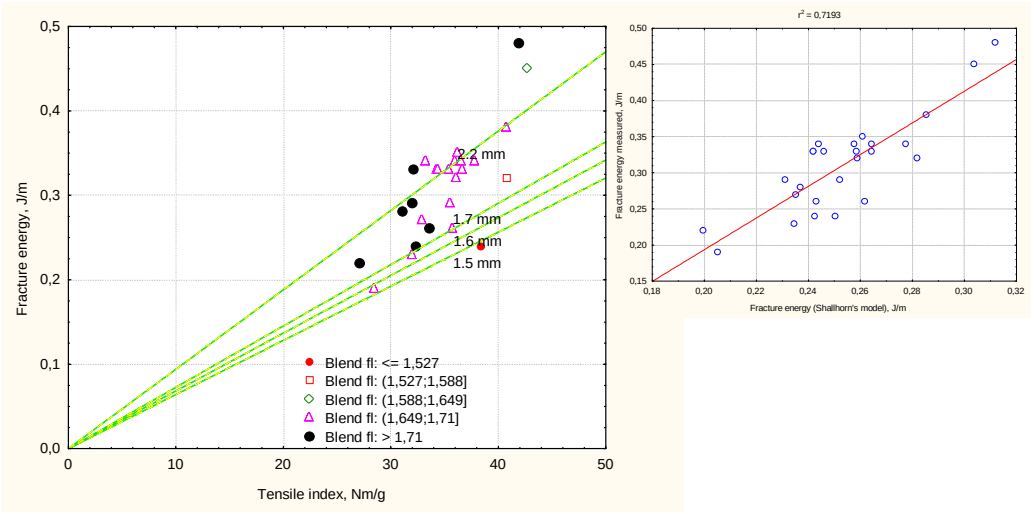


Figure 5-6. Predicted fracture energy vs. tensile index using Eq. 25. r^2=0.719 (n=26). The level curves are for average fibre length of 1.5 mm, 1.6 mm, 1.7 mm and 2.2 mm. Fracture energy index is converted to fracture energy using the average basis weight (39 g/m²) of the handsheets. Points are categorized based on the average fibre length. Measured vs. predicted fracture energy values are plotted in the small graph.

The goodness of fit (r^2=0.719) of the Shallhorn model is somewhat lower than the Seth model or the modified Niskanen model. It is obvious from Fig. 5-6 that the ordinary average fibre length of the furnish hardly explains the variation in the fracture energy in the current data set (Series II). The correlation coefficient of the model was somewhat higher than with the tensile index solely, but the coefficient increased only a little when the fibre length was taken to the model. Mathematically this was in line with the low correlation between the average fibre length and fracture energy.

In summary, the handsheet series of TMP/long fibre blends indicated that bonding, judged with tensile strength, is an important contributor to the fracture energy.

5.5 Comparison of different test series

The laboratory series (preliminary study and Series II) indicated that the properties where mechanical pulp differs from chemical reinforcement pulp are fibre flexibility and fibre strength. Therefore, when planning the pilot trial much

emphasis was put on maintaining the fibre strength and increasing flexibility. Gentle, multi-stage refining and sulphonation were used as a tool to achieve the desired properties. The pulps manufactured this way were called MRP (Mechanical Reinforcement Pulp) and CMRP (Chemimechanical Reinforcement Pulp), see Chapter 4.2.1. The starting points for the series differed which makes the comparison somewhat difficult, but not impossible. The properties of the MRP and CMRP pulps are compared with the most interesting and comparable pulps or fibre fractions from the proceeding laboratory series in Table 5-4. It is striking that the bonding properties of the long fibre fractions of TMP are so poor. The long fibre fraction of the refined TMP rejects is somewhat better but still quite poorly bonded. The MRP and CMRP were significantly better in that respect. The tensile strength of the MRP was virtually equal with the normal TMP rejects and it had a somewhat lower TEA index. However, taking its high average fibre length, high tear index and low fines content (see also Table 4 in Chapter 4.2.1) into consideration, it can be said that it was a better reinforcement pulp than the normal refined TMP reject pulp. The CMRP was developed one step further and it had a very high tensile strength, tensile stiffness and TEA index for a (chemi)mechanical pulp. The tear strength was somewhat lower but the fracture energy higher than the MRP. Its high density is an indication of a high fibre flexibility which was confirmed by the single fibre flexibility analysis. Thus, a good starting point for an interesting pilot test existed.

Table 5-4. Key properties of selected pulps from the three test series.

	Series I -Preliminary laboratory series (Paper I)			Series II - Main laboratory series (Papers II and III)		Series III - Pilot series (Papers III and IV)	
	TMP	TMP 30 mesh	TMP 16 mesh	Refined TMP rejects	Refined TMP rejects 16+30 mesh	MRP	CMRP
CSF	57	703	723	75	n.a.	94	88
Fibre length, mm	1.59 (FS-200)	1.75 (FS-200)	2.54 (FS-200)	1.68 (FS-200)	2.43 (FS-200)	2.21 (FibLab)	2.20 (FibLab)
Density, kg/m³	472	283	282	486	330	478	583
Tensile index, Nm/g	51.2	18.4	17.8	64.0	23.7	65.5	71.3
Tensile stiffness index, MNm/kg	4.47	2.44	2.41	5.7	3.39	6.2	7.8
Tear index, mNm^2/kg	7.0	4.6	7.5	7.5	7.6	8.4	7.5
TEA index, J/kg	857	135	114	1050	158	943	1179
Scott bond, J/m²	332	55	50	310	48	207	271
Fracture energy index, mJm/g	8.1	2.5	2.7	n.a.	n.a.	10.6	11.3

Figure 5-7 illustrates how different pulps and pulp fractions reinforced TMP in the three separate trial series. The base TMP with which the pulps and fractions were mixed was different in different series. In addition, the softwood chemical pulp (kraft) was different. Moreover, there were significant differences in the handsheet making procedures. In spite of these reservations, it is fair to compare general trends in the different trial series. The very first trial series clearly

demonstrated for the first time, how adding mechanical long fibre fractions (for clarity, the results with the 30-mesh fraction are not shown in Fig. 5-7) increased the fracture energy of TMP only slightly even though the average fibre length was increased. Softwood kraft pulp gave a much higher fracture energy at the same average fibre length.

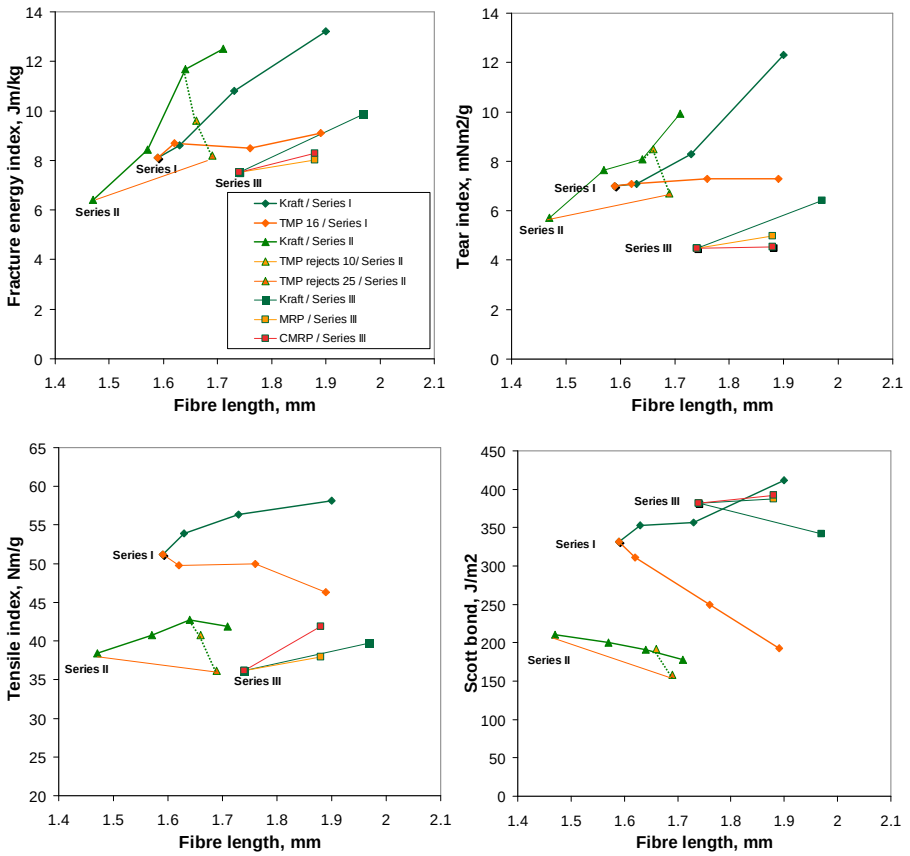


Figure 5-7. Fracture energy index, tear index, tensile index and Scott bond vs. fibre length. Series I - preliminary laboratory series, standard handsheet (60 g/m²), no filler. Series II - main laboratory series, low-grammage handsheets (38 g/m²) with semi-automatic handsheet mould, 10% of filler clay. Series III - pilot series, geometric mean of pilot paper (48 g/m²), 10% of filler clay. In Series II, 10% or 25% of kraft pulp was replaced with TMP rejects at 35% of reinforcement pulp. These points are connected with a dashed line. The points of Series II with 10% of kraft pulp are connected with a solid line.

The results of the second series were in good agreement with the first series. Increasing the amount of kraft pulp consistently increased the fracture energy and the tear index. Instead, mechanical fibres in the form of the long fibre fraction of the refined TMP reject pulp were not advantageous for the fracture energy even though they were somewhat better bonding than the long fibre fractions of TMP. The poor bonding of the mechanical pulp long fibre fractions in the first two series reflected also very clearly in the tensile index and the Scott bond. In the pilot study (Series III) with the well-bonding MRP and CMRP, the tensile index improved particularly with CMRP. Both the MRP and CMRP

maintained the Scott bond which is an essential difference compared to the first two series. It is hard to say exactly to what degree the good bonding of the MRP and CMRP contributed to their fracture energy that they gave to the pilot paper. However, it can be said that the improved bonding with its various manifestations did have a positive impact on the fracture toughness of the pilot paper. The difference to the kraft pulp reference was definitely smaller than in the two laboratory series.

As discussed above, there were remarkable differences in the experimental design and testing procedures of the three series which complicated interpretation of the results on one hand. On the other hand, using different approaches increases the weight of evidence. One possibility to get easily understandable results is to study how increasing the average fibre length of the furnish by a certain amount affects the handsheet properties. In Table 5-5, the relative changes in the key handsheet properties caused by a 0.1 mm increase in the fibre length are given.

Table 5-5. Relative change (%) of some paper technical properties when the average fibre length of the furnish is increased by 0.1 mm using different pulps or pulp fractions. The figures are attained by interpolation from the graphs of Figure 5-7. In Series I and III, the starting point is TMP with no additional reinforcement fibres and in Series II, the point with 10% of kraft pulp.

	Series I		Series II		Series III		
	Kraft	TMP 16 mesh	Kraft	TMP rejects 16+30	Kraft	MRP	CMRP
Fracture energy	22	7	31	11	14	5	7
Tear index	12	3	34	8	18	5	1
Tensile index	8	-3	6	-3	4	4	11
Scott bond	7	-17	-5	-11	-4	1	1

The Series I and II had clear common features: kraft pulp was markedly better as a reinforcement pulp than the mechanical counterpart. In Series III, the situation was changed. The (chemi)mechanical reinforcement pulps increased bonding of the sheet which is likely to be the main reason why the gap between the kraft pulp and the MRP and CMRP was reduced in terms of the fracture energy. For the tear strength, where the role of bonding is less, the kraft pulp was markedly better. It can be deduced from this that developing the bonding properties of the mechanical pulp fibres is advantageous for the fracture energy, but still room for improvement remains.

The test results discussed above revealed that mechanical pulp fibres can be detrimental for the bonding properties of handsheets judged with tensile index and Scott bond. However, it is worth noticing that the drop due to mechanical fibres was not actually as big as could be deduced from the properties of the pulp components. The matrix pulp, TMP in these trials, can integrate poorly bonding fibres to the fibre network to some degree. It seems that it is more important that the sheet is bonded and that the matrix pulp can in a way absorb poorly bonding fibres rather than to say that mechanical fibres have a high

bonding ability as such. Moss and Retulainen (1995) have shown that fines significantly contribute to the strength and other properties of handsheets made of TMP long fibres. Hiltunen et al. (2002) observed that in TMP/chemical pulp (60/40) mixtures beating of the latter component did not improve the fracture energy (in-plane tear). They explained that highly refined TMP provided a sufficient amount of bonding to the mixture sheets and thus the normally positive effect of beating chemical pulp vanished. Accordingly, it can deduced that in these series the mechanical pulp component was able to 'tolerate' poorly bonding fibres so well that the effect of increased bonding ability of the mechanical pulp fibres was only modest.

In Series I (see Paper I), the fraction handsheets were made without circulation water in the mould. This approach was adopted because collecting pulp fractions to be used for handsheet making using the Bauer-McNett classifier is very time consuming. However, two fractions (16-mesh fractions of TMP and kraft) were tested also with white water circulation in the sheet mould. With circulation, the fines retention is higher than without circulation. Although the fines content in the 16-mesh fractions is low and consequently the amount of fines in the handsheets could not increase much due to the water circulation, their effect was surprisingly clear. The tensile index and the Scott bond of the TMP 16-mesh fraction increased 59% and 14%, respectively. As for kraft pulp, the increase was lower in relative terms (11% both for tensile index and Scott bond), but in absolute terms, the increase was considerable. In fact, the highest toughness figures (tear index and fracture energy) of all the pulps tested in this research were measured for the 16-mesh fraction of kraft pulp.

As stated in Chapter 5, Kettunen's 'damage width model' suggests that in a reasonably well-bonded paper sheet the fracture energy is independent of the degree of bonding. That would mean that e.g. increasing the bonding ability of mechanical pulp fibres should not improve the fracture energy of the paper sheet. However, the results presented above and the models suggested by several researchers (Niskanen et al. 2005, Shallhorn 1994, Seth and Page 1975, Toven et al. 2008) indicate otherwise. How could this contradiction be explained? Kettunen's observation of the linear dependence of the fracture energy and the damage width has been confirmed by other researchers (e.g. Hiltunen 2003) and there are good reasons to believe that such a general rule really exists. However, Kettunen's observation was based on a relatively few observations and there was considerable scatter in the results for normal papers with a damage width of ca. 2 mm. Åström et al. (1993) investigated how beating of kraft pulp affects the fracture toughness of groundwood pulp/kraft pulp mixtures. The fracture toughness increased slightly with beating with all GW/kraft pulp mixtures. Supposing that the beating did not change the average fibre length of the mixtures, at a given average fibre length, increased beating (=bonding) did increase the fracture toughness. Increasing the refining degree from 20 to 30°SR increased the tensile index by about 15%. At the same time, the increase in the fracture toughness was less than 7% at 10% filler content. Apparently, the effect of bonding depends on the furnish and the properties of the component pulps.

One way to evaluate whether the handsheets are well-bonded, has been presented by Lehtonen (2004). He suggested, based on the tensile-tear

relationship between different mechanical pulp blends, that there is a domain transition from the failure negligible domain to significant failure at a 0.3-0.45 bonding index (tensile strength over zero-span tensile strength) and 30-40 Nm/g tensile index. In the pulp blends of Figures 5-3, 5-5 and 5-6, the average tensile index was 35.2 Nm/g (27.1-42.7 Nm/g). Thus, it is evident that most of the pulp blends were such that fibre failure contributed to the handsheet strength. The pulps in the pilot series (Papers IV and V) were clearly in the fibre failure domain (tensile index 50.5-77.7 Nm/g, bonding index 0.51-0.65). The LWC base papers made of those pulps were also in the fibre failure domain based on the MD tensile strength even though they contained 10% filler clay (MD tensile index 58-68 Nm/g).

In summary, the tests carried out in this research showed that bonding is a major contributor to the fracture energy. Improving the bonding ability of mechanical pulp fibres improved the fracture energy of the furnish. However, the effect is smaller than expected particularly when the bonding ability of the fibres is sufficient. It seems that the level for sufficient bonding is rather low and in practical terms, the possibilities to increase fracture energy by increasing bonding via increased refining are also limited.

Since other strength properties, such as tensile strength, Scott bond and even tear strength are valuable in many loading situations, increasing bonding of mechanical pulp fibres is not without value.

5.6 Rheology

The stress-strain curve of softwood kraft pulp differed essentially from the curves of long-fibre mechanical pulps (Paper IV), see Fig. 4-13 in Chapter 4.2.1. Transposing the curves with an efficiency factor (Seth and Page 1983) reveals how the shape of the mechanical pulp curves is similar, as Fig. 5-8 illustrates.

The curves of mechanical pulps superimpose which can be regarded as an indication of their similar nature. Seth and Page (1983) observed similar phenomena with coarse Southern pine kraft pulp refined to different beating degrees. The pulp was poorly bonded and beating increased the elastic modulus considerably. By transposing the curves with different beating degrees superimposed. Wet pressing revealed similar results with certain prerequisites. The efficiency factor describes how efficiently the stress is transferred in the fibres in a sheet. In a loose sheet structure, the elastic modulus of single fibres is not fully utilized. In the current research the refining treatments and sulphonation of mechanical pulps densified the sheet structure meaning that the bonded area increased which increased the efficiency factor. Normally, the sheet density and the tensile strength correlate strongly with each other. That was also true for the pulps of Fig. 5-8. However, the MRP and the TMP deviated from the trend line, the former having a higher and the latter a lower strength at a given density than expected. This could be interpreted such that the MRP had somewhat higher bonding strength than the other pulps. The low tensile strength at a given sheet density might be partly due to its low fibre length and high fines content.

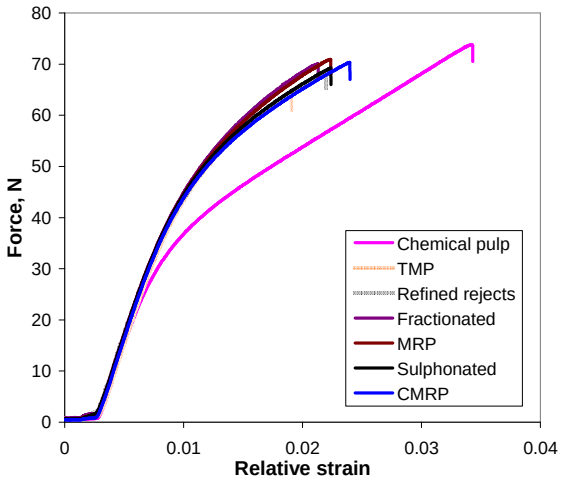


Figure 5-8. Transposed stress-strain curves of long fibre mechanical pulps and softwood kraft pulp (Data from Paper IV). Transposing has been made by dividing the original curves by the efficiency factors determined from the ratio of the modulus of each curve to the highest modulus (CMRP).

The stress-strain curve of the chemical pulp differed drastically from the mechanical pulps. According to Seth and Page (1983), the shape of the curve originates from within the fibre wall, for instance misalignments of the fibrils and microcompressions. This fits well with the observations that were made of the fibre properties of mechanical and chemical pulps. The high stretch at break of the chemical pulp can be explained by the above mentioned factors and fibre length, kinks, curl, flexibility and also by higher fibre strength. Many of these are such that mechanical pulp can be modified to resemble chemical pulp but some of them are so fundamental that reaching the properties of chemical pulp is not possible.

A high tensile stiffness is normally desired for printing papers as controlling a paper sheet with a high tensile stiffness is easier than that of a less stiff sheet. The tensile stiffness analysed from the handsheets of the pure pulps translated to the tensile stiffness of machine made papers and the CMRP paper had the highest tensile stiffness followed by the chemical pulp reinforced paper, the MRP paper and the pure TMP paper with no reinforcement pulp (Fig. 9-5). The stress-strain curves in Fig 5-9 show that the CMRP paper and the kraft paper were stiffer than the MRP and TMP papers both dry and rewetted. An interesting feature is that the TMP paper had a surprisingly high breaking strain.

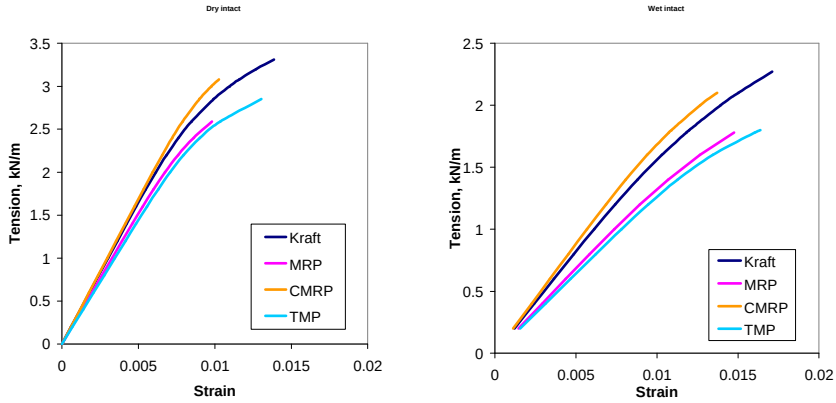


Figure 5-9. Stress-strain curves of pilot papers drawn from data gained from the KCL AHMA tests. Left: dry paper (moisture content ca. 5%). Right: rewetted paper (moisture content ca. 10%).

Transposing the curves of Fig. 5-9 similarly to Fig. 5-8 would show that the curves superimpose and the paper with kraft pulp as reinforcement would not differentiate from the rest. This indicates that the basic straining behaviour of the paper webs, when stressed, is similar.

It can be said that the kraft pulp gave the best reological properties to the pilot paper as a whole since the tensile stiffness was almost as high as with the CMRP but the breaking strain was much higher. It can be hypothesized that a high breaking strain produces a kind of safety margin for paper which is useful when there are local tension peaks in the paper web for instance due to a bad profile or formation. In a rigid paper sheet with a limited breaking strain local, microscopic fractures are formed at an earlier stage than in a more flexible paper. The initial fractures are starting points for a catastrophic failure of the sheet. Although the tension of paper for instance in a printing press is kept modest (<0.5 kN/m) and consequently the strain is not large compared to the breaking strain, a high breaking strain is a valuable thing for the runnability. The strain in the fracture zone can be two to three times higher than the external strain (the measured total strain) (Korteoja et al. 1998). This could be interpreted such that even before a paper web breaks localized areas must exist where the strain is markedly higher than the average. The KCL AHMA tests with intentionally defected webs brought forth the importance of the web uniformity. The breaking tension and the breaking stretch of the webs with defects were less than 50% of those of intact webs.

5.7 Number of fibres

The number of fibres (per unit weight of pulp) is a parameter in a number of equations that have been derived to predict paper strength. The Page equation (Eq. 12) can be used to get an idea about the effect of the fibre number on the tensile strength. At a given fibre length, the fibre number depends on the fibre length and the density of the fibre wall. With these prerequisites the fibre number is proportional to the cell wall area and the fibre coarseness. Increasing fibre coarseness by 15% decreases tensile strength by about 3% when the

parameters of the Page equation are adjusted to give a tensile strength of about 70 Nm/g. When the coarseness is increased by 30%, the difference in tensile index is about 6%. The 15% and 30% differences are roughly the same as what was observed between chemical pulp and the (chemi)mechanical reinforcement pulps CMRP and MRP, respectively. Applying the Shallhorn-Karnis model (Shallhorn and Karnis 1979) where the tensile strength is proportional to fibre number and inversely proportional to fibre coarseness, would lead to even larger differences in the tensile strength when coarseness is varied. When using the models, one has to remember that they are developed for idealistic situations and they do not for instance take into consideration possible interactions between the mechanical pulp and the reinforcement pulp. Moreover, in practise, adjusting one parameter usually affects other parameters. In spite of these reservations, the evident effect of fibre number and coarseness on the strength properties cannot be disregarded.

The fibre number (or coarseness) is a parameter also in the tear strength models presented by Shallhorn and Karnis (1979) and Kärenlampi (1996). In the former the tear strength is inversely proportional to coarseness. Interestingly, in the latter one it is inversely proportional to the square of coarseness when the sheet is loosely bonded and fibres do not break. Instead, when bonding is higher and fibre breakage occurs, the fibre coarseness has no effect on the tear strength.

Seth and Page (1988) studied chemical pulp with different coarseness and observed that at a given tensile strength there was no clear relationship between fibre coarseness and tear index. However, by correcting the tear index for the fibre strength (basically in a similar way as in this research) and plotting the tear index against sheet density, coarse fibres were shown to give higher tear strength. For low-coarseness pulps at high bonding levels, the effect of coarseness was diminished. From this it can be deduced that in the base papers of this research the effect of coarseness was likely modest.

In a later work, Seth (1996) confirmed that coarse softwood pulp fibres give good tear strength but poor fracture toughness whereas with fine fibres the situation is opposite and they give good fracture toughness and poor tear strength. According to him, fine, low coarseness fibres give a well-bonded sheet which is advantageous for in-plane strength properties.

Yu et al. (2000) tried to clarify the effect of coarseness on the fracture energy by mixing different chemical pulps to TMP in various ratios. Their results disagreed with Seth's result in that coarse-fibred abaca pulp gave a much higher fracture energy and toughness than fine-fibred abaca pulp. In the study of Yu et al. the fine abaca was clearly finer than the fine pulp in Seth's research. Yu et al. concluded that the reason for the poor performance of the fine abaca was the high number of fibre failures.

According to the percolation theory discussed in Chapter 2.6.1 there should be a threshold concentration of reinforcement pulp at which the reinforcement fibres begin to form a continuous network causing a non-linear, antagonistic behaviour of paper strength. The threshold concentration is proportional to fibre coarseness and inversely proportional to fibre length. Since chemical pulp fibres are

normally less coarse and longer than mechanical pulp fibres, the threshold concentration is lower for them.

However, the test results of this research do not give any clear evidence of the existence of a threshold concentration. The fracture toughness increased linearly when kraft pulp or its 16-mesh fraction was added to the base TMP and there is no sign of a percolation threshold, Fig. 5-10. This observation is in agreement with the findings of Kärenlampi et al. (1997). The 30-mesh fraction of kraft pulp gave a good fracture energy value at a low proportion, but the single point can well be an outlier. The mechanical pulp long fibres showed a very slight synergistic feature. It is evident that the pure fractions suffered from their very low bonding ability and mixing them with well-bonding TMP adduced some synergy.

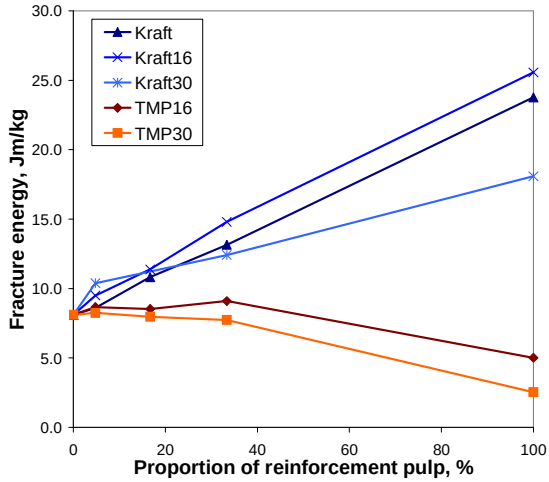


Figure 5-10. Fracture energy vs. proportion of reinforcement pulp. Data from Paper I. Starting point is 100% LWC TMP. The results for pure 30-mesh fractions are from handsheets made without recirculation.

The experimental design in other series was such that it did not allow making direct conclusions about the existence of the percolation threshold. However, some remarks can be made. In the second laboratory series (Chapter 4.1.3, Paper III) the fracture energy increased constantly with the increased proportion of kraft pulp. This observation is in agreement with the first series and the literature. Another observation from the second series is that in most cases a partial replacement of chemical pulp with mechanical pulp long fibres caused an immediate drop in most strength properties including the fracture energy. Apparently relatively coarse and stiff mechanical pulp fibres disturbed the consolidation of the handsheets containing a rather big proportion of chemical reinforcement pulp. The quite extensively refined TMP reject pulp behaved almost linearly.

It seems that the prevalence of the percolation theory is not supported by the results of this research at least inasmuch as chemical reinforcement pulp would get any decisive advantage over mechanical reinforcement pulps.

The reduced importance of fibre coarseness on the tear strength with increased bonding may explain why there are contradictory experimental results in the literature. This is also important because it means that the high coarseness of mechanical pulp is not as detrimental as the strength models, particularly the Shallhorn-Karnis model, predict.

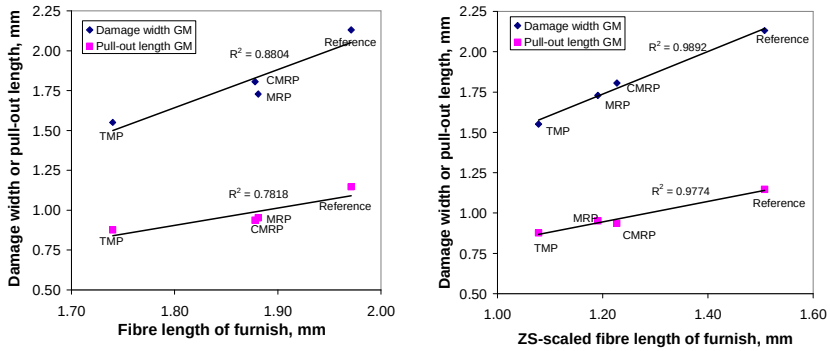
Based on the results referred above, striving towards low coarseness would not necessary be a primary target in mechanical pulping. A low coarseness brought about by extensive refining of mechanical pulp fibres would likely reduce the fibre strength and consequently, fracture energy. To gain a high fracture energy for a paper sheet, fibres must be such that they bond well and are strong enough. The independent effect of fibre coarseness is minor. Thus, high coarseness or low number of mechanical pulp fibres is not a fundamental hindrance for high fracture energy.

5.8 Fibre strength

In Papers IV and V it was shown that the average fibre length scaled with the zero-span tensile strength (ZS) can be used as an estimate for the damage width, and used instead of it in the fracture energy model presented by Niskanen et al. (2005). Using the ZS to correct a property is not a new idea. Seth and Page (1988) corrected the tear index for fibre strength by dividing it by the square of the ZS. In this way, they showed that the corrected tear strength is higher the coarser the fibres.

In this research, the ZS-scaling was first introduced in Paper IV. There it was shown to improve the coefficient of determination of fracture energy when fracture energy was explained using the modified Niskanen's equation (Eq. 23). In that work, the handsheets were not analysed for the damage width and no comparison between the estimate and the measured value could be made. In Paper V, where the pilot paper results were reported, the trial papers were analysed also for the damage width. The correlation between the fibre lengths of the paper furnishes and the damage width was non-linear but when the fibre length was corrected for the fibre strength, the correlation appeared to be linear.

ZS-scaling brought the pulps reinforced with mechanical and chemimechanical long fibres onto the trend line. This can be regarded as evidence of the impact of the fibre strength on the damage width. Since the damage width correlated extremely well with the fracture energy of the pilot papers, there seems to be a direct link from the ZS-scaled fibre length to the paper strength. This interpretation does not leave much room to the effect of bonding. As stated previously, according to Kettunen (2000) the fracture energy of reasonably well-bonded sheets depends on the damage width and through that on the fibre length. It can be assumed that the papers in this study were reasonably well bonded and therefore their fracture energy was mainly fibre-length dependent. Scaling the fibre length with fibre strength then adds some more precision to the rule.



a b

Figure 5-11. a) Damage width and pull-out length vs. fibre length of furnish and b) vs. zero-span scaled fibre length of furnish. The 'Reference' is a 27/63 blend of kraft pulp and TMP. 'MRP' and 'CMRP' are 27/63 blends of those pulps and TMP. All points contain 10% kaolin filler.

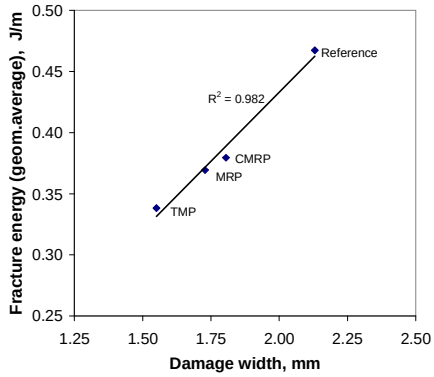


Figure 5-12. Fracture energy (geometric mean of CD and MD) vs. damage width of base paper. Abbreviations as in Fig. 5-11.

The effect of the fibre strength can be estimated from data plotted in Fig 5-11a and 5-12. If the MRP and CMRP were located on the line between TMP and the reference, their damage width should be 1.9 mm which in turn would give a fracture energy of 0.42 J/m for both pulps supposing that there is a fully linear relationship between the damage width and fracture energy as Fig. 5-12 indicates. The estimated fracture energy corresponds to an increase of 13% for MRP and 10% for CMRP, compared to their measured values. These results would mean that about a half of the difference in the fracture energy of the trial papers could be explained by the fibre strength and the other half by the fibre length of the paper furnish.

Another way to get an idea about the importance of the fibre strength is to use Equation 23. Basically it suggests that the fracture energy (G) is a function of fibre length (l), fibre strength represented by the relative zero-span tensile strength (ZS') and a bonding term (T') consisting of tensile strength and tensile stiffness. Equation 23 becomes:

$$G = T'*ZS'*l \qquad \text{(Eq. 25)}$$

Given that T' and l are equal for two pulps, a 50% difference in ZS (e.g. pulp A 100 Nm/g and pulp B 150 Nm/g) would mean that pulp A would have a 33% lower fracture energy than pulp B. If the share of these pulps in a paper furnish were 30% and a linear mixing rule were valid, pulp A would give a 10% lower fracture energy for the furnish which is in accord with the results of the pilot run.

These calculations are somewhat schematic, but taking into account that there is a sound scientific basis for Niskanen's equation (Eq.16) from which Eq. 23 is derived and that the fibre strength has been shown to have an effect on the fracture energy by several authors, the calculation results are likely not to be just coincidental.

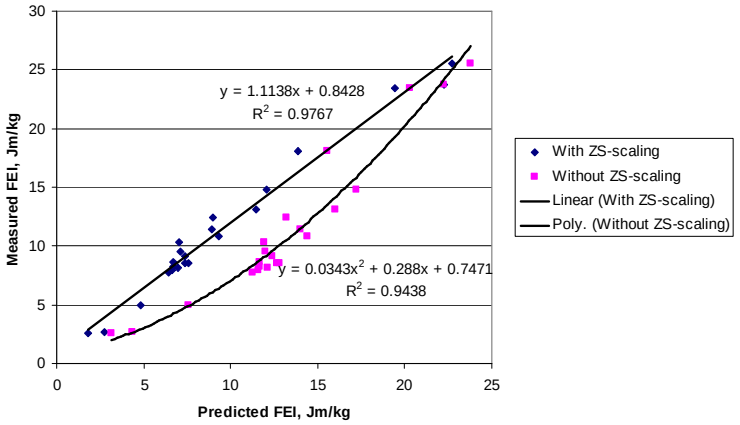


Figure 5-13. Measured vs. predicted fracture energy index. Data from Paper I. Prediction done using Eq. 23 with and without ZS-scaling. ZS-values were calculated from estimated ZS-values for the component pulps. The models were normalized to give comparable values with the measured values.

The model worked quite well also for the very heterogeneous data from Paper I. If the fibre length is not scaled for the fibre strength, a polynomial curve fitting is good. When the scaling is made, a linear fit describes the dependence very well (Fig. 5-13).

5.9 Runnability of pilot papers

As discussed above, the mechanical pulp fibres studied in the first parts (Papers I-III) of this research had several handicaps compared to chemical reinforcement pulp, the most striking features being lower bonding ability, lower flexibility, lower fibre strength (zero-span tensile strength) and also lower average fibre length. In the final part of the study (Papers IV and V) the idea was to make mechanical and chemimechanical reinforcement pulp with improved properties, and then study the effects of the replacement of chemical reinforcement pulp with mechanical reinforcement pulp on a pilot scale.

The bonding ability of the MRP and CMRP evaluated based on the tensile index was quite high, approaching the level of moderately beaten softwood chemical pulp for LWC paper. If the evaluation is based on the internal bond (Scott bond), particularly the MRP showed a fairly low Scott bond value, evidently because the fibres were still relatively stiff and did not conform effectively to create a high bonding area. Moreover, the medium and fines fractions, which are important for the sheet consolidation in the case of mechanical pulps, were small compared to normal TMP. Sulphonation (CMRP) improved the situation somewhat due to higher flexibility and conformability.

Comparing the tensile strength of the whole pulps and the long fibre fractions opens an interesting point of view to the development of bonding, see Fig. 5-14. The strength of the chemical pulp is largely formed by the long-fibre fraction or looking from another point of view, the strength of the long-fibre fraction does not need much contribution from the finer fractions. In the case of pure mechanical pulps, the situation is the opposite. Sulphonation (CMRP) improved the bonding ability of fibres significantly.

A remarkable finding is that the tensile index of the MRP long fibres did not improve much due to refining. However, the whole pulp was considerably stronger than the refined rejects. This means that the additional refining that the MRP experienced did not improve the bonding ability of the fibres very effectively. Instead, it obviously generated well bonding fines and other small sized fractions that enhanced the strength of the whole pulp. This claim is supported by the observations reported in Papers II and IV in which the changes between unrefined and refined rejects were rather small in terms of fibrillation and flexibility. The present results are in accord with those of Moss and Retulainen (1995) who demonstrated the great effect of fines on the bonding of TMP fibres. In their study, the tensile strength of handsheets made of a blend consisting 70% of TMP long fibres and 30% TMP fines was almost four times higher than that of the long fibres without fines. Besides the amount of fines, their quality matters as Luukko (1999) has shown. According to him, fibrillar fines increase the tensile strength of mechanical pulp effectively. It is likely that in the case of the MRP it was the increased content of fibrillar fines that gave the high tensile index. Retulainen et al. (1993) have shown that the strength of kraft pulp fibres is also significantly increased by fines addition. In their study, the long fibre fraction was the +20-mesh fraction, whereupon it contained fewer fines than the long fibre fraction of the present study. Therefore, the starting level of the tensile index was lower and the effect of fines bigger than here.

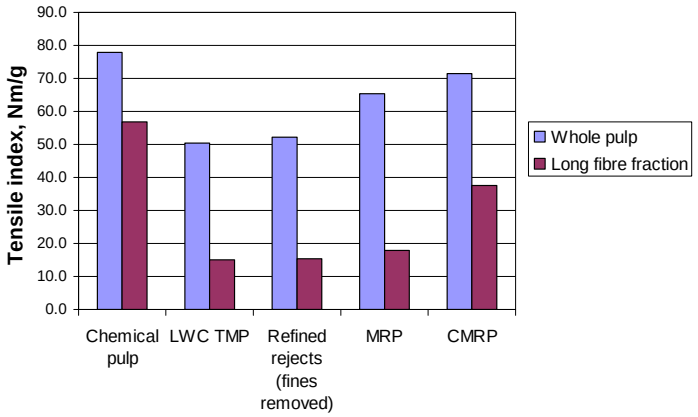


Figure 5-14. Tensile index of whole pulps and their long fibre fractions (+30-mesh) used in the pilot test. 'Refined rejects' (fines were removed after mill refining as described Paper IV) was the starting point for MRP and CMRP.

It can be questioned if the gentle, multi-stage refining was the best possible way to improve fibre properties. The reason for selecting that approach was the idea of saving fibre strength. A small energy input is accompanied by a large plate gap in refining in which case the refining intensity is low and fibre damage supposed to be limited. On the other hand, internal fibrillation and fibre splitting may not take place to a desired degree. Studying different ways to refine pulp was not within the scope of this research and therefore the question raised cannot be answered based on the results of this research. In any case, the strength of the MRP was better than that of a normal TMP reject pulp and thus the target to create a strong mechanical pulp was met.

However, the pilot trial demonstrated that the best LWC base paper was made of chemical pulp as a reinforcement pulp. In this trial the reinforcement pulps were realistic in the regard that the average fibre length was allowed to differ in different trial points, the chemical pulp containing paper got an advantage from its higher fibre length. It explained a major part of the differences in the strength properties. It was also observed in the pilot trial that the fibre strength of the reinforcement pulp (evaluated with the zero-span strength measurement) contributed to the fracture properties of the papers. As the papers were evidently fully activated and well-bonded, the MRP and CMRP pulps with longer fibres than ordinary TMP were supposed to give a higher fracture energy in a linear proportion to their damage width. Indeed, this was the case when the geometric means of the pulps were considered, see Fig. 5-15.

The ratio between damage width and pull-out length has been used as an activation indicator (Hiltunen 2003). If the ratio is below two, the paper is fully activated. The ratio for the same LWC base papers was within the range of 1.77-1.93 (geometric mean of CD and MD values). Thus, the paper sheets of the different trial points were well activated by web straining during the paper manufacture process.

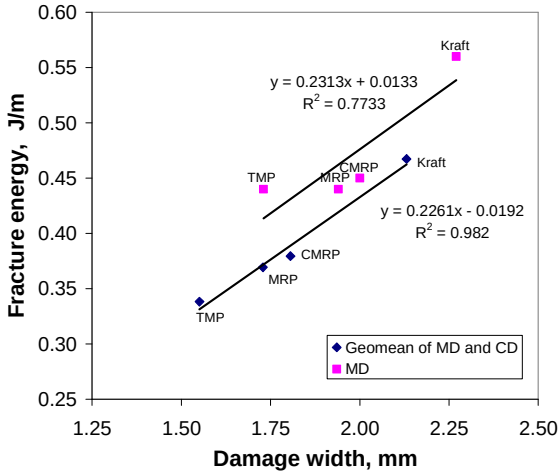


Fig. 5-15. Fracture energy vs. damage width of base paper. Geomean = geometric mean. Redrawn from Paper V.

The result is in good agreement with the results of Kettunen (2000) that found in reasonably well bonded sheets there is a linear correlation between the damage width and the fracture energy. A deviation to the right of the trend line would mean decreasing bonding. If the graph is drawn from MD data, a slight move of the MRP and CMRP to the right can be seen. This could be interpreted as an indication of somewhat lower bonding degree of those points.

The average fibre length of the furnish correlated fairly well with the damage width (Fig. 5-11) and consequently with the fracture energy (Fig. 5-16). However, the MRP and CMRP pulps had clearly lower fracture energy than their fibre length would suggest. The correlation improved markedly when the fibre length of the furnish was scaled with the zero-span strength of the pulp components and the points then fit to a straight line.

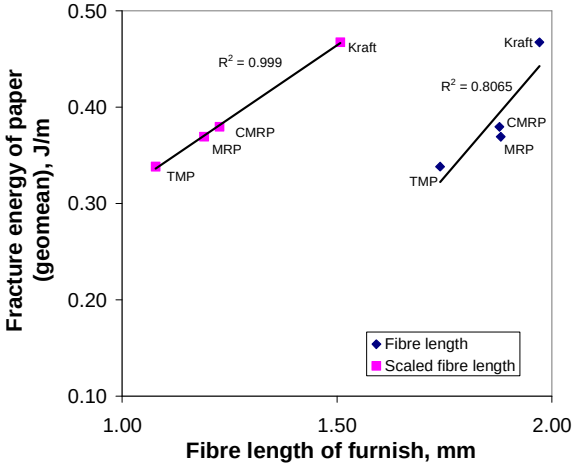


Figure 5-16. Fracture energy (geometric mean of MD and CD) vs. average fibre length of the furnish with and without the zero-span scaling of fibre length. Data from Paper V.

Since the zero-span scaled fibre length and the damage width correlate so well, the former can be seen as an estimate for the latter. As the scaled fibre length of the furnish predicted the fracture energy almost to 100%, applying Eq. 23 could not give any better result, in other words, introducing a bonding term in the form of the ratio between the tensile strength and tensile stiffness was not needed. This result deviated somewhat from the laboratory series with the pure pulps presented in Paper IV.

The finding that the damage width or its estimate of scaled fibre length explained well the fracture energy of the paper sheet confirms also the idea that the pilot paper sheets were "reasonably well bonded".

It was expected, based on the good strength properties of the handsheets, that the runnability results from the KCL AHMA would have been better for the MRP and CMRP papers than they were. Surprisingly, they had low breaking strain, low breaking tension and a low threshold tension for the dry intact paper sheet. The corresponding properties of wet paper were low particularly for the MRP. The low Weibull m modulus of both MRP and CMRP indicated that there was plenty of scatter in the results which as such explained the contradiction between the laboratory analyses and the dynamic strength values from KCL AHMA. The low m modulus is an indication of irregularities or flaws in the paper web. However, no clear reason could be identified. The MRP and CMRP papers had somewhat worse formation than the TMP paper with no reinforcement pulp, but on the other hand, the kraft paper had the worst formation and still it performed best. The shives content of the MRP and CMRP papers were slightly higher than the reference papers. However, the absolute shives level was so low that is should not have caused any problems. During the pilot paper manufacture, no abnormalities were recorded in runnability, pulp flows, consistencies, steam pressures etc. Thus, it can be only speculated that there were some unidentified defects in the MRP and CMRP papers that caused those papers to break at an unexpectedly low web tension. It is not likely that the pulps as such were the cause for the possible irregularities or defects in the paper web.

The results with the defected webs were more logical than those with intact webs. Obviously the intentionally made defects overrule the effect of the random irregularities and in consequence the fibre properties get a more pronounced role. In the rewetted, defected web, the good strength properties and high fibre length of the MRP and CMRP were even more visible than in the dry web.

In brief, the pilot trial confirmed that it is possible to improve the runnability of TMP by mechanical or chemimechanical reinforcement pulps, though one has to confess that the kraft pulp is better in virtually all respects.

6 CONCLUSIONS

The work hypotheses presented in Chapter 1.4 are discussed in the following:

1. Weaker fibres

Fibre strength was evaluated based on the zero-span tensile strength. The evaluation showed that mechanical pulp fibres are markedly weaker than chemical pulp fibres. It was shown that the fibre length scaled with the zero-span tensile strength explained the strength of the handsheets and paper much better than the normal fibre length. Thus, fibre strength is probably the most important difference between mechanical and chemical pulps. In other words, the low fibre strength of TMP fibres is a central reason for their relatively low reinforcement ability. In a weakly bonded sheet the fibre strength would not be that important, but it was shown that the handsheets studied and above all the pilot LWC base papers were well-bonded and activated meaning that fibre breakage takes place.

2. Less fibres in mechanical pulp

Another hypothesis was that possibly chemical pulp reinforces better than mechanical pulp because its fibres are less coarse. Thus, in a weight unit there are more chemical pulp fibres than mechanical pulp fibres at a given average fibre length. Theoretically, a higher fibre number results in a lower percolation consistency and earlier formation of a continuous network. Controlling the fibre number of a wood pulp without affecting other properties is very difficult on a large scale. The coarseness of mechanical fibres could be decreased by extensive refining, but it is likely that fibres would become damaged at the same time. Therefore, arranging a comparable trial set-up is very difficult and it was not done in this research.

The literature revealed that the practical meaning of the percolation theory in papermaking is insignificant. Neither the tests carried out in this research, where long fibres were mixed to a base TMP, did not give any clear indication of the existence of a percolation threshold. Consequently, chemical pulp does not get any advantage from its high fibre number. In addition, it has been shown with different kraft pulps that coarse but well bonding fibres give the highest reinforcement ability.

On these grounds it can be concluded that high coarseness combined with low fibre number is not a handicap for mechanical pulp.

3. Poorer bonding

When the work hypotheses were formulated, poor bonding of mechanical pulp fibres was thought to have a bigger influence on the strength properties than what it seemed to have in reality. Although their bonding ability proved to be low, fines and medium fraction can enhance the bonding of the network so much that the bonding ability of the plain fibre fraction can be lower than one might suppose. Bonding could be improved by refining and sulphonation, but in

particular when no chemical treatment is involved, generation of well-bonding fines seems to be a more important matter than the improved bonding of the actual long fibres. In the case of sulphonation, the improved fibre conformability promoted bonding. Based on theoretical models, increased bonding improves fracture properties. However, the overall bonding of handsheets with and without filler and that of pilot paper was so high that increasing the bonding of mechanical or chemimechanical reinforcement pulps did not seem to be a very effective way to increase their reinforcement ability.

4. Different reological properties

The reological properties - in this case limited to tensile stiffness and stretch at break - were shown to be different for mechanical and chemimechanical reinforcement pulps and kraft pulp. The tensile stiffness of mechanical pulps can be developed to the level of chemical pulp by extensive refining possibly combined with chemical treatment (sulphonation). Instead, the stretch at break or extensibility of chemical pulp is much higher than that of any mechanical pulp. Although during the manufacture of paper and in the printing house the paper web is not operated in the plastic region on average, high stretch at break dampens possible tension peaks inside the web and is likely to give extra potential to tolerate defects and irregularities.

Other

The starting point for this research was to compare mechanical and chemical pulp fibres at a given average fibre length. That set-up was reasonable when trying to find an answer to the differing reinforcement ability. In practise, it is difficult to get as high fibre length with mechanical pulp as chemical pulp. This is due to totally different manufacturing principles. Therefore, mechanical reinforcement pulp would suffer from somewhat lower fibre length that would negatively affect all planar strength properties like fracture energy and tensile and tear strength.

One of the biggest differences between mechanical and chemical pulp fibres is the lower flexibility of the former ones. It could be improved by sulphonation, however, the level of chemical pulp could not be reached. Since sulphonation also changes other things than the flexibility, it is not possible to say exactly what its role was. In spite of its much higher flexibility, the sulphonated CMRP was not superior compared to the pure mechanical MRP in terms of reinforcement ability. From this it can be deduced that the reinforcement ability is not heavily dependent on the fibre flexibility. Yet, the suitability of chemical reinforcement pulp arises partially from its flexibility that certainly increases the total and local extensibility of the paper web.

This research concentrated on the properties of a dry sheet. However, the tests with the KCL AHMA device gave some indications on the impact of different long fibres on the rewetted paper web. The results can be interpreted such that the advantage of long mechanical pulp fibres is biggest just in a wet web, where the fibre strength has a smaller role due to decreased inter-fibre bonding.

This research has shown that the reinforcement ability of mechanical pulp fibres is lower than that of chemical pulp fibres, and that developing their properties in this respect is very challenging. This does not mean that it would be useless to develop mechanical pulps and their fibres, improve their bonding and keep them long and strong. In the final analysis, the question is about the balance between production costs of mechanical pulp and the need and price of chemical pulp.

Recommendations for future work

In the present research, the pulp samples were chosen based on advance information of the pulp quality from different processes. No attempt was made to affect the properties. Thus, the data, particularly from Series I and II, were basically random in nature. A more systematic (statistical) study of the effects of various fibre quality parameters would complete and confirm the results.

This research was made on a laboratory and pilot scale. No mill studies were included. It would be very interesting to study whether the current findings would apply on a mill scale.

The low fibre strength was found to be a serious handicap of mechanical pulp fibres. The violent manner in which the fibres are detached from the wood matrix in mechanical pulping is the primary reason for the weakness. How much the different groundwood and refiner processes and process parameters affect the fibre strength, should be investigated.

The development of TMP can be seen as a balance between energy consumption, printability (optical and surface properties) and strength properties. This balance could be further studied while taking into account the new information of the limits of the strength enhancement of mechanical pulp fibres.

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Appendix A

Table A1. Pulp and paper technical properties of long fibre fractions (composite of 10, 16 and 30-mesh fractions) of some mechanical and chemical pulps (Huurre 2001, Papers II and III). Fibre lengths are length weighted average values. TMP1 to TMP5 are different TMP's. TREJu = unrefined TMP rejects, TREJr = refined TMP rejects, MDF = medium density fibre board, BKPu = unrefined and BKPr=refined bleached kraft pulp.

Analysis	Unit	GW	PGW	TMP1	TMP2	TMP3	TMP4	TMP5	TREJu	TREJr	MDF	BKPu	BKPr
Fibre length (FS-200)	mm	2.42	2.51	2.49	2.5	2.67	2.74	2.58	2.53	2.43	2.6	2.77	2.84
Fibre length (MorFi)	mm	1.47	1.56	2.03	2.08	1.92	2.16	1.99	2.09	1.94	1.51	2.46	2.45
Fibre length (Fibermaster)	mm	1.97	2.38	2.49	2.62	2.53	2.85	2.71	2.56	2.36	2.11	2.82	2.78
BNM 10	%	2.7	8.9	13.4	12.6	24	18.4	12.7	24.9	12.6	26.6	46.5	29.4
BMN 16	%	6.0	9.5	19	18.2	14.9	12.5	14.2	26.8	28.1	25.3	29.8	37.3
BMN 30	%	12.7	15.5	17.5	18.4	15.3	18.7	16.9	18.9	17.9	25.1	16.9	15.7
Grammage	g/m^2	59	60.4	60.5	59.1	61.8	60.8	59.8	59	60.9	55.9	60.4	59.5
Density	kg/m^3	319	296	277	261	216	225	262	269	330	200	618	643
Bulk	cm^3/g	3.13	3.38	3.61	3.83	4.62	4.45	3.824	3.71	3.03	0	1.618	1.56
Tensile Index	Nm/g	13.6	15	13.7	10.5	7.1	8.6	11.5	12.9	23.7	0	35.7	56.5
Elongation	%	0.94	1.15	0.95	0.9	1.91	1.3	1.44	0.89	1.17	-	3.61	3.08
TEA Index	J/kg	72	84	70	48	64	62	90	60	158	-	951	1160
Tensile Stiffness Index	kN/m^2	2.56	2.6	2.35	1.88	1.87	2.78	4.33	2.27	3.39	-	6.99	6.78
Breaking Length	km	1.39	1.53	1.4	1.07	0.72	0.88	1.17	1.31	2.42	-	3.64	5.76
Tear Index	Nm^2/kg	4.53	5.26	5.01	3.71	3.16	3.62	4.68	5.59	7.58	0.47	24.85	23.88
Bonding Strength SB low	J/m^2	61	58	50	41	38	43	43	46	48	-	135	161
Brightness	%	51	57.8	58.2	56.9	56.4	53.7	53.4	60.6	61.3	32.3	86.8	85.8
Light Scattering Coefficient	m^2/kg	34.2	34	28.2	28.4	27.5	25.3	27.3	27.9	28	19.7	26.1	23.8
Absorption Coefficient	m^2/kg	2.92	1.81	1.36	1.61	1.55	1.69	1.9	1.14	1.07	5.39	0.19	0.23

Table A2. Special analysis of the long fibre fractions (Huurre 2001, Papers II and III). Abbreviations as in Table A1.

Analysis	Unit	GW	PGW	TMP1	TMP2	TMP3	TMP4	TMP5	TREJu	TREJr	MDF	BKPu	BKPr
Fibre dimensions													
FS-200 Fibre Length	mm	2.42	2.51	2.49	2.5	2.67	2.74	2.58	2.53	2.43	2.6	2.77	2.84
Fibre wall thickness (mean) LM	µm	4.5	4.7	4.5	4	4.4	5	5.2	4.2	4.1	5.6	5.6	5.2
- 95% confidence	µm	0.21	0.24	0.24	0.21	0.24	0.27	0.28	0.24	0.24	0.24	0.3	0.32
Fibre width (mean) LM	µm	38.4	39.6	40	41.1	40.1	43.3	42.7	41	41.7	36.3	39.6	40.2
- 95% confidence	µm	1.52	1.44	1.6	1.56	1.73	1.59	1.54	1.54	1.66	1.39	1.59	1.47
Cell wall porosity													
FSP	g/g	0.595	0.585	0.65	0.62	0.64	0.725	0.535	0.635	0.665	0.54	1.26	1.12
FBW	g/g	0.165	0.195	0.235	0.215	0.225	0.21	0.23	0.26	0.26	0.16	0.5	0.485
NFW	g/g	0.36	0.35	0.36	0.34	0.35	0.375	0.365	0.33	0.345	0.35	0.31	0.285
WRV	%	1.08	1.28	1.34	1.31	1.48	1.23	1.22	1.27	1.38	1.05	1.54	1.63
Fibre strength													
Zero-span Tensile Index Dry	Nm/g	87.2	87.7	89.5	96.8	89.1	96.6	97.3	90.8	99	65.6	142.5	142.5
Zero-span Tensile Index Wet	Nm/g	72.5	72.8	78.9	83.1	78.5	82.7	77.7	87.2	93.8	na	127.7	134.9
External fibrillation (LM)													
Slightly fibrillated	%	12	12	71	61	65	20	12	67	66	79	96	84
Fibrillated	%	44	49	22	32	28	69	71	26	27	18	3	14
Broken	%	44	39	7	7	7	11	17	7	7	3	1	2
Simons staining													
Blue (green) stained fibres	%	56	15	22	42	21	31	20	31	23	52	26	15
Yellow stained fibres	%	15	32	31	18	24	28	34	26	27	15	74	85
Two-coloured	%	17	22	21	16	25	21	25	18	14	22	0	0
Colourless	%	12	31	26	24	30	20	21	25	36	11	0	0
Fibre stiffness TD&K													
stiffness (mean)	10-12Nm2	-	-	25	21.6	37.9	53	24.5	16.5	13.2	48.2	-	-
stiffness (median)	10-12Nm2	-	-	16.9	13.5	23.4	26	11.6	11.1	9.3	32.8	-	-

LM = Light Microscopy

Appendix B

Table B1. The properties of the trial pulps. The manufacture of MRP and CMRP is described in Chapter 4.2.1. Chemical pulp is mill beaten NBSK collected from a Finnish LWC paper mill. LWC TMP is peroxide bleached spruce TMP from another Finnish paper mill. (Paper IV)

		Chemical pulp	LWC TMP	MRP	CMRP
Pulp properties					
CSF	ml	505	42	94	88
LW Avg. fibre length (FiberLab)	mm	2.51	1.74	2.21	2.2
Coarseness (FiberLab)	mg/m	0.182	0.252	0.243	0.207
Curl (FiberLab)	%	16.1	11.2	13.5	12.0
L-factor	%	93.1	55	75.1	77.4
BMN 16	%	72.4	24.1	46.7	50.4
BMN 28	%	7.9	11.1	10.8	9.4
BMN 48	%	12.8	19.8	17.6	17.6
BMN 200	%	6.8	18.2	13.3	12.2
BMN P200	%	0.1	26.8	11.6	10.4
Somerville (0.08mm sieve)	%	0.33	0.15	0.5	0.22
Hand sheet properties					
Grammage	g/m²	61.4	58.2	60.3	59.1
Apparent density	kg/m³	702	529	478	583
Tensile index	Nm/g	77.7	50.5	65.5	71.3
Elongation	%	3.4	2.4	2.5	2.5
TEA index	J/kg	1586	829	943	1179
Tear index	mNm²/g	15.5	6.9	8.4	7.5
Fracture energy index	mJm/g	21.3	8.0	10.6	11.3
Bonding strength (Scott bond)	J/m²	359	301	207	271
Opacity	%	70.0	87.6	91.9	85.0
Brightness ISO	%	76.9	71.4	51.9	51.9
Light scattering coefficient	m²/kg	23.8	58.0	40.6	28.3
Absorption coefficient	m²/kg	0.41	0.72	3.19	2.52
Air permeance G-H	s	38.9	337	148	252
Roughness Bentsen	ml/min	120	64	198	136
Zero-span tensile strength					
Zero-span, dry	Nm/g	153	94.5	100	109
Zero-span, wet	Nm/g	138	74.6	91.5	97.5

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