Rolf Wathén

Studies on fiber strength and its effect on paper properties

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Rolf Wathén

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Forest Products Technology, Helsinki University of Technology for public examination and debate in PUU 2 Auditorium at Helsinki University of Technology (Espoo, Finland) on the 24th of November, 2006, at 12 noon.

Keywords: fibre properties, strength properties, cellulose, hemicellulose, zero span tensile strength, runnability, degradation, fracture, deformation, damage, ultrastructure, fibril, angle

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ABSTRACT

The objective of this work was to study factors affecting the strength of pulp fibers used in papermaking and how their strength affects the properties of the fiber network, i.e. the paper. All the structural levels contributing to fiber strength starting from the organization of cellulose chains in microfibrils through to visible defects and fiber deformations were considered. Due to its wide availability, zero-span strength was used as an indication of fiber strength.

Industrially made pulp fibers are mechanically damaged and thus weakened in the fiber line. Fiber strength may also degrade chemically. Chemical degradation may be homogeneous or heterogeneous, and the effects of these on fiber and paper properties differ. In this work, acid vapor-induced degradation was found to cause more heterogeneous degradation of fibers compared to ageing treatment at elevated temperature and humidity. In both treatments degradation occurs via the same mechanism – acid hydrolysis – but the difference is attributed to initial fast reaction of the acid vapors at fiber disorder sites. Z-directional fiber strength is less sensitive to fiber degradation than axial fiber strength. Spruce pulp fibers require the viscosity to drop below 400 ml/g before any difference can be detected in the Scott-Bond values. For birch pulp fibers the same happens at a viscosity of 700 ml/g. Neither treatment was observed to affect inter-fiber bonding.

Zero-span strength measurements were shown to follow a normal distribution. This was expected based on the Central Limit Theorem and was also predicted by modeling. The variation in zero-span strength was found to increase as functions of decreasing sheet thickness and increasing span length. The former was predicted by the model. The reason for the latter is that the properties of the fiber network start to show in the measurement.

Contrary to some earlier studies, it is suggested here that fiber curl itself maybe does not affect the zero-span measurement results. One reason for the often observed increase in zero-span strength during beating could be the favorable organization of fibrils. The Jentzen effect was not observed in the experiments probably because the test pulps likely had very few misaligned fibrils and on average a low fibrillar angle.

Fiber properties have a significant effect on the fracture properties of paper. In general, decreases in fiber length and strength lead to a decrease in fracture energy. Higher fiber curl means higher fracture energy, lower breaking tension and higher breaking strain of a paper web. Once the fracture process of paper has initiated, strains deviating from the ordinary breaking strain occur in the fracture process zone. The most significant contribution to these strains comes from the fibers orienting towards the direction of the tension. Even though significant to fracture energy, fiber strength did not have a clear effect on the strains in the fracture process zone.

TIIVISTELMÄ

Työn tarkoituksena oli tutkia paperinvalmistuksessa käytetyn kuidun lujuuteen vaikuttavia tekijöitä sekä tämän lujuuden vaikutusta paperin ominaisuuksiin. Huomioon otettiin eri rakenteelliset tasot selluloosamikrofibrillien järjestäytymisestä kuidussa näkyviin vikoihin ja kuitudeformaatioihin. Kuidun lujuuden mittana käytettiin ns. zero-span -mittausta sen hyvän yleisen saatavuuden vuoksi.

Teollisessa massan valmistuksessa kuidut kärsivät kuitulinjoilla mekaanisia vaurioita, jotka heikentävät niiden lujuutta. Kuidun lujuus saattaa pudota myös kemiallisista syistä. Kemiallisista syistä johtuva lujuuden pudotus voi olla luonteeltaan homogeenista tai heterogeenista, joilla on erilaiset vaikutukset kuitujen ja paperin lujuuteen. Tässä työssä happohöyryllä aiheutettu lujuuden pudotus oli luonteeltaan heterogeenisempaa kuin pudotus, joka saatiin aikaan vanhennuskäsittelyllä korotetussa lämpötilassa ja kosteudessa. Molemmissa käsittelyissä hajoamismekanismi oli sama - happohydrolyysi - mutta happohöyryillä reaktionopeus on alussa nopeampi kuitujen epäjärjestyskohdissa. Kuitujen z-suuntainen lujuus ei ole yhtä herkkä kuidun hajoamiselle kuin aksiaalinen lujuus. Kuusimassoilla Scott-Bond-mittauksessa havaittiin pudotus viskositeetissa 400ml/g, koivumassoilla viskositeetissa 700ml/g. Kummankaan käsittelyn ei havaittu vaikuttavan kuitujen väliseen sitoutumiseen.

Zero-span-mittausten todettiin noudattavan normaalijakaumaa. Tämä oli odotettavissa keskeisen raja-arvolauseen (Central Limit Theorem) perusteella ja sama tulos saatiin myös mallintamalla. Vaihtelu mitatussa zero-span-lujuudessa kasvoi arkin paksuuden pienetessä tai vetovälin kasvaessa. Johdettu malli ennusti arkin paksuuden vaikutuksen vaihtelulle. Vetovälin kasvun ja vaihtelun yhteyteen on syynä verkosto-ominaisuuksien näkyminen mittauksissa.

Vastoin joitakin aikaisempia tutkimustulosten tulkintoja, tässä työssä esitetään tulkinta, jonka mukaan kuitujen kiharuudella ei ole vaikutusta zero-span-mittaukseen. Syy usein nähtyyn zero-span-arvon kasvuun jauhatuksessa voi olla mikrofibrillien suotuisa järjestäytyminen. Ns. Jentzen-efektiä ei havaittu tässä työssä tehdyissä kokeissa, mahdollisesti koska tutkituissa kuiduissa todennäköisesti oli hyvin vähän epäjärjestäytyneitä kohtia sekä keskimäärin pieni fibrillikulma.

Kuitujen ominaisuuksilla on merkittävä vaikutus paperin murtumaominaisuuksiin. Yleisesti ottaen alhaisempi kuidunpituus ja lujuus johtavat matalampaan murtoenergiaan. Kiharammat kuidut johtavat verkoston korkeampaan murtoenergiaan, alhaisempaan vetolujuuteen sekä korkeampaan murtovenymään. Murtoprosessin alettua murtovyöhykkeellä tapahtuu normaalista murtovenymästä poikkeavia venymiä. Näihin venymiin vaikuttavat eniten vedon suuntaan orientoituvat kuidut. Vaikka kuidun lujuus vaikuttaa murtoenergiaan, sillä ei todettu olevan selkeää vaikutusta venymiin murtovyöhykkeellä.

PUBLICATIONS INCLUDED:

Publication I: Wathén, R., Rosti, J., Alava, M., Salminen, L. and Joutsimo, O. (2006): Fiber strength and zero-span strength statistics –some considerations, Nordic Pulp and Paper Research Journal, 21(2):193-201.

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Publication III: Wathén, R., Batchelor, W., Westerlind, B. and Niskanen, K. (2005): Analysis of strains in the fracture process zone. Nordic Pulp and Paper Research Journal, 20(4):392-398.

Publication IV: Joutsimo, O., Wathén, R. and Robertsén, L. (2005): Role of fiber deformations and damage from fiber strength to end user, Trans. 13th Fund. Res. Symp., Cambridge, UK, 2005, pp.591-611.

Publication V: Joutsimo, O., Wathén, R. and Tamminen, T. (2005): Effects of fiber deformations on pulp sheet properties and fiber strength, Paperi ja Puu – Paper and Timber, 87(6):392-397.

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AUTHOR'S CONTRIBUTION:

Publication I: Design of the experiments, analysis, first version of the manuscript

Publication II: Design of the experiments, main part of the analysis, first version of the manuscript

Publication III: Design of the experiments, main part of the analysis, first version of the manuscript

Publication IV: Design of the experiments in part, analysis in part, first version of the manuscript together with the first author

Publication V: Design of the experiments in part, main part of the analysis regarding tensile properties and fracture mechanics properties, manuscript in part

PREFACE

This work has been done under the TEKES financed Wood Material Science Research Programme (BUNDLE, Fibre wall modelling). I want to thank them for the possibility as well as the Finnish Cultural Foundation and Jenny and Antti Wihuri Fund for personal monetary support.

Next it is order to thank professor Tapani Vuorinen for fruitful co-operation in writing and publishing this work. I think it was easy for us to agree how things need to be organized. I am also grateful for professor Mark Kortschot and associate professor Lennart Salmén for acting as pre-examiners of my work resulting in significant improvements.

My supervisors Dr. Tarja Tamminen and Dr. Mikko Alava should both be praised for carrying me through this project. For which I am naturally very grateful. Tarja: I think I have thought everything I possibly know about paper physics, and also learnt a lot in return. During the years I think it was you and not me who became the real expert in fiber physics and chemistry. I hope it was worth the trouble. It was for me. Mikko: What can I say? You are getting softer when you get older. Good for me. In addition to Tarja and Mikko, one more person deserves my special gratitude. Dr. Olli Joutsimo. Olli you have been a constant source of amusement and even on occasion inspiration to me, in addition for being co-author in many of the papers we published. I all too rarely let these people know how much I appreciate their advice and especially friendship. Anyway. I do.

In addition to above mentioned, I need to thank also some other people. As my co-authors, Mr. Jari Rosti, Dr. Lauri Salminen, Dr. Warren Batchelor, Dr. Bo Westerlind, PhD Kaarlo Niskanen and Dr. Leif Robertsén have naturally helped be immensely. Sincerest thanks to you all. Skillful technicians from KCL also made very significant contribution to this work. I do my best to keep you busy also in the future.

In the end of the preface it is customary to thank loved ones for their love, support, tolerance, patience etc. These I have received from my parents as well as from my wife Kukkis and sons Matias, Niilo and Kasper more than I possibly deserve. Thank you.

Espoo, October 2006

Rolf Wathén

TABLE OF CONTENTS

1 INTRODUCTION

Natural cellulosic fibers are the most important raw materials of paper and paperboard, as well as of many hygiene products. In the year 2003, 187 million tons of pulp and 325 million tons of paper and board were produced in the world (Peltola 2004). The properties of fibers and other raw materials define the properties of the end products. For paper and paperboard, strength, the ability to tolerate applied stresses, is one of the most relevant properties. Single fiber strength is very important to paper and paperboard strength (Van Den Akker et al. 1958). Also fibers' abilities to swell and form inter-fiber bonds are important for the strength of paper and paperboard.

Fibers used in paper and board making are of natural origin. The most usual source is wood. Fibers are extracted from woods in chemical, mechanical or chemi-mechanical processes. Wood raw material has a very significant effect on the properties of the received fibers, as does the process used in defibration.

The main chemical components of fibers are cellulose, hemicelluloses and lignin. Fiber ultrastructure is the ordered patterns of these components. Cellulose is the main strength delivering component. It is a long linear polymer and has a strong tendency for intra- and intermolecular hydrogen bonding, which leads to formation of microfibrils. These have excellent mechanical properties due to ordered structure and effective atomic level load sharing. Microfibrils further aggregate into fibrils or fibril aggregates. These fibrils are wound at an angle called microfibrillar angle around fiber axis, and can be thought to form a number of co-centric lamellae. Fibers have distinct layers; primary wall and secondary wall, which consist of three separate sub-layers (S1, S2 and S3). Middle lamellae is a layer between fibers. Fiber layers have different chemical compositions and microfibrillar angles. In addition to defects in fibers, the microfibrillar angle of the thickest secondary wall layer, the S2-layer, has been shown to have the most significant effect on fiber strength (Page et al. 1972). However, one should not assume that the other layers do not play any role (Mark 2002).

As mentioned, visible fiber defects greatly decrease fiber strength (Page 1972). However, fiber structure can also be damaged internally (Joutsimo 2004). In chemical pulping fibers go through extensive mechanical treatment, for example hit the turns in pipe lines or are mishandled by the fluidisizing rotor of the medium consistency pumps. These treatments damage fiber structure and lower

its strength (McLeod et al. 1995, Tikka and Sundquist 2001). In addition to damage, fiber deformations like curl and kinks are introduced in the pulping process. These deformations affect the properties of fiber networks (Page and Seth 1980), i.e. paper and paperboard.

Fiber strength may also decrease in chemical treatments when fiber components, especially cellulose, are degraded. The effect of chemical degradation depends on its extent and location in fiber. Homogeneous or random degradation causes very little loss in strength, whereas localized or heterogeneous degradation may weaken fibers significantly (Gurnagul et al. 1992, Berggren 2003). The intermediate stages of acid sulphite cooking and the final stages of kraft cooking combined with mechanical damage are said to cause heterogeneous degradation (Gurnagul et al. 1992).

The physical size of individual fibers is quite small, fiber length being few millimeters (mm) and perimeter some tens of micrometers (μm). This makes the testing of individual fibers very laborious and time consuming. There is also a large amount of variation in strength between individual fibers. Despite of the pain and trouble, testing of individual fibers has been done (Kim et al. 1975, Page et al. 1972, Hardacker 1970, Mott et al. 1995), but alternative ways to determine fiber strength have also been employed. In pulp and paper industry zero-span strength, tensile testing of papers or pulp handsheets with nominally zero span-length, is often taken to be an indicator of mean fiber strength (Seth and Chan 1999). However, zero-span strength as such tells little of the variation in fiber strength. Another way to measure single fiber strength is the Single Fiber Fragmentation test, where a number of fibers are embedded in resin and the cured resin bar strained in a tensile tester. This method gives the breaking strain distribution of fibers, thus revealing also the variation in fiber strength.

Identifying the components and structures delivering strength in fibers is very important. Since the zero-span strength is commonly used as a fiber strength index, it is relevant to know how fiber deformations, fiber damage and variation in individual fiber strength in addition to fiber ultrastructure are seen in the measurement results. Also the mechanisms and ways by which these affect the properties of paper products are of keen interest. In the following, some additional rays of light are shed upon these issues.

2 THE OBJECTIVE AND THE OUTLINE OF THE STUDY

The objective of this work was to study different factors affecting the strength of papermaking pulp fibers and how that strength affects the properties of fiber network, i.e. paper. All the structural levels contributing to fiber strength starting from the organization of cellulose chains in microfibrils going to visible defects and fiber deformations were considered.

The ultrastructure and properties of papermaking fibers are investigated based on literature in chapter 3. On the molecular level, cellulose and its fibrillar structure, hemicelluloses and lignin are discussed. On a higher structural level, the microfibrillar angle and the pore structure of fibers are addressed. Next level considered consists of fiber morphology and fiber deformations and damages, which are also connected to some end-use properties.

Chapter 4 reviews and discusses the different methods applied to measure fiber strength; testing of individual fibers, single fiber fragmentation test and zero-span strength test. In chapter 5 different aspects of fiber and cellulose degradation are addressed. Considered topics are degradation patterns, measurement of degradation and degradation in pulping. Chapter 6 goes through the modelling of fiber strength. Chapter 7 reviews literature on the role of fibers in paper fracture.

Chapter 8 describes the different materials and methods used in this study. Chapter 9 reports and discusses the results from the experiments performed to study the phenomena of fiber degradation. Chapter 10 deals with zero-span strength measurement experiments. Topics include the effect of fiber deformations, the variation in zero-span measurement plus a preliminary model of how zero-span strength variation is connected to variation in fiber strength. Chapter 11 discusses the role of fiber deformations and damages to different paper properties. The so called post-fracture strain is also considered. Chapter 12 gives the overall conclusions and some suggestions for further research.

3 ULTRASTRUCTURE AND PROPERTIES OF PAPERMAKING FIBERS

Natural fibers are cells with intriguing structure. Typical fibers used in papermaking are about 1-4mm long and roughly 30μm wide. The thickness of the cell wall is around 4μm. A lot of variation exists in these dimensions. Papermaking fibers are chemically mostly composed of cellulose, hemicelluloses and lignin, see Figure 1b. Fiber cell walls consist of different layers, middle lamella between fibers, primary wall and secondary wall, Figure 1a. Middle lamella and primary wall, together known as combined middle lamella, are usually very thin (~0.1μm) (Hakkila 1998), though also thicker regions exist. According to Retulainen et al. (1998) they are usually lost in pulping. However, Duchesne and Daniel (2000) have observed primary layers in fibers after kraft pulping. S2-layer is the thickest of the layers, ~74% of softwood fiber volume (Hakkila 1998), and is to a large degree thought to be responsible for the mechanical properties of fibers (Retulainen et al. 1998). Secondary wall layers are composed of lamellas of spiraling cellulose fibrils, which are surrounded by hemicelluloses and lignin. In S1-layer the spiraling angle, the microfibrillar angle (MFA), is around 50-70°. In S2 typical values are from 10° to 30° and in S3 from 60° to 90° (Hakkila 1998).

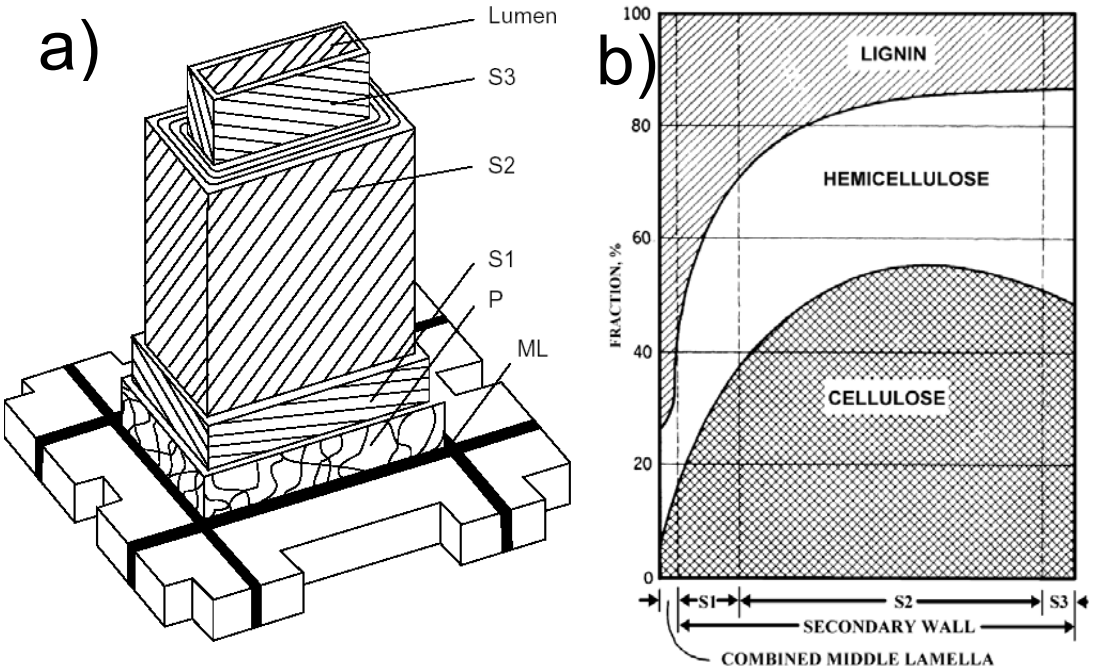


Figure 1. a) Different layers in a softwood fiber (Retulainen et al. 1998). b) Chemical composition of combined middle lamella and secondary walls (Jensen 1977). ML=Middle lamella, P=Primary wall, S1-S3= secondary wall.

The arrangement of chemical components and the number and size of the structural units in fibers is still under investigation, even though a significant amount of research has been conducted on the topic. One suggestion for the structure of native fiber and the location of the different chemical constituents with-in is given by Åkerholm (2003) and is presented in Figure 2.

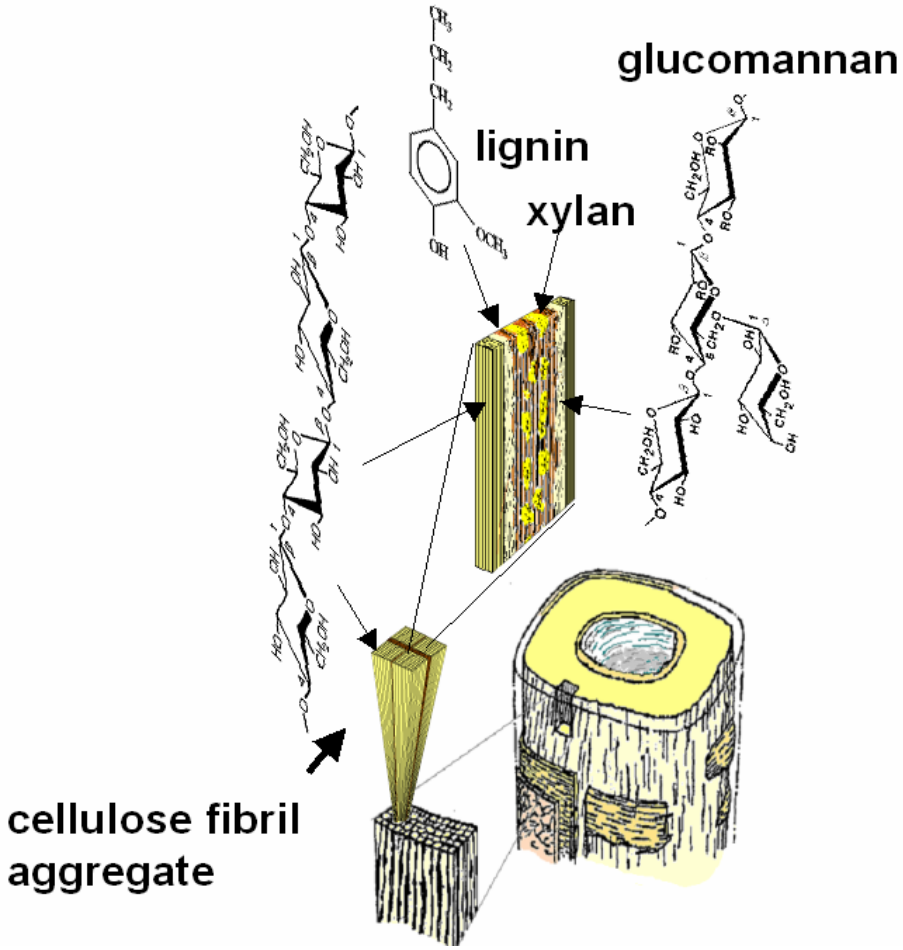


Figure 2. Proposal for the structure of native softwood fiber. Adapted from Åkerholm 2003.

3.1 Cellulose and its fibrillar structure

Cellulose is the main load bearing component in fibers. It is a linear polymer composed of glucose units joined together by β-1,4 glycosidic bonds, see Figure 3. Cellulose has a strong tendency for intra- and intermolecular hydrogen bonding, which leads to the formation of microfibrils with excellent mechanical

properties. According to Hinterstoisser et al. (2001) the carbon-oxygen-carbon bonds in addition to hydrogen bonds are the ones deformed when cellulose molecules are mechanically loaded.

The degree of polymerization, DP, or the number of glucose units in a cellulose chain of a native softwood fiber is above 10000, dropping in chemical pulping to around 500-2000. Mechanical treatment of fibers has very little effect on the DP.

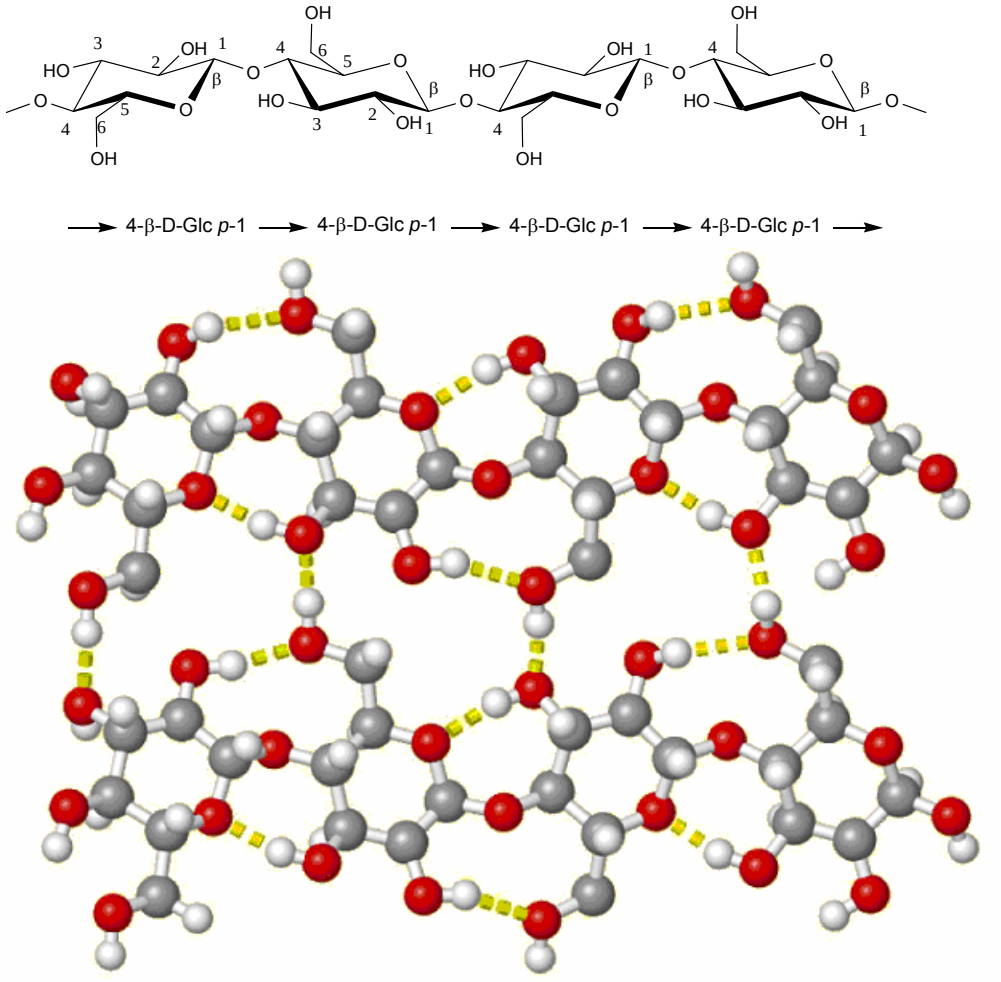


Figure 3. Chemical structure of cellulose and the hydrogen bonding pattern of cellulose Iα (Horton et al. 2001).

There are two different crystalline forms of native cellulose, cellulose I, designated as Iα and Iβ (Atalla and VanderHart 1984). The two differ in hydrogen bonding pattern. Physical bending of microfibrillar cellulose can cause an interconversion between the forms (Jarvis 2000). The proportion of Iα and Iβ

forms depends on the cellulose origin. Primary walls of conifer tissue contain more cellulose Iα, secondary walls more cellulose Iβ (Kataoka and Kondo 1998).

There are other crystalline forms of cellulose, such as cellulose II, but also other forms have been characterized. These forms do not exist naturally, but can be obtained from cellulose I by different chemical treatments. In chemical pulping some conversion of cellulose I into cellulose II may occur locally (Mohlin et al. 2003). According to Mohlin et al. (2003), these other forms are mechanically inferior to cellulose I, which can by seen from the Figure 4. As the relative amount of cellulose I decreases, the zero-span tensile strength also decreases.

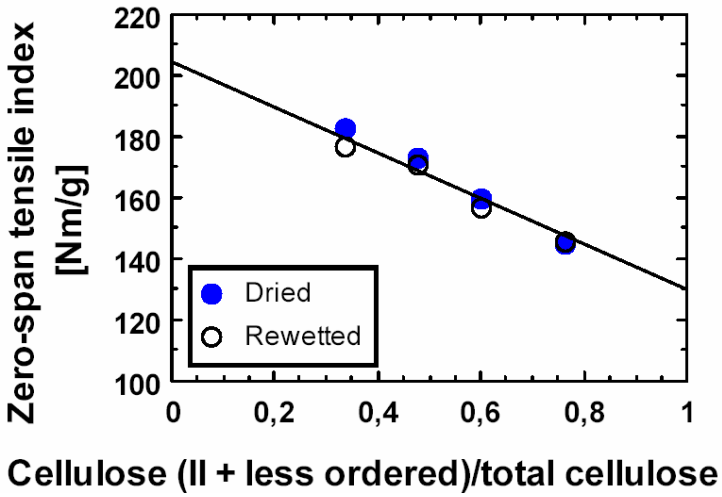


Figure 4. Zero-span tensile index of laboratory cooked unbleached kraft pulp was reduced when the Cellulose II content was increased by merceration. The slope of the line drawn agrees with the expected slope based on the differences in elastic modulus (Mohlin et al. 2003).

The next larger structural unit from single cellulose chains is elementary fibril or microfibril, which consists of 30-40 parallel cellulose chains. A microfibril with 36 chains would have dimension of around 3.5*3.2nm, but also smaller ones have been reported (Paavilainen 2002). Microfibrils again aggregate into what are called fibrils or fibril aggregates, with the size of around 20nm. Microfibrils have excellent but naturally anisotropic mechanical properties, the elastic modulus in chain direction being approximately 140 GPa depending on the measurement method (Mark 2002). Fibril cross-direction moduli are about 1/3 or 1/10 of the

chain direction values measured respectively parallel or normal to cellulose chain sheets.

Whether some cellulose in fibrils exists in amorphous form in fibrils is still an open question. One model that would seem plausible suggests that microfibrils consist of crystalline structure, but some disorder is present in fibril surfaces. These disorders would come in the form of distortions, twists and strained sections as presented by Rowland and Roberts (1972), see Figure 5.

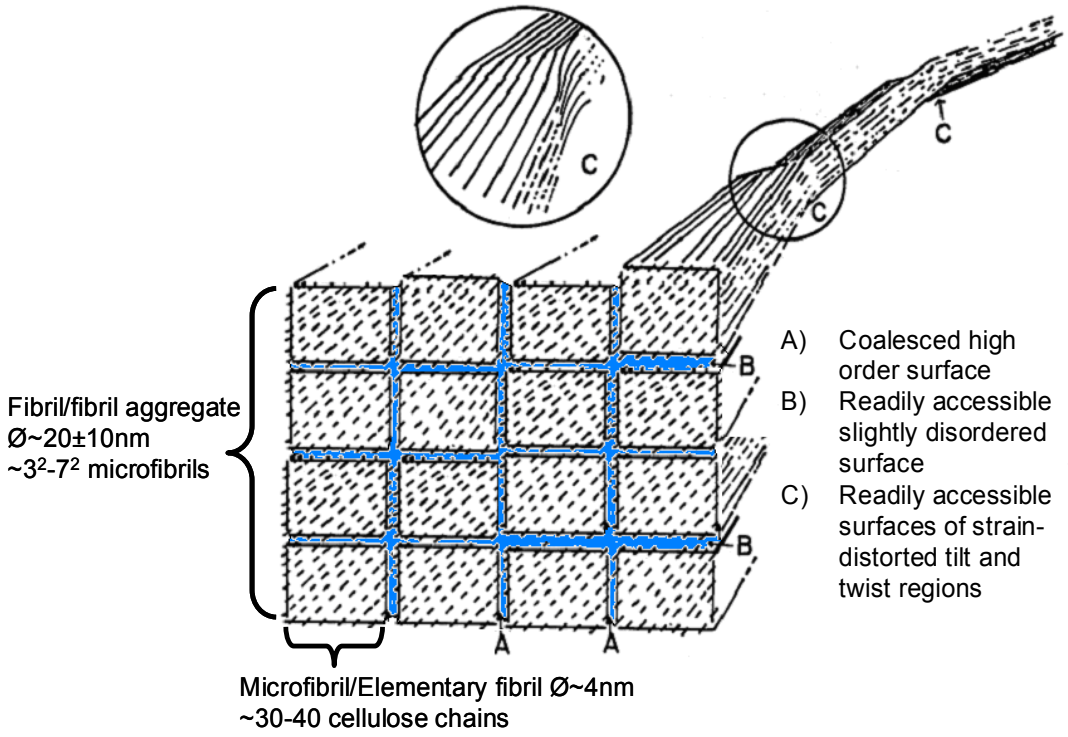


Figure 5. Approximate sizes of microfibrils and fibrils in wood pulp fibers and a theory of cellulose crystallinity according to Rowland and Roberts (1972). Figure adapted and modified from Rowland and Roberts (1972).

In unprocessed wood the mean cellulose aggregate side length has been measured to be around 18nm, where as in chemical pulp the measure was slightly larger (Fahlén and Salmén 2003). According to Fahlén and Salmén, cellulose aggregates increase in size at the initial phase of kraft cooking. This was caused by the thermally induced rearrangement of the cellulose molecules.

Bardage et al. (2004) analyzed Norway spruce kraft pulp samples using transmission electron microscopy and image analysis. They found S1 and S2 layers to contain a wide range of microfibril/aggregate sizes. A significant number of aggregates of a size of 18-20nm was found. This would suggest that there is a tendency of 4^2 to 5^2 (in aggregate cross-section) microfibrils to aggregate into larger units.

Duchesne and Daniel (2000) measured the development of Norway spruce fiber surface in kraft cooking by using field emission-SEM, allowing the determination of surface aggregate size distribution. Mean aggregate widths, with significant variation, increased as the cook proceeded, from 16nm after 19 minutes to 20nm after 266 minutes. The sizes of the aggregates are larger and more compact the less hemicelluloses there are left after kraft cooking (Duchesne et al. 2001).

The mechanical properties of polymers, like cellulose, are visco-elastic, i.e. time-dependent. Thus cellulosic fibers exhibit visco-elastic behavior. Visco-elasticity of polymers is due to Van der Waals forces (Andersson 1995). Especially the time dependence of polymer stiffness is dependent on these forces. If strain rates are lower, molecules have sufficient time to move in relation to one another. When the strain rate is increased, forced molecular motion produces friction, which leads to higher stresses required for material to deform. In addition to time, polymer properties are also dependent on moisture and temperature. The influence of moisture and temperature on the viscoelastic properties of cellulose has been studied by Berger and Habeger (1989) and Berger et al. (1989). Stiffness of various cellulosic materials decreased with increasing moisture and temperature.

Cellulose fibrils are the load carrying elements in fibers. Gurnagul and Page (1989b) have suggested that also the main components influencing the viscotic response of fibers are the cellulose fibrils. This conclusion was based on testing of the zero-span strength of various chemical and mechanical pulps using different loading rates. The rate-dependence was very similar between fibers having different chemical composition.

3.2 Hemicelluloses

As shown in Figure 1, hemicelluloses constitute about 25-40% of wood material. Hemicelluloses are polysaccharides with a DP of 50-300. Hemicelluloses found in hardwoods are different from those found in softwoods. The major hardwood hemicellulose is a partially acetylated 4-O-methylglucurono xylan with a minor proportion of glucomannan also present. Partially acetylated galactoglucomannans are the most common softwood hemicelluloses. Xylan is also present in softwood, where it is substituted by furanosidically linked arabinose units in addition to 4-O-methylglucuronic acid groups (Whistler and Chen 1991).

High hemicellulose content in fibers may in some cases be beneficial for the recycling purposes, since according to Oksanen et al. (1997) it may lead to lower tendency to hornify in drying. Higher hemicellulose content of kraft pulps may also lead to a more porous surface structure of kraft pulp fibers (Duchesne et al. 2001).

The contribution of hemicelluloses to fiber strength has been widely discussed and is not entirely clear. Spiegelberg (1966) studied the contribution of hemicelluloses to single holocellulose fiber strength. He found that as the amount of hemicelluloses decreased, so did the tensile strength, elastic modulus and work-to-rupture of fibers. According to Spiegelberg, xylan is the most significant hemicellulose from the fiber strength perspective. Also Sjöholm et al. proposed that the removal of xylan from hardwood may decrease fiber strength (2000). Hemicelluloses in fibers allow fibrils to flow and organize more favorably when fibers are dried (Kim et al. 1975). This reduces fibrillar angle and straightens dislocations and other potential weak spots. According to Kersavage (1973) hemicelluloses act as an effective stress-transfer matrix, especially in moist fibers with moisture content around 10%. When fibers become wetter, the matrix starts to considerably lose stress transfer ability. The same applies when fibers become drier but the effect is not that drastic. Liitiä et al. (2005) have speculated with the relationship of glucomannan solubility to fiber strength. According to them mechanical damage to fibers may destroy interactions between cellulose and glucomannan. This would impair the stress-transfer matrix.

Surface hemicelluloses seem to affect significantly the formation of fiber-fiber bonds. Schönberg et al. (2001) studied the role of xylan in spruce kraft pulp

fibers. The location and the charge of xylan greatly influenced the formation of inter-fiber bonds. Sjöberg et al. (2004) found some correlation between the amount on surface hemicelluloses and pulp handsheet tensile strength, but not with the amount of internal hemicelluloses and handsheet tensile strength.

There is evidence that hemicelluloses really affect fiber strength, and we believe that they might. One way or another, hemicelluloses do affect the strength of the final fiber network formed, even if they did not have an effect on single fiber strength. This is due to the hydroxyl groups in hemicelluloses that are connected to the swelling of wet fibers (see chapter 3.5 Pore structure and swelling). Swelling itself can maybe internally organize a fiber favorably, but the main effect comes when a wet fiber network is dried. Swollen fibers shrink in drying, and while doing so activate segments in other fibers connected via inter-fiber bonds. This has a favorable effect on the fiber network strength properties, and the more swollen the fibers are, the more favorable the effect. This phenomena can be associated with the Jentzen-effect (Jentzen 1964), the improvement of single fiber strength properties when dried under tension. In connection to the above discussed positive effects of surface hemicelluloses, it might be possible that higher surface hemicellulose content leads to higher surface swelling, which leads to stronger inter-fiber bonds (Forsström et al. 2005b), but this increase in surface swelling is not significant to total fiber swelling and corresponding shrinkage in drying, and is thus not seen as improved activation.

3.3 Lignin

Around 15-30% of wood fibers are composed of lignin, see Figure 1. Its role is to act as cement between fibers and as a stiffening agent within fibers (Goldstein 1991). It also serves as a barrier to the enzymatic degradation of the cell wall. Lignins consist of phenylpropane units and form very complicated structures, Figure 6. Softwood and hardwood lignins differ in methoxyl content and in the degree of cross-linking. Lignin is largely removed in chemical pulping, making wet fibers porous and flexible. Ander et al. (2003) recently claimed that delignification does not affect the tensile stiffness of fibers, but does affect tensile strength probably due to formation of discontinuities (dislocations, pores) in cooking. Lignin is also responsible for most of the color of papermaking fibers. Different

pulp bleaching methods either remove lignin and/or change its structure so that fibers become brighter.

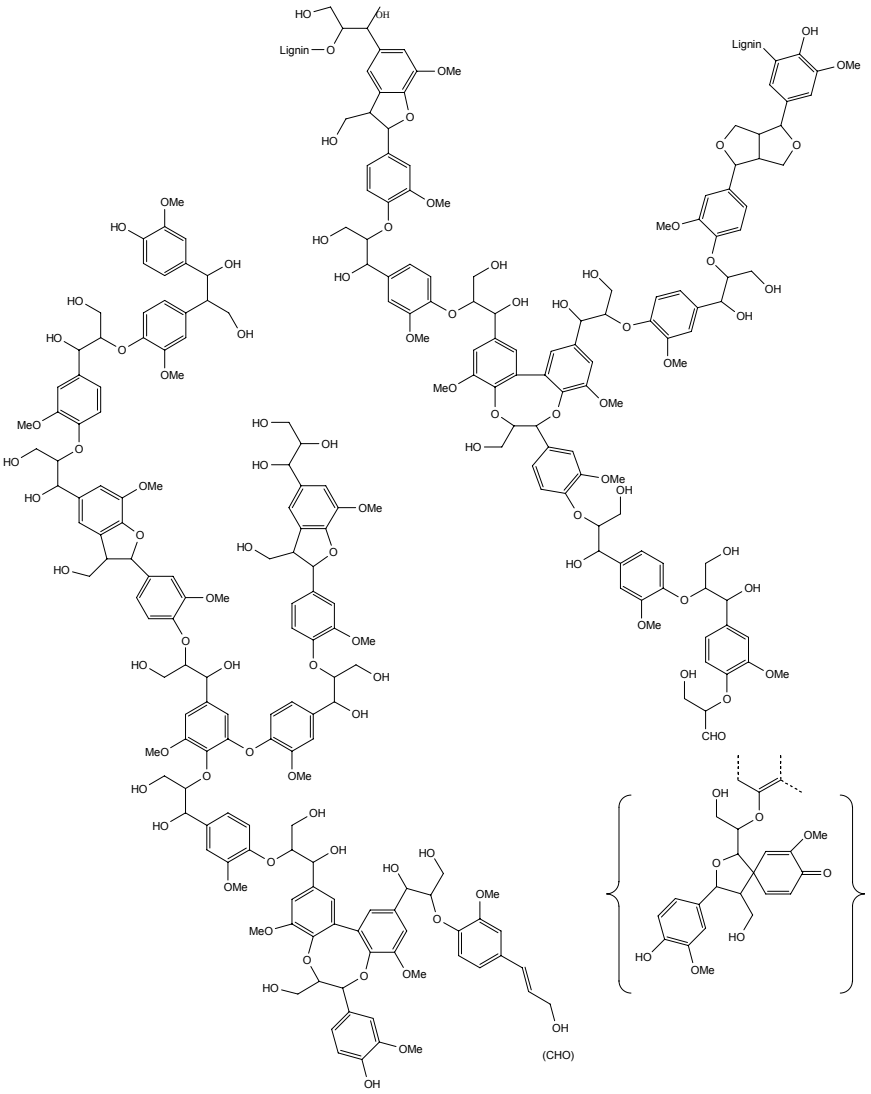


Figure 6. The structure of lignin according to Brunow et al. (1998).

3.4 Fibrillar angle

Since S2-layer constitutes most of the fiber and has the largest amount of cellulose, its microfibrillar angle (MFA) has a great influence on the mechanical properties of fibers. If the S1-layer is still present and relatively intact after pulping and subsequent operations, fibers' mechanical properties are not solely dominated by the S2-layer (Mark 2002). However, in general, the lower the microfibrillar angle, the stronger and stiffer a fiber is. With low MFAs fibrils and cellulose chains are loaded in the direction of cellulose chains when tension is applied in fiber length direction. When the MFA increases, the fibrils are loaded more and more to their cross-directions, which have inferior mechanical properties compared to the chain direction. Figure 7 presents results from one study of how the tensile stiffness of individual fibers is affected by the MFA. Also Reiterer et al. (1999) measured a strong decrease in tensile strength and tensile stiffness and a significant increase in fiber breaking strain as a function of increasing MFA.

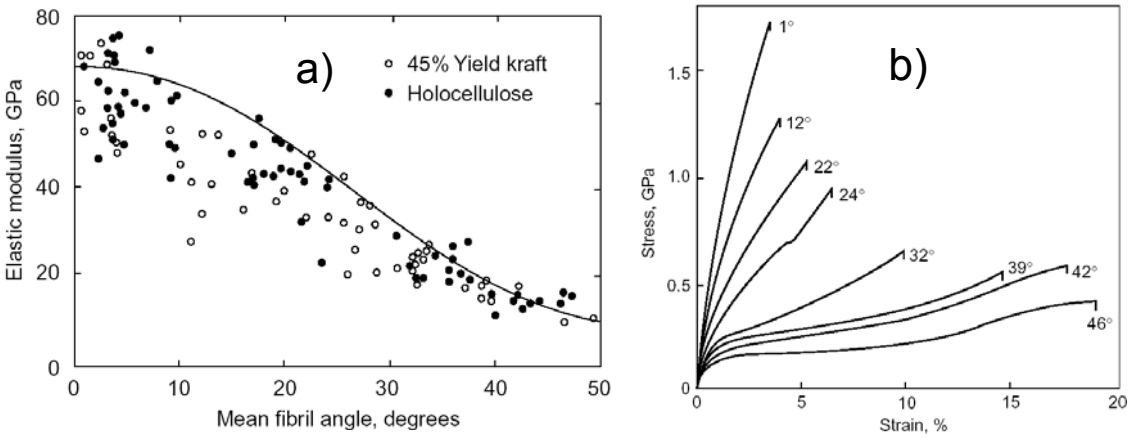


Figure 7. a) Elastics modulus of fibers vs. the fibril mean angle of the S2-layer. The solid line gives a theoretical prediction (Page et al. 1977). b) Load-elongation curves for 45% yield black spruce fibers at different fibrillar angles (Page and El-Hosseiny 1983).

Low MFA makes fiber stress-strain curves almost linear, at higher angles one can observe significant non-linearity. This has been shown by Page and El-Hosseiny (1983), see Figure 7b. Hill (1967) tested the creep properties of longleaf pine

holocellulose fibers. He found that when fibers are subjected to tension for time periods of 12-48 hours, fibrillar orientation towards fiber axis increases (MFA decreases). This leads to increased fiber strength and elastic modulus.

As do many other fiber properties, MFA varies between fibers from a same tree. Latewood fibers usually have slightly lower MFA than earlywood fibers (Paakkari and Serimaa 1984), though opposite views are also presented (Lichtnegger et al. 2000). MFA also varies between growth rings. X-ray diffraction measurement of Norway Spruce by Serimaa et al. (2000) revealed MFAs from 20° to 40° in the five first growth rings counting from the pith. In growth rings farther from the pith the MFAs were from 6° to 10°. Similar values are measured by Lichtnegger et al. (2000), even measuring MFAs very close to 0° for some earlywood fibers.

3.5 Pore structure and swelling

The cell walls of dry cellulose fibers are quite non-porous (Stone et al. 1966). The entry of water into fibers causes debonding and separation of the solid elements (Scallan 1983). Thus in wet state cellulose fibers, whether native or processed, have a porous structure (Stone and Scallan 1965). The porosity has a large effect on fiber swelling, a relevant property to fibers' ability to build strong networks. In chemical pulping material is removed from cell walls, resulting in fibers that have a more porous structure compared to native fibers. Porosity is also introduced into fibers in mechanical treatments like refining.

Fiber swelling is also affected by fiber charge (Scallan 1983). The water swelling the fibers attaches itself mainly to hydroxyl groups found in cellulose and hemicelluloses. Cellulose and hemicellulose absorb up to 4-5 times more water than lignin at water saturated conditions at temperatures around 20°C (Cousins 1978).

The form of the counter ions of the anionic groups within the fiber wall is very significant to fiber swelling (Scallan 1983). Changing the counter ions changes fiber swelling. Since the degree of swelling is also dependent on the mechanical properties of the fiber wall, adjusting the degree of swelling by changing the counter ions can also be used to determine the elastic properties of the fiber walls (Scallan and Tigerström 1992). The connection of fiber swelling and the counter ions is due to a dependency of the osmotic pressure inside the fibers on the

number of ions in water close to acidic groups (Scallan 1983). Water is sucked into fibers to dilute the solution and reduce this pressure (Scallan 1983). This again breaks intra-fiber bonds and causes fiber swelling. Forsström et al. (2005b) pointed out that changing the counter ion of the carboxyl groups changes the surface swelling properties of fibers but flexibility is only moderately affected.

Counter ions and surface charges also influence many paper making properties of fibers. These effects have been discussed in a review by Lindström (1992). In one recent study changing the counter ion from Na^+ to Ca^{2+} or into acidic form lowered the bond strength between fibers by more than 50% (Forsström et al. 2005b).

There exist two often used methods for measuring fiber swelling and its ability to retain water, WRV, water retention value, and FSP, fiber saturation point. The two do not always give consistent results. The differences have been discussed amongst others by Scallan and Carles (1972) and Forsström et al. (2005a). The differences can be attributed to measurement procedures. The WRV measurement is more sensitive to changes in fiber surface than FSP (Forsström et al. 2005a)

The pore size distribution of mechanical and chemical fibers was studied by Berthold and Salmén (1997) by using ISEC, inverse size-exclusion chromatography. Pores in untreated TMP fibers were relatively small. Unbleached kraft fibers showed a larger proportion of larger pores while the proportion of smaller pores decreased compared to TMP fibers. Bleaching drove the same effect further. Similar phenomena were observed by Maloney and Paulapuro (1999). Their studies used thermoporosimetry to show that only micropores exist in wood and mechanical pulp fibers. During mechanical pulping micropores, but not macropores, are created. Also at the early stages of kraft pulping the volume of micropores increased, macropores were created through the whole cooking process. Treimanis (1996) pointed out that the rate of pore formation depends on the delignification method.

When water is removed from the pores of kraft pulp fibers, larger pores with magnitudes in the micrometer class lose their water first, followed by smaller pores in the nanometer class (Topgaard and Söderman 2002). In drying of fibers some pores are closed, and cannot be reopened by refining fibers (Wang et al. 2003). A schematic illustration of what happens to pore structure according to

Wang et al. in drying and in subsequent refining is given in Figure 8. The model would suggest that aggregation of microfibrils occurs in drying. However, recent investigations by Fahlén (2005) with holocellulose fibers show that no aggregation occurs in drying, so pore closing in drying is not related to aggregation. With holocellulose fibers refining also closed pores (Fahlén 2005).

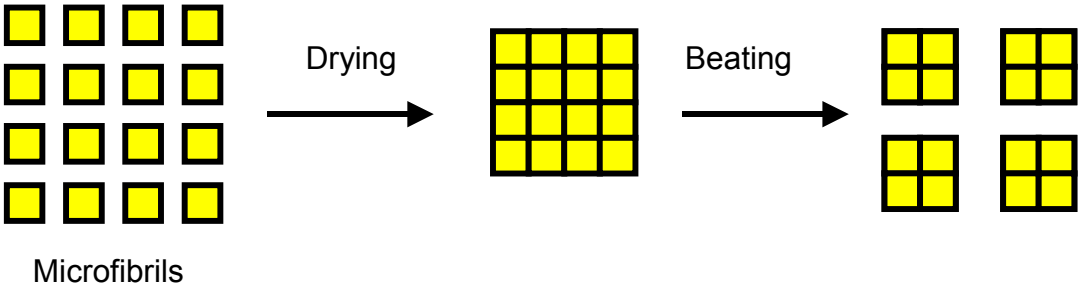


Figure 8. A schematic illustration of possible changes in pore structure resulting from beating previously dried pulps (After Wang et al. 2003).

Forsström studied the influence of pore structure and the water retaining ability of unbleached kraft pulp fibers on different paper strength properties (Forsström et al. 2005a). The pore structure was determined with NMR relaxation measurements and the water retaining ability with WRV and FSP measurements. WRV changes at different pulp yields were associated with changes in the water associated with fiber surfaces. Generally larger pore radii led to a higher tensile index of pulp handsheets. However increased yield led to smaller pores and increase in tensile index, which might be due to smaller fiber damage.

3.6 Fiber morphology

Morphological properties include fiber length, fiber width and cell wall thickness. These vary a lot between wood species, within annual growth rings, different stem parts and are also affected by the growing conditions (Paavilainen 2002). Some variation in the fiber thickness in a pulp is illustrated in Figure 9a. Variation in Scots Pine fibers from saw mill chips has been measured by Ekenstedt et al. (2003), Figure 9b. Some morphological properties of different papermaking fibers are presented in the Table 1.

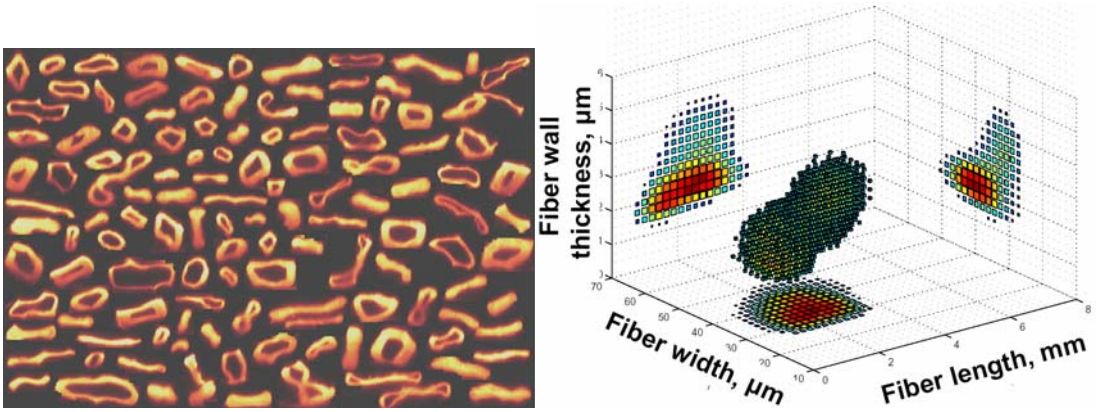


Figure 9. a) A CLSM image of TMP fibers showing variation in fiber wall thickness. Figure courtesy of KCL. b) Variation in morphological properties of Scots Pine saw mill chip fibers (Ekenstedt et al. 2003).

In a single pulp the morphological properties between fibers vary a great deal. One can ask, what is actually the most representative single value to represent some morphological property. For example the fiber length affects the tensile strength, breaking strain and fracture toughness of dry paper, and is especially important for wet web strength (Retulainen et al. 1998). Jang and Seth (2004) have argued recently that mass weighted mean fiber length is the most relevant pulp fiber length measurement over arithmetic mean or length weighted mean fiber lengths.

Table 1. Some morphological properties of typical pulpwood fibers (Peel 1999).

English name	Latin name	Length, mm	Width, μm	Cell wall thickness, μm	Fiber coarseness, mg/m
Softwoods					
Balsam fir	Abies balsamea	3-3.5	28-35	2.1-3	0.22-0.25
Scots pine	Pinus sylvestris				
Norway spruce	Picea abies				
Lodgepole pine	Pinus contorta				
Black spruce	Picea mariana				
White spruce	Picea glauca				
Loblolly pine	Pinus taeda	3.5-4.2	35-40	2.6-4.2	0.29-0.48
Slash pine	Pinus elliottii				
Longleaf pine	Pinus palustris				
Shortleaf pine	Pinus echinata				
Douglas fir	Pseudotsuga taxifolii				
Western hemlock	Tsuga heterophylla				
Radiata pine	Pinus radiata				
Hardwoods					
Birch	Betula pendula, Betula papyrifera	1.0-1.2	18-30	2-4	0.08-0.11
Beech	Fagus sylvatica, Fagus grandifolia	1.0-1.3	16-29	3-5	~0.12
Eucalyptus	Eucalyptus globulus, grandis, etc.	0.9-1.0	11-13	3	0.05-0.08
Poplar, aspen	Populus spp.	1.0-1.2	10-35	~4	
Others					
Cereal straws	Various	~1.5	8-18	~4	
Bamboos	Various	1.8-2.8	~14	3-9	
Bagasse	Saccharum officinarum	1.8-3	20-30		
Cotton rags	Gossypium herbaceum	20-40	25-30	4-7	

3.7 Fiber deformations, damage and defects

In pulps fibers are rarely straight but have some degree of curl. In wood fibers are relatively straight, but some deformations may exist due to growth stresses (Kibblewhite 1977, Nyholm et al. 2001). In industrial pulping, fiber curl, deformations and damage can originate from a number of sources like chipping, defiberization, medium-consistency unit operations and hitting the turns in pipe lines (Abitz 1991, Bennington and Seth 1989, Seth and Bennington 1995, McLeod et al. 1995, Tikka and Sundquist 2001). These treatments may lead into lower pulp strength. Fiber deformation often occurs simultaneously with fiber damage, but deformation and damage are two different phenomena. Fiber deformation can be beneficial to some paper properties, but fiber damage is usually something to avoid. Fiber deformations influence the fiber network properties (Page and Seth 1980). They affect the tensile strength and the bonding ability of fibers in a network. A large part of fiber deformations are removed in pulp beating, and the strength properties return close to those of the undeformed pulp (Kibblewhite 1976, Mohlin and Alfredson 1990, Seth 2001). The morphological properties of the fiber wall affect the development of fiber deformations. For example, medium-consistency fluidization induces more curl and microcompressions in thick-walled fibers than in thin-walled fibers (Seth and Bennington 1995). Page and Seth (1980) have illustrated the effect of fiber curl and dislocations on the stress-strain behavior of fibers in a network, Figure 10.

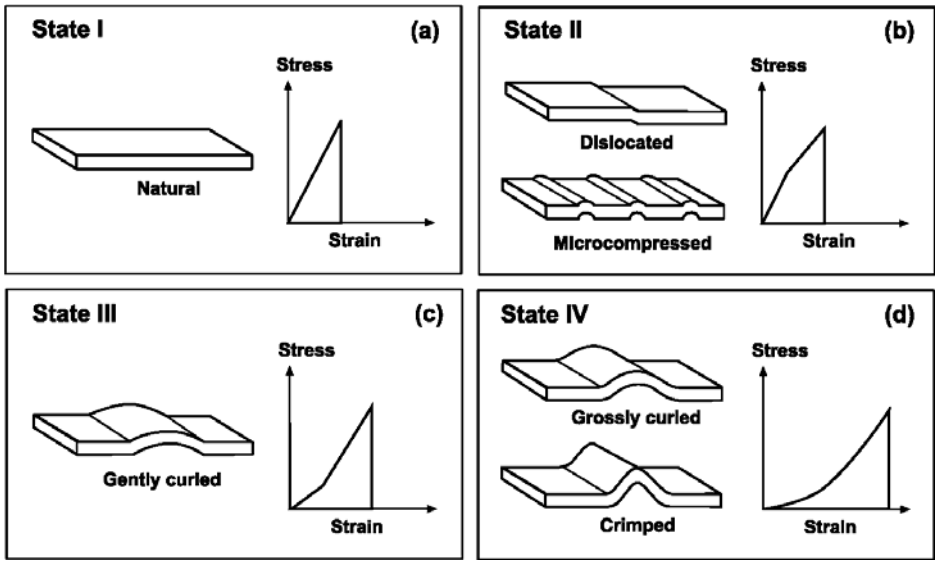


Figure 10. Various states of fibers and the corresponding stress-strain curves (Page and Seth 1980).

The use of curly fibers in papermaking will lead to low tensile index, but may also lead to high tear-index (Page et al. 1985a, Seth and Page 1988). This was also observed in publications IV and V and has been explained by the uneven distribution of stresses along the length of a curled fiber in a fracture zone (Page et al. 1985a). More specifically, curly fibers are more likely to be pulled out instead of failing in the tear-test. This pull-out consumes more energy than fiber failure (Anon. 1944). Curly fibers also tend to form sheets having a lower elastic modulus but higher stretch than sheets made from straight fibers (Page et al. 1979, Page and Seth 1980, Fellers et al. 2001).

Compared to fiber curl, fiber kink can be described as a sudden change in the direction of the fiber axis. The fiber kink is calculated as part of fiber curl, but it has a different effect on paper properties. Kinks affect the wet strength and wet rupture energy of the pulp (Pihlava 1998). Curl and kink are illustrated in the Figure 11.

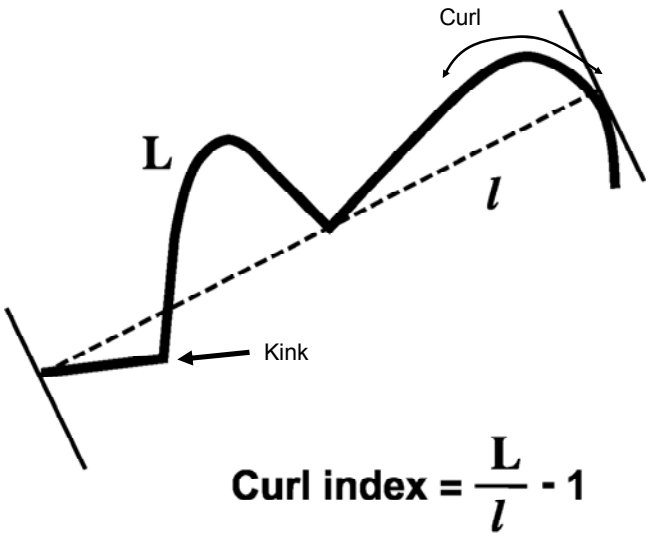


Figure 11. Illustration of fiber curl and kink. Curl index according to Page et al. (1985a).

Fiber dislocations are parts of the cell wall where the alignment of the microfibrils is locally disturbed (Page et al. 1985a). A fiber lacking dislocations is rigid, but already a small number of dislocations can significantly reduce the bending stiffness of fibers. Some delamination occurs in the dislocated regions, which partly explains the decrease. When a fiber containing dislocations bends, it forms

a polygon rather than a continuous curve (Hartler and Nyren 1968, Hartler 1995). Similar to fiber curl, the presence of dislocations reduce the elastic modulus of the sheet (Page et al. 1979). Dislocations can become weak sites in the fibers, defects in fracture mechanics sense, reducing the strength of the individual fibers, thus leading to a decrease in average effective fiber length (Hartler and Nyren 1968, Hartler 1995, Mott et al. 1995). It has also been suggested that an increase in the number of dislocations increases the tear strength and stretch while decreasing bonding strength through creation of discontinuities that act as points of bond failure in stressed fiber networks (Kibblewhite 1976).

The definition of fiber damage is not as clear as that of fiber deformation. If desired, some degree of separation can also be made between fiber damage and fiber defects. In fracture mechanics sense, any discontinuity or anomaly from a normal structural pattern (a fiber with totally intact ordered ultrastructure) can be considered a defect (or damage). It is possible that even though no visible defects are present in fibers, they still may be damaged because their internal structure is disordered compared to undamaged fibers (see chapter 10.1). This leads to impaired internal stress-transfer between fibrils, thus leading to weakened fibers.

The fiber damage can be a result of chemical degradation during pulping, but it may also arise from mechanical treatment. Defects can also be natural. Fiber pits are often considered to be such defects, but Iribarne suggests otherwise (Iribarne 2002). The evidence gathered by Iribarne indicates that areas where fibers have been located adjacent to ray tissues are the most common natural defects in fibers.

Fiber damage is usually seen as a reduction in strength of the dry or wet fibers and fiber networks. The effect of fiber damage is often difficult to determine, since several other factors also affect fiber network properties. According to Mohlin et al. (1996), reversible deformations can be removed by PFI beating while irreversible damage cannot. They also suggested that irreversible damage could be defined as the difference in zero-span tensile index between undamaged and damaged fibers after they have been straightened by beating.

It must be noted that visible defects do not necessarily much lower the strength of dry fibers. However, the situation changes when fibers are wetted. A clear decrease in strength of wetted fibers as a function of defects has been reported by Mohlin et al. (2003), see Figure 12, as also concluded by Gurnagul and Page

(1989a). Some discussion whether the drop in the zero-span tensile measurement is actually due to de-bonding of fibers is presented in chapter 9.1. The changes moisture content in general can increase or decrease fiber strength depending on the fiber structure and the level of moisture (Leopold and Thorpe 1968, Kersavage 1973).

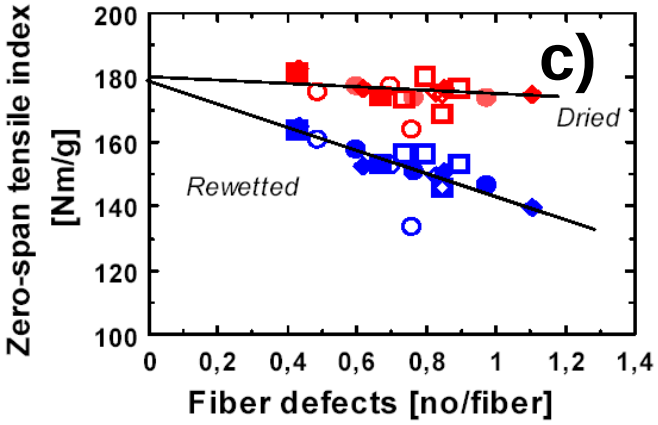


Figure 12. Effect of fiber defects to zero-span tensile strength according to Mohlin et al. (2003).

4 FIBER STRENGTH MEASUREMENTS

In the field of pulp and paper science it is a commonly known problem that measuring the strength of single fibers is a tedious task. Studies around measuring single fiber strength can be divided into three categories based on the measurement method:

1. Tensile testing of single fibers using suitable tensile testers

2. Single Fiber Fragmentation (SFF) tests where a number of fibers are embedded in resin. After curing this sample is strained stepwise in a tensile tester and fiber breaking strains are determined from images taken after each step.

3. Zero-span tensile strength, where paper or pulp handsheet sample is strained to failure between very closely located clamps, which have a nominal zero span-length.

These tests are discussed further in the following subchapters.

4.1 Tensile testing of individual fibers

Testing individual fibers is a very tedious task. Still, an extensive amount of single fiber strength testing with specifically tuned tensile testers was done from the 1960's to early 1980's (Duncker and Nordman 1965, Ehrnrooth 1982, El-Hosseiny and Page 1975, Hardacker 1970, Hardacker and Brezinski 1973, Kersavage 1973, Kim et al. 1975, Leopold and Thorpe 1968, Page and El-Hosseiny 1976, Page et al. 1972, Page et al. 1977). The issue continues to be relevant, and also recent papers are published on the subject. For example, Mott et al. (2002) measured the mechanical properties of individual southern pine fibers. For the elastic modulus of earlywood fibers the value of 14.8 GPa was measured, the corresponding tensile strength being 604 MPa. For latewood the values were 33% and 73% higher. The difference was attributed to microfibril angle and pitting. Stress-strain curves exhibited significant non-linearity when fibers were from annual growth ring 5 and 10. The non-linearity decreased towards the top of the tree. The non-linearity can be attributed to microfibrillar angle (Page and El-Hosseiny 1983), as discussed previously.

Burgert et al. (2003) point out that measuring the strain of the fibers when individual fibers are tested is much more difficult than measuring force. Therefore they presented a system where the strain is determined using an optical video system. Dunford and Wild (2002) presented an apparatus to measure the cyclic transverse compression of single pulp fibers. For each load cycle apparent elastic modulus and mechanical loss coefficients are obtained. Interestingly, the apparent transverse elastic modulus increased in cyclic loading. This and other observed changes were attributed to physical and chemical changes occurring in fiber wall, but no details of the nature of these changes were given.

4.1.1 Statistics of individual fiber strength

Being natural and not artificial, two individual fibers are never exact copies of one another. Therefore, one may also expect variation in fiber strength measurements.

The Weibull-distribution, the simplest form given in Eq.(1), is often used to describe the variation in material strength. It has also been applied in the context of fiber strength distributions of Single Fiber Fragmentation tests (Andersson et al. 2002). There exists 3- and 2-parameter versions of the distribution, of which the 2-parameter version is considered here. The parameter β in Eq.(1) can be thought to be a scale parameter, revealing the strength level of the material in question, where as the parameter α, Weibull-modulus, describes the variation. The lower the value of α, the more variation there is in the strength of a material.

$$F(s_{fiber}) = 1 - e^{-\left(\frac{s_{fiber}}{\beta}\right)^{\alpha}} \qquad (1)$$

$$\ln\left(\ln\left(1 - F_{\exp}(s_{fiber})\right)^{-1}\right) = \alpha \ln(s_{fiber}) - \alpha \ln(\beta) \qquad (2)$$

If one rearranges Eq.(1) and takes twice natural logarithms of both sides, and replaces the cumulative distribution function $F(s_{fiber})$ with one that has been experimentally measured, say $F_{exp}(s_{fiber})$, Eq.(2) is obtained. This equation is used in so called Weibull-plots. Plotting the left side of the Eq.(2) against $\ln(s_{fiber})$ should be linear if the data follows the Weibull-distribution. Using Eq.(2) is also one way to determine α (and β) using linear regression.

Page and El-Hosseiny (1976) have measured the strength distributions of individual fibers. Some re-plots of their data are presented in Figure 13. Measurements of single fibers from the same pulp do not give consistently same values because of significant variations in fiber structures.

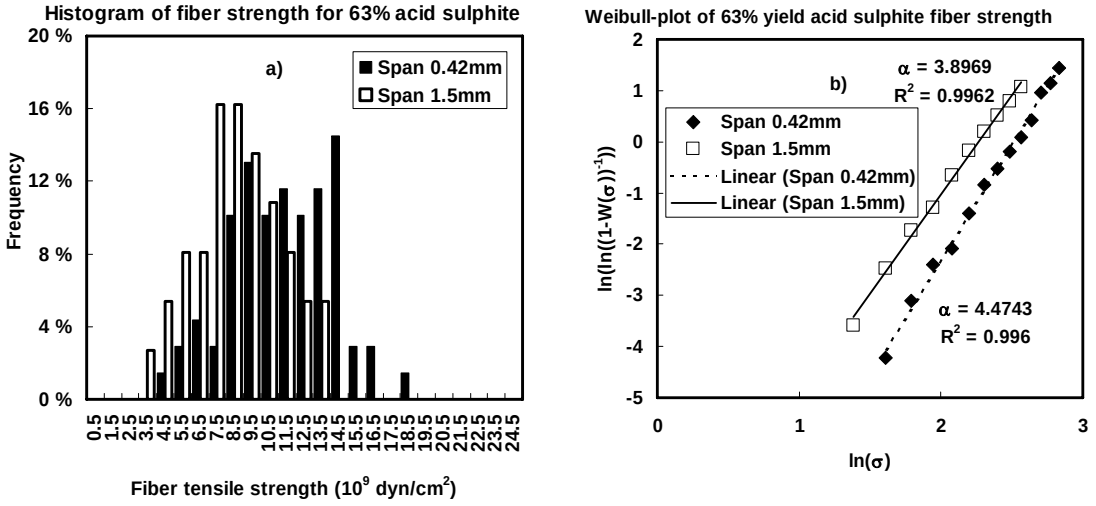


Figure 13. a) Strength distribution of 63% yield acid sulphite fibers from Page and El-Hosseiny 1976. b) Corresponding Weibull-plot.

In fracture mechanics defects, or exceptions from uniform structure are sites where failures initiate. Page and El-Hosseiny (1976) measured fiber strength distributions with two different span-lengths, and used the weak-link theory presented by Peirce (1926) to predict the strength of the longer span from the shorter span with excellent results. Peirce weak-link theory was also applied by Hardacker (1970). If one extracts the data from the histograms published by Page and El-Hosseiny (1976) and plots them in Weibull-plots, Weibull shape parameter values from 2.9 to 4.5 are received. These are on the same magnitude level as those measured by Andersson et al. (2002) and Ljungqvist et al. (2002).

In papers published from 1960's to 1980 as well as in the recent studies of Ander et al. (2003), the mean values of single fiber strength have been the main interest, not the strength distributions. A few papers present the measured distributions as histograms (Duncker and Nordman 1965, Hardacker and Brezinski 1973, Page and El-Hosseiny 1976). Hardacker and Brezinski (1973) found that fiber strength distributions could often be described with a log-normal distribution, but no more specific mathematical form for the single fiber distributions was found in the literature of this period.

4.2 Single Fiber Fragmentation test

Single Fiber Fragmentation test, or SFF, has been applied to measure the effect of different fiber properties to fiber breaking strain. The principle of the SFF-test is presented in Figure 14. SFF test gives subjective breaking strain distribution of fibers. This should not be directly convertible to fiber strength distribution because it does not reveal the strain-stress relationship of fibers. One can of course pick a suitable value for the tensile stiffness from the literature and assume that fibers are linear-elastic. Some arguments could be presented against this. First, fibers are linear-elastic only at very small fibrillar angles (Page and El-Hosseiny 1983). Tensile stiffness on the other hand is dependent at least on the strain rate and fibrillar angle. These would be needed to be determined for all the fibers. However, the SFF method gives at least some indication of the variation in fiber strength relatively easily.

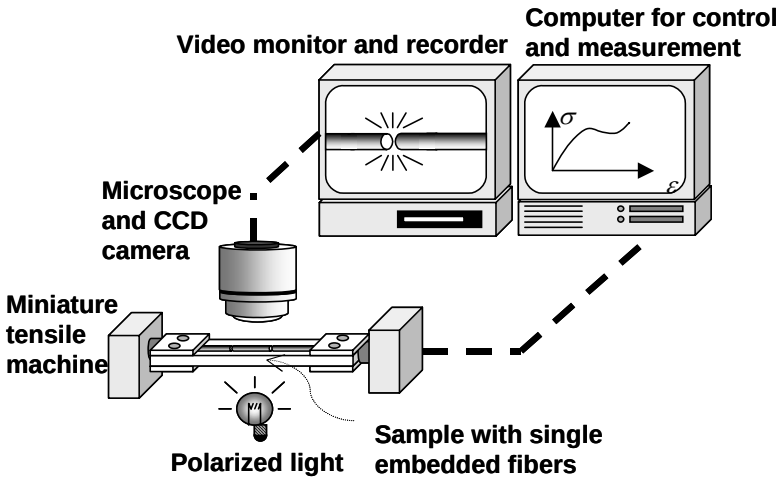


Figure 14. Equipment and principle for the Single Fiber Fragmentation test. Courtesy of Fredrik Thuvander, Karlstad University.

4.3 Zero-span strength

The zero-span measurement was first suggested in 1925 by Hoffman-Jacobsen. The measurement is carried out using a tensile tester in which a paper strip is clamped between two jaws that are practically in contact with each other so that there is no apparent gap between them, i.e. the span length is zero. Zero-span strength might be taken as a measure of fiber strength, if there is no stress transfer between fibers, i.e. network effects are absent. The concept of zero-span has been the subject of numerous studies and much controversy. A good review of zero-span measurement has been presented by Bronkhorst and Bennett (2002). Relating zero-span strength to actual fiber strength involves problems such as the application of load through shear in the clamps, prevention of lateral contraction, and the question of how many fibers carry the load and how uniformly. Figure 15 presents the principle of zero-span testing.

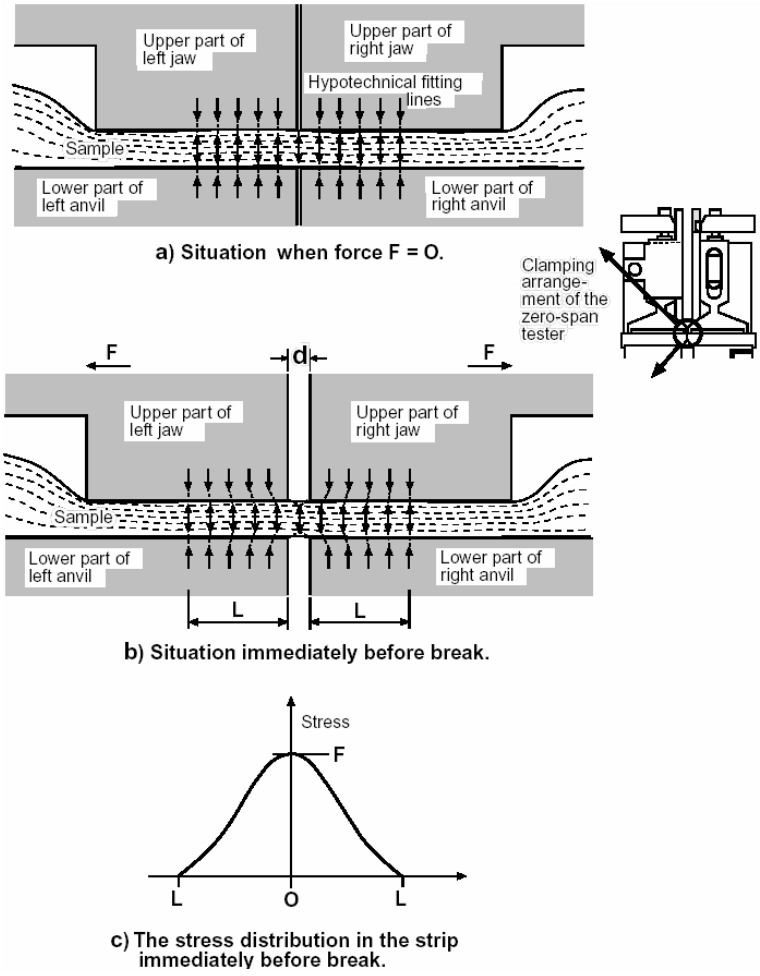


Figure 15. Principle of zero-span testing (Levlin 1999).

Short-span measurements are performed with the zero-span measurement device using very short but finite spans of the magnitude of 0.2-0.6mm. Increasing the span length causes decrease in the measurement values (Cowan and Cowdrey 1974) because network structure and fiber bonding become issues. Batchelor and Westerlind (2003) have developed a method of subtracting the displacement-load curve of the zero-span measurement from the short-span load-displacement curve to get the load-displacement curve of the free span. They point out that fiber properties measured from individual fibers are not necessarily the same as those measured from fibers in handsheets. For example drying stresses affect fiber properties. The method presented by Batchelor and Westerlind thus provides a more relevant measure of the fiber stress-strain characteristics.

Seth and Chan (1999) have demonstrated that zero-span results are greatly affected by fiber kinks and crimps, which must be removed before zero-span can be used as a representative value of fiber strength. Seth therefore recommends the use of refined straight fibers in the measurements, since low-consistency refining removes kinks and crimps. Mohlin et al. (1996) demonstrated a strong correlation between rewetted zero-span tensile index and the number of fiber deformations that change the direction of the fiber axis. However, it is shown in publication V that straightness itself is not an issue in the zero-span measurement, as curly defect-free fibers have the same zero-span strength as straight defect-free fibers. The span is so short that no significant straightening occurs.

The effect of inter-fiber bonding to zero-span strength has created a lot of discussion (Bronkhorst and Bennett 2002). According to Gurnagul and Page (1989a) and Seth (2001), inter-fiber bonding has very little to do with zero-span strength measurement. However, for example Iribarne (2005) disagrees with this. The results and analysis presented in this work support the argument that zero-span strength is very little if at all affected by inter-fiber bonding. Inter-fiber bonding however quickly becomes relevant when the span-length is increased.

Seth has shown that fiber length does not affect zero-span results. The model of El-Hosseiny and Bennett (1985) agrees with this, but shows that fiber length distribution has a significant impact if the span is increased. El-Hosseiny and Bennett estimate the actual span in a zero-span measurement to be 0.1mm.

Very little has been published on the mechanism in which the fibers fail in the zero-span test. For example, do the weakest ones fail first or do all fibers fail simultaneously? In the zero-span test load is gradually increased and spread to fibers, though likely not evenly (Hägglund et al. 2004). It is reasonable to think that fibers which are weakest and/or carry the highest load fail first. We have adopted this view in publication I.

Variations in a measurement can be illustrated with probability distributions. The distribution of zero-span values has been little studied. To the author's knowledge at the time of writing this, the only one to address the issue even marginally were El-Hosseiny and Bennett (1985), who applied the binomial distribution to describe the strength distribution in the zero-span measurement.

5 FIBER DEGRADATION

Fibers and cellulose may degrade chemically or mechanically. Degradation can be defined as a deleterious change in the chemical structure or physical properties. Joutsimo (2004) has recently shown that mechanical degradation, or damage, rather than chemical degradation in pulping lines is the major cause of fiber strength loss. However, the two may be connected. Mechanical damage to fiber introduces disorder into fibers, making them more susceptible for chemical degradation. In chemical degradation cellulose chains are clipped, degraded. Chemical degradations can be classified for example into acid hydrolytic, oxidative, alkaline, thermal and microbiological (enzymatic) degradation (McGinnis and Shafizadeh 1991).

5.1 Degradation patterns and conditions

Degradation may occur in two different modes. It can be heterogeneous or homogeneous. In heterogeneous degradation the degrading is strongly concentrated to certain location, where in homogeneous it is not. This is illustrated in Figure 16. It is also important to define the scale of the degradation phenomena studied. For example, even though the chemical reactions are the

same, it is important to consider whether one studies the degradation at the fiber level or at fibril level.

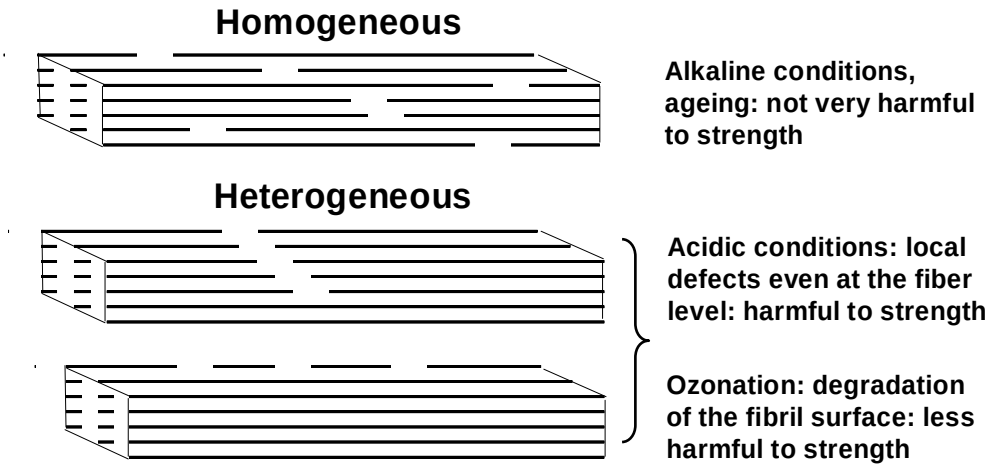


Figure 16. Illustration of homogeneous and heterogeneous degradation. Adapted from Berggren et al. (2003).

According to Berggren (2003) and Berggren et al. (2001, 2003), the cellulose degradation pattern depends on the conditions inducing the degradation. Thus, the same average cellulose chain length may result from, say, acidic or oxidative alkaline pulp treatment. However, in the case of acidic degradation, cellulose damage is localized at certain points, whereas alkaline degradation is more homogeneous throughout the cellulose fibrils. As a result of these different degradation patterns, acidic degradation is more detrimental to fiber strength when evaluated at the same average cellulose chain length. The effect of acid depends on the acid species, acid concentration, exposure time and temperature (de Souza Lima and Borsali 2004).

The effect of hydrolysis conditions and raw material on the acid hydrolysis of industrial pulps was studied by Håkansson and Ahlgren (2005). They found the leveling-off degree of polymerization (LODP) to be independent of reaction temperature, acid concentration and acid type. The intrinsic viscosity of the starting material altered by using Gamma rays affected the LOPD only a little. Gamma-rays cause homogeneous degradation of fibers (Sjöholm et al. 2000). Degradation induced by Gamma-irradiation thus occurs mainly at different locations than acid hydrolysis, which causes more severe degradation.

In the field of paper conservation it is very popular to study the effect of ageing on paper by accelerating the degradative reactions by exposing papers to warm and humid conditions for certain periods of time. Strlič et al. (2003) have demonstrated with pullulans, which have a structure comparable to cellulose, that this leads to homogeneous degradation. Zou et al. (1996a, 1996b) have studied the phenomenon and given a formula for the change in the degree of polymerization as a function of paper moisture content, temperature and activation energy. Barański et al. (2004) have applied the formula to various papers.

5.2 Measuring degradation

The extent of degradation can be measured by measuring the degree of polymerization, DP. However, one has to keep in mind that the degree of polymerization is not a good indication of fiber strength, particularly when two pulps from different origins are compared (Seth and Chan 1999, McLeod et al. 1995)

A popular way to measure the degree of polymerization is Size Exclusion Chromatography (SEC). SEC gives the distribution of polymer chain lengths in a given sample, from which different descriptive numbers can be calculated. A popular way to measure the DP in pulp and paper industry is to measure the intrinsic viscosity of pulps. Formulas have been given for converting the viscosity into DP (Immergut et al. 1953, Evans and Wallis 1989). Hemicelluloses may interfere the determination of cellulose DP. If SEC is used, statistical methods can be used to separate hemicelluloses from celluloses, as has been done for example by Vaaler et al. (2003). For the determination of cellulose DP from intrinsic viscosity in the presence of hemicelluloses, a method has been presented by da Silva Perez and van Heiningen (2002).

5.3 Cellulose degradation in pulping

In kraft pulping carbohydrates, celluloses and hemicelluloses, degrade. According to Page et al. (1985b), the more cellulose degrading the pulping process is, the more the strength of the received fibers deviates from their potential. However, because cellulose has higher DP and is crystalline, hemicelluloses are degraded to a larger degree. In alkaline pulping the most important reactions related to carbohydrate losses and reduction in their chain lengths are (Alén 2000):

- Dissolution of undegraded and degraded carbohydrate chains
- Deactelylation of acetyl groups in hemicellulose chains
- Peeling of different end units in carbohydate chains (primary peeling)
- Formation of alkali-stable end units in carbohydrate chains (the stopping reaction)
- Alkaline hydrolysis of glycosidic bonds in carbohydrate chains and the formation of new alkali-labile end units required for the peeling reaction (secondary peeling, chain-scission)

Agarwal and Gustafsson (1995) pulped holocellulose fibers at 170°C in 50g/L NaOH (liquid:wood, 9:1) for 40, 80 and 120min. Part of the samples were treated with borohydride to remove the reducing end-groups where primary peeling occurs. They suggested, based on the observation that after 40 minutes cooking the zero-span strength increased for samples that had not been borohydride treated, that primary peeling had beneficial effect on fiber strength. However, samples were compared at different yields and thus a more likely reason is the early removal of low DP hemicelluloses which causes a relative increase in the cellulose content of the fibers per unit mass. Thus neither primary nor secondary peeling had yet affected fiber strength, but the cellulose content of the tested fibers/handsheets had increased.

5.4 Degradation and fiber strength

Gurnagul et al. (1992) have studied the effect of different cellulose degradation methods on fiber strength. They used kraft cooking, vapor and liquid-based acid hydrolysis and hydrolytic enzyme treatment to degrade chemical pulp fibers. Their results indicate that enzyme treatment and liquid-based acid hydrolysis degrade fibers more heterogeneously than kraft cooking and vapor-based acid hydrolysis. The latter two treatments were said to cause homogeneous degradation of fibers.

Ander and Daniel (2004) used liquid based HCl treatment to induce fiber cleavage. Depending on the HCl concentration and treatment time, the number of cleavages per fiber at 80ºC varied from 0 with 0.1M HCl and 4h treatment time to 6.34 with 2M HCl and 4h treatment time. The number of cleavages was used to characterize the number of dislocations and other weak points since HCl cleaves fibers at these locations.

Seth and Page (1988) used vapor-based acid hydrolysis in degrading fibers. This procedure is particularly interesting for this kind of study because it is performed on handsheets and not pulps. Network structure, drying stresses, level of bonding and fiber activation all depend on fiber properties. Altering fiber properties before sheeting thus influences the structure and type of sheets formed. This introduces a speculation factor into the analysis of measurements – for example, has fiber tensile stiffness decreased or are the fibers simply less activated? During pulp treatments hemicelluloses dissolve, thus changing the chemical composition of the fibers. This does not occur when handsheets are treated. Treating handsheets with hydrochloric acid vapor has been shown not to affect fiber tensile stiffness (Seth and Page 1988, Kärenlampi and Yu 1997) based on the fact that the tensile stiffness of handsheets did not change. After a very harsh treatment, however, a decrease in tensile stiffness has been observed (Kärenlampi and Yu 1997). According to Seth and Page (1988), inter-fiber bonding is unaffected by acid vapor treatment if evaluated using the Page-equation (Page 1969).

6 MODELS OF FIBER STRENGTH

A number of models have been developed for fiber strength. The objective for these models is to gain understanding of how stresses are distributed in fibers when subjected to forces and strain. When a model is created and verified with experimental data, it can be used to study, depending on the model of course, how changes in for example time, temperature, damage or moisture content affect fiber strength. For example Astley et al. (1998) applied Finite Element Method (FEM) models to relate the elastic properties of softwood fibers to wall thickness, moisture content and microfibrillar angle. For a comprehensive review of the mechanical models of fibers from 1960s to 1990s one can look up the work of Mark (2002).

Many fiber models are based on the theories and knowledge of fiber reinforced composite materials. A composite itself is defined as a structural material that consists of two or more combined constitutients that are combined at a macroscopic level and are not soluble in each other (Kaw 2006). Of these constituents one is called the reinforcing phase which is embedded in the matrix phase. A single fiber can be thought to be a laminated composite structure with different cell wall layers like S2 as lamina, fibrils as the reinforcing phase while hemicelluloses and lignin act as the matrix.

Building a mechanical model starts from micromechanics. This is the construction of the lamina, or in the case of a fiber, the cell wall layer, properties from the properties of individual constituents, fibrils and the hemicellulose/lignin matrix. This has been done by Harrington et al. (1998) who calculated the elastic constants of the cell-wall idealizing it as a unidirectional fiber-reinforced composite. The properties of the composite were then determined from the properties of the individual fiber components, celluloses, hemicellulose and lignin and their amount in fiber wall. Testing and evaluating properties of a lamina and laminated structures is macromechanics. Laminated structures consist of combined laminas.

Xu and Liu (2004) have modeled the elastic modulus of microfibrils. Their model produced similar behavior of elastic modulus of fibers as presented in Figure 7. Similar behavior was also observed by Gassan et al. (2001), who modeled the elastic modulus of holocellulosic fibers as antisymmetrical laminated structures.

Berg and Gradin (1999) have modeled the stiffness degradation of wood fiber as a function of introduced damage. Wood fiber was loaded as a two layer structure. The outer layer was assumed to be linearly-elastic and anisotropic, inner layer correspondingly linear-elastic and reinforced by fibrils running at angle against the axial direction of the fiber. The model predicted that tension loads damage fibers to a larger degree than shear loads.

El-Hosseiny and Page (1975) treated fibers as helically wound fiber-reinforced tubes. They applied two theories derived for the strength of such materials to connect the variation in MFA to fiber strength. The other one of the theories fitted the measured fiber strength data well, as illustrated in Figure 17.

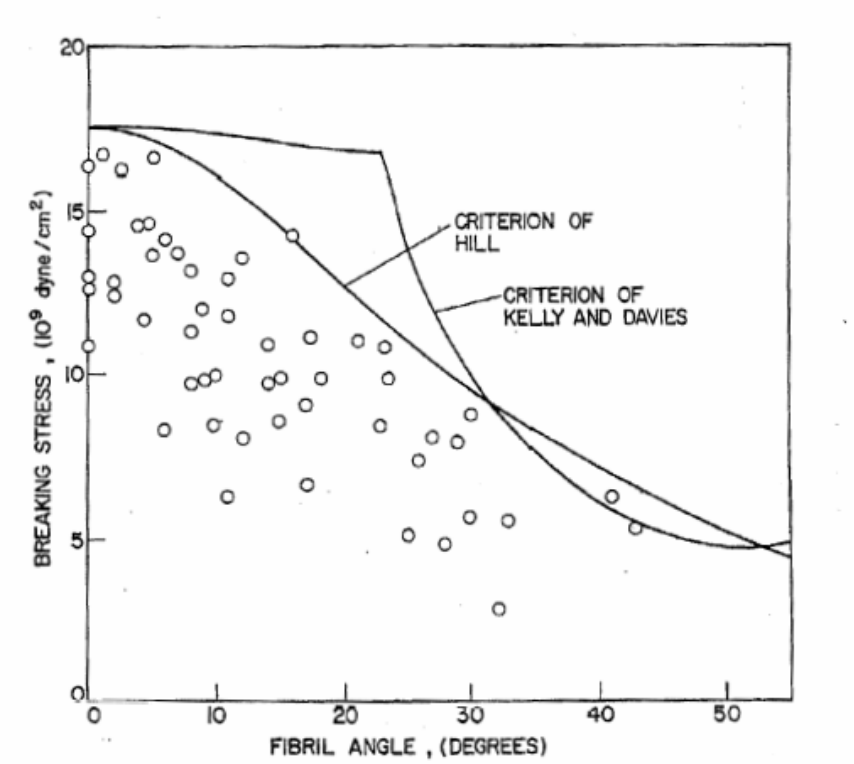


Figure 17. Experimental values of fiber strength for 60% yield spruce kraft pulp fibers. Kelly-Davies' criterion and Hill's criterion are fitted to the upper bound of strength (El-Hosseiny and Page 1975). For details on the models see the reference.

7 ROLE OF FIBERS IN PAPER FRACTURE

In 1958 Van Den Akker et al. showed that fiber strength is very important for paper strength by demonstrating with dyed fibers that a significant amount of them fail in paper fracture. Yan and Kortschot (1997) measured the load-displacement curves of single fibers pulling them out from the paper network. The load on the fiber dropped around 75% when it was debonded, but there was a tail in the curve decaying in proportion of the remaining embedded length of the fiber. Therefore even if a fiber is debonded from the network in fracture, there are still significant frictional forces to overcome. Thus significant energy is consumed also in pulling the debonded fiber out of the network.

Niskanen et al. (1999) used computer simulations to show that if fibers and bonds have equal strength, the same breaking force in Newtons, the failure of one fiber consumes the same amount or slightly more energy than the failure of one bond. They concluded that since fibers used in papermaking are much stronger than the bonds between them, fiber failure must have a great contribution to fracture energy of paper. Based on the data of Davison (1972), they calculated the failure of one fiber to consume as much energy as the failure of 5-6 inter-fiber bonds. In another study Niskanen et al. (1996) concluded that a drop in fracture energy occurs if either bonding or fiber strength becomes proportionately much larger than the other.

Fiber strength, bonding and fiber length are all important to fracture energy, the amount of energy consumed per unit length of an advancing crack. They also affect damage width, the spatial extent of the damage in the fracture process zone, where the majority of the deformations and the actual failure occur and where the actual fracture energy is consumed. The FPZ is located around the tip of the advancing crack. In fracture mechanics in general, and also in paper, the size of the fracture process zone is related to fracture energy and has been extensively studied by Kettunen (2000), whose results are summarized in Figure 18. Decreasing fiber strength and length both decrease damage width and fracture energy. When the fiber strength decreases, the probability of a fiber breaking increases (Kärenlampi and Yu 1997).

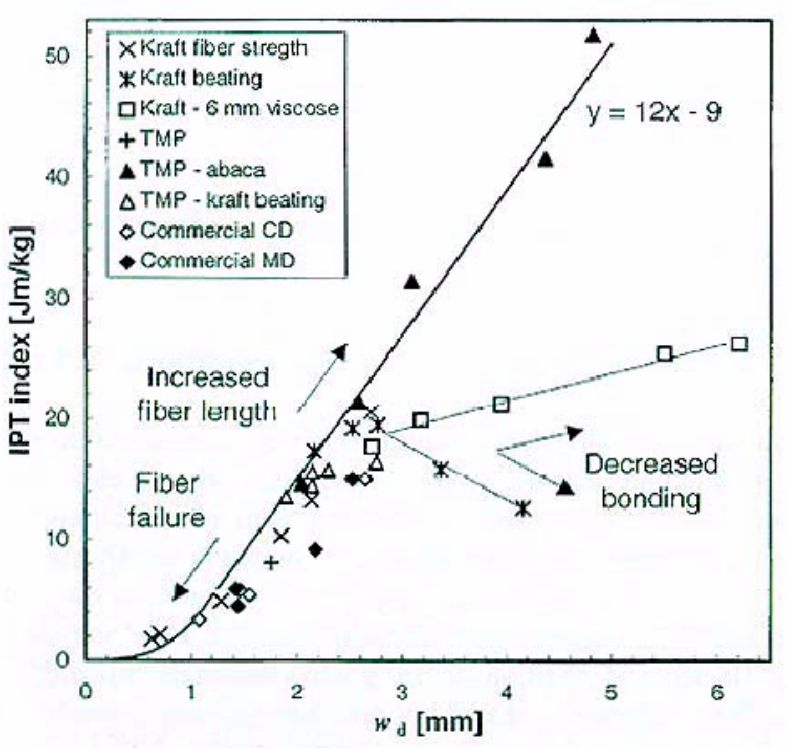


Figure 18. Damage width w_d vs. in-plane tear-index (Kettunen 2000).

8 MOTIVATION, MATERIALS AND METHODS

8.1 Motivation

Fiber strength is important for paper strength, which among other things also depends on fiber deformations and fibers' abilities to swell and form inter-fiber bonds. In fibers, cellulose fibrils, microfibrillar angle and fiber damage/defects are the main strength defining factors. Clarifying the role of hemicelluloses to fiber strength requires further studying. They do however affect paper strength. In the experimental part we take a small step in studying the role of hemicelluloses in fiber strength.

During processing from wood to a fiber in a paper sheet a fiber can experience both mechanical and chemical degradation. Both can be heterogeneous or homogeneous in nature. Degradation may affect single fiber strength properties as well as the ability of the fibers to form fiber networks. Assuming that pulp sheets are used in studying the effects of degradation and degradative treatments are applied before sheeting the pulps, it is difficult to distinguish the changes in single fiber strength from changes in the ability to form fiber networks. Chemical composition of the fibers may also change. Therefore we studied the nature and effect of chemical degradation on fiber strength and sheet properties by applying two different chemical degradation methods to pulp handsheets. Mechanical degradation is studied by damaging fibers in the end of the cook by stirring, then sheeting them and measuring sheet properties. The effects of fiber deformations which are related to fiber damage, or mechanical degradation, were also studied.

In a pulp, there exists a lot of variation in fiber strengths. These variations are due to variations at least in cellulose content, microfibrillar angle and fiber defects and damage. Testing the strength of individual fibers is also a challenging and time consuming task. Due to its wide availability and easy usage, zero-span strength measurement is often used to evaluate pulp fiber strength. However, variation in this test and how variation in fiber properties affect it are scarcely studied, but of interest, and are thus studied experimentally in this work.

In industrial pulping one does not try, or at least one maybe should not try, to make individual fibers with as good mechanical and optical properties as possible. Instead, one should try to make fibers that give paper that has as good mechanical, optical and other end-use properties as possible. We studied how fiber properties like fiber strength and deformations affect some paper properties. Particular attention is paid to runnability and fracture mechanics, particularly to so-called fracture process zone strain (FPZ-strain). The FPZ-strain describes strains in the area where the actual failure of paper or board occurs.

8.2 Materials and methods

The raw materials and their preparation are described in detail in the publications attached to this thesis, and thus only a short description is given here. Handsheets from pulps were made according to ISO 5264-2. In publications I and IV we made 40 g/m^2 sheets with bleached laboratory pulps instead of 65 g/m^2 because the undamaged pulp fibers were very strong and could not be tested with heavier handsheets. In publication III we used also oriented sheets. Test materials, sheeted pulps or used papers, are summarized below:

Publication I:

- Gently cooked DED-bleached laboratory pulps from Norway spruce and birch.
    - Refined 3000 PFI and unrefined
    - Refined 3000 PFI and homogenized (treatment to induce curl)
- DED-bleached Norway spruce laboratory pulp that was damaged in the end of the cook by mixing
    - Refined 3000 PFI
    - Bleached 3000 PFI refined mill pulp

Publication II:

- Gently cooked DED-bleached laboratory pulps from Norway spruce and birch refined 3000 PFI (same chips but different cook than in publication I).

Publication III:

- Gently cooked DED-bleached pulps from Norway spruce refined 3000 PFI (same chips but different cook that in publications I and II). Oriented sheets using dynamic sheet former. 3 different orientation levels.
- DEDED-bleached softwood laboratory pulp
    - Refined 1000 PFI and 3000 PFI. Plate dried
    - Refined 1000 PFI. Added 1% starch.
    - Refined 3000 PFI. Freely dried.
- Commercial SC-paper
- Commercial LWC-base paper

Publication IV:

- Gently cooked DED-bleached laboratory pulp from Norway spruce from publication I.
    - Refined 3000 PFI
    - Refined 3000 PFI and homogenized (treatment to induce curl)
- DED-bleached Norway spruce pulp that was damaged in the end of the cook by mixing from publication I.
    - Refined 3000 PFI.
- Unbleached gently cooked Norway spruce laboratory pulp used also in publication V.
    - Refined 2000 PFI
    - Refined 2000 PFI. Homogenized.
    - Homogenized. Refined 2000 PFI.
- Unbleached Norway spruce laboratory pulp damaged in the end of the cook by mixing
    - Refined 2000 PFI

Publication V:

- Unbleached gently cooked Norway spruce laboratory pulp used also in publication IV.
    - Refined 2000 PFI
    - Refined 2000 PFI. Homogenized.
    - Homogenized. Refined 2000 PFI

Scan or ISO standards were followed when they existed for the measurement in question. Detailed information is given in individual papers. Deviations from standards are mentioned in text. Fiber curl and kinks were determined using PulpExpert. Measurement of post fracture strain is explained in publication III. The evaluation of damage width and pull-out width was done as described by Kettunen (2000). Statistical analysis methods to determine the statistical distributions of zero-span strength values are explained in publication I.

Results and discussions

9 EXPERIMENTS ON FIBER DEGRADATION (PUBLICATION II)

Two cellulose degradation methods for spruce fibers and one for birch were used to investigate the effect of the cellulose degradation methods and patterns on fiber strength properties. The used treatments were acid vapor hydrolysis and thermal ageing treatment. It was unfortunate that we were not able to produce too similar levels of degradation with the two methods. This may cause some controversy in the interpretation of our results. In general, acid vapor hydrolysis caused greater degradation of pulp handsheets.

The effects to fiber strength were analyzed based on zero-span strength measurement and other measurements using pulp handsheets, since unfortunately we had no way of measuring fiber strength directly. Since network structure affects measured handsheet properties, also degradation treatments were performed with handsheets instead of pulps, in order to ensure a constant network structure and chemical composition. Based on our measurement results, we discuss the effect of the different degradation mechanisms on axial and Z-directional fiber strength. In addition, the potential role of softwood hemicelluloses in enforcing fiber strength is addressed.

9.1 Degradation modes and axial fiber strength

Figure 19 shows how zero-span measurements react to decreasing viscosity. We interpret the results so, that when dry zero-spans are compared at the same viscosity, acid treatment weakens the fibers more heterogeneously. Gurnagul et al. (1992) say that acid vapor treatment of handsheets leads to homogeneous degradation of fibers, but that acid treatment in the liquid phase results in heterogeneous degradation. The latter finding is attributed to acid hydrolysis occurring at kinks and nodes. In a review article Nyholm et al. (2001) conclude that dislocations may contain cracks that facilitate the penetration of cell wall degrading chemicals and enzymes. Our fibers were quite carefully prepared, but

some irregularities and discontinuities certainly exist in the fiber structure. We consider it possible that acid vapor treatment would, at least initially, also prefer these locations, while the ageing treatment would be more homogeneous. Acid vapor induced hydrolysis is a very fast reaction compared to ageing, which may also contribute to its heterogeneity.

The difference between the most degraded thermal treatment test point and the least degraded acid vapor treatment dry zero-span strengths is statistically significant at p=0.10, which indeed leaves room for interpretation. It might be possible to interpret the data so that both degradation treatments produce similar degradation and the results in Figure 19a can be described with one S-shaped line.

It can be argued from the theoretical point of view that in the zero-span measurement heterogeneous degradation of fibers should always result in smaller or equal strength when compared to homogeneous degradation. In order to do this one has to make some assumptions about the zero-span test which are not entirely accurate. First we assume that all fibers share the load equally and when a fiber fails the load is distributed evenly to fibers that have yet to fail (global load-sharing, see publication I). Secondly we assume that homogeneously and heterogeneously degraded fibers are at the same level of degradation when the mean strength between the sets of fibers is the same. Or put in another way, both sets of fibers, homogeneously and heterogeneously degraded, have experienced the same amount of strength reducing events.

Now let us consider theoretical sets of fibers A and B, both consisting N intact fibers of unit strength. Note that such sets do not exist in nature but fiber strengths vary and have a strength distribution, which in publication I we assume to be Weibull-distribution. We now apply homogeneous degradation treatment to set A, and heterogeneous treatment to set B. In heterogeneous degradation treatment X percent fibers have lost Y percent of their strength, while 100-X percent of fiber retain their strength of one (1) unit. In homogeneous degradation all fibers lose equal amount of strength. The percentage Z that the fibers in the homogeneously degraded set A retain of their strength at the same level of degradation than in set B is given by

$$Z=X(1-Y)+(1-X). \qquad (3)$$

Because all fibers in set A have equal strength, they will all fail simultaneously when the load applied reaches $N*Z*1$. Set B on the other hand contains both intact

and degraded fibers. Degraded fibers will fail when the load reaches $N^*(1-Y)^*1$, and this load is then distributed to other fibers. The intact fibers will fail at the load $N^*(1-X)^*1$. Note that the failure load of heterogeneously degraded set depends only on the proportion of the degraded fibers, not on the extent of degradation.

Since we said that the failure load in zero-span measurement is expected to be lower or equal in the heterogeneous than in the homogeneous case at the same level of degradation, inequality

$$N^*Z \geq N^*(1-X) = Z \geq (1-X) \quad (4)$$

must hold. Rearranging Eq.(3) results in

$$Z = 1-XY \quad (5)$$

Which inserted into inequality Eq.(4) gives

$$1-XY \geq (1-X) = Y \leq 1. \quad (6)$$

Based on this reasoning it can be expected that the zero-span strength in homogeneously degraded handsheets is indeed higher than in heterogeneously degraded handsheets. However, one must bear in mind that with real fibers the strength distribution before and after degradation treatments is very different from the simple ones used in the example above, and this will naturally have its implications to the real measurement results.

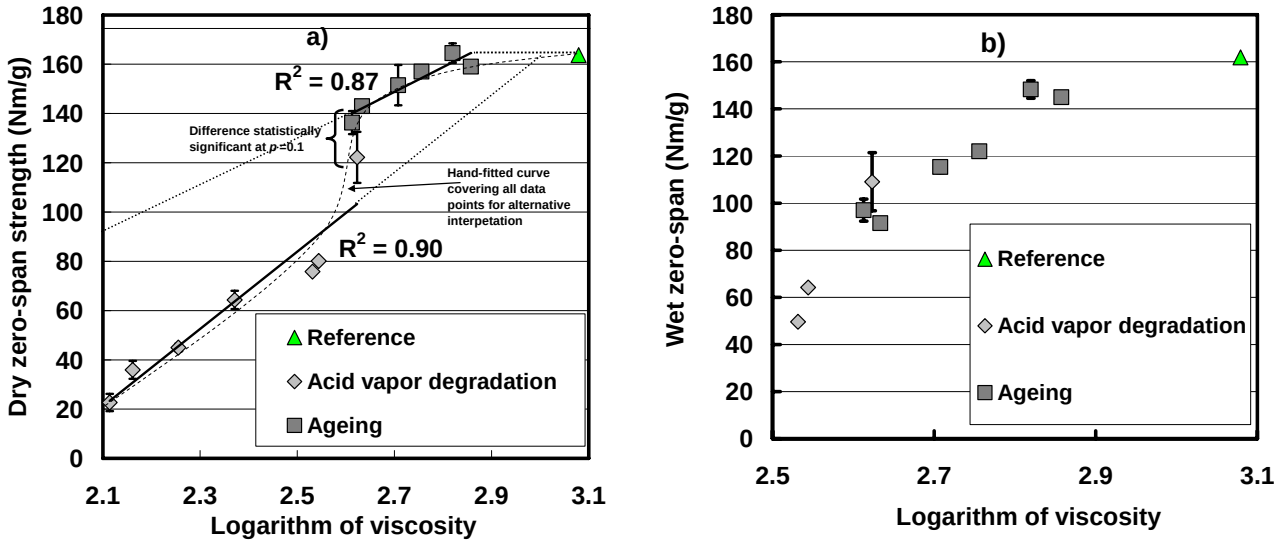


Figure 19. Dry zero-span strength a) and wet zero-span strength b) as a function of viscosity for acid vapor-treated and aged spruce handsheets. Error bars for 95% confidence interval of the mean.

Mohlin et al. (2003) attributed the difference between wet and dry zero-span measurements to fiber defects, wet zero-span being more susceptible to fiber defects than dry zero-span. In our experiments for spruce, both treatments decreased wet zero-span strength more than dry, though with the ageing treatment the difference was larger. We hypothesize that hydrogen bonds reinforce aged fibers more effectively than they do acid vapor-treated fibers, and their removal during wetting causes the greater decrease in wet zero-span. Mohlin et al. (2003) showed wet zero-span to differ more from the dry measurement the larger the number of defects per fiber. This would imply that there are more defects in the aged fibers than in the acid vapor-treated fibers, even though the defects measured by Mohlin et al. are probably very different from those in our fibers. The analogy here is as follows: the more heterogeneous acid vapor treatment produces fewer but more serious fiber defects than the more homogeneous ageing treatment, which produces a larger number of smaller fiber defects.

According to Gurnagul and Page (1989a), the difference between wet and dry zero-span measurements can be attributed to degradation of the hemicellulose-lignin matrix, which allows the fibrils to slide against each other in the wet state. They state that the weaker the supporting matrix, the larger the reduction in zero-span strength on wetting. With chemical pulps, this matrix has been removed to a large extent in cooking. We thus think that the contribution from the above mentioned fiber defects is larger.

For our acid degradation series of birch handsheets, the situation is very interesting indeed. Dry zero-span actually drops more than wet, and for two test points wet zero-span strength is actually higher than dry-zero span. Having higher wet zero-span than dry zero-span is not totally unheard of, for example Gurnagul and Page (1989a) observed this for well beaten unbleached black spruce kraft. According to Kersavage (1973), moist fibers at around 10% moisture content have higher strength than dry or totally wet fibers due to ideal ability of the hemicellulose matrix to transfer stresses inside the fibers and due to higher ductility of the moist cellulose than dry cellulose. Even though test strips are soaked in water prior to testing of the wet zero-span, it is possible that most fibers can be considered moist rather than wet. Introducing degradation in the fibers may in this case allow water to enter the fibers in such way that their strength in enforced.

Figure 20 plots the two zero-span measurements against each other. In a prepared response to publication II in the Cambridge conference (Iribarne 2005), Iribarne presented Figure 21 and claimed that the difference between dry zero-span and wet zero-span is due to fiber bonding. However, the data presented here shows that bonding measured with Scott-Bond test did not change in initial acid or ageing treatments, even though changes occurred between dry and zero-span measurements. Also, it would be very difficult to explain why we had higher wet-zero span than dry zero-span strengths for two of our birch test points or why for well refined and thus bonded spruce handsheets wet and dry zero-span strengths are practically the same. This supports the views of Gurnagul and Page (1989a) and Seth (2001) that zero-span measurement, wet or dry, is not affected by inter-fiber bonding and this view is adopted in this analysis.

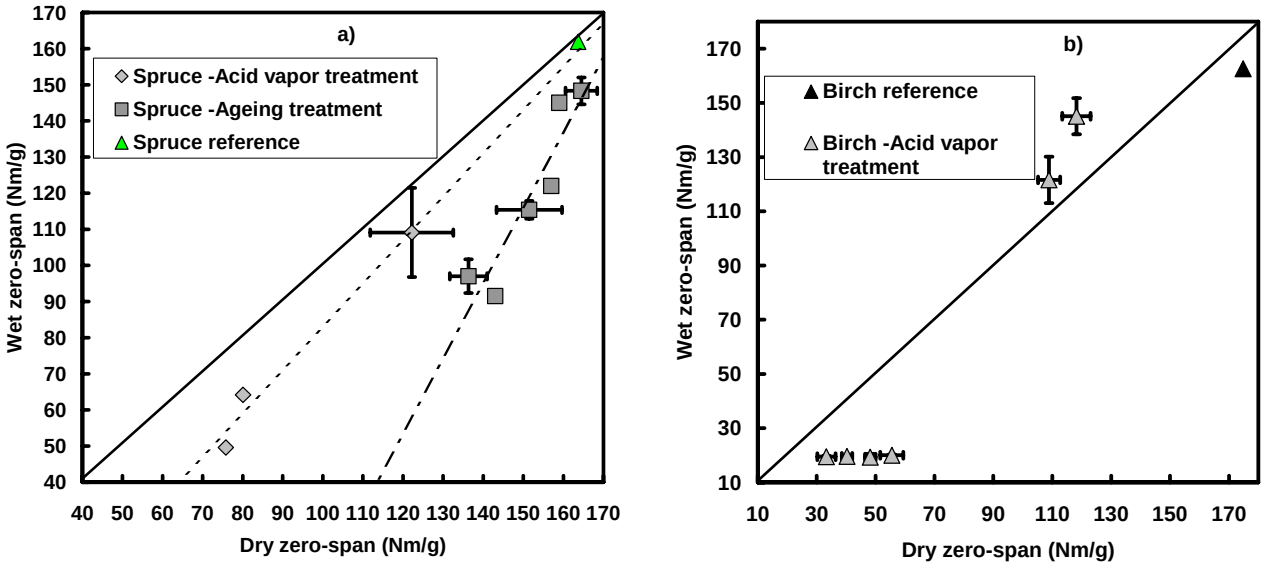


Figure 20. Dry zero-span vs. wet zero-span measurements for spruce a) and birch b). Error bars for 95% confidence interval of the mean.

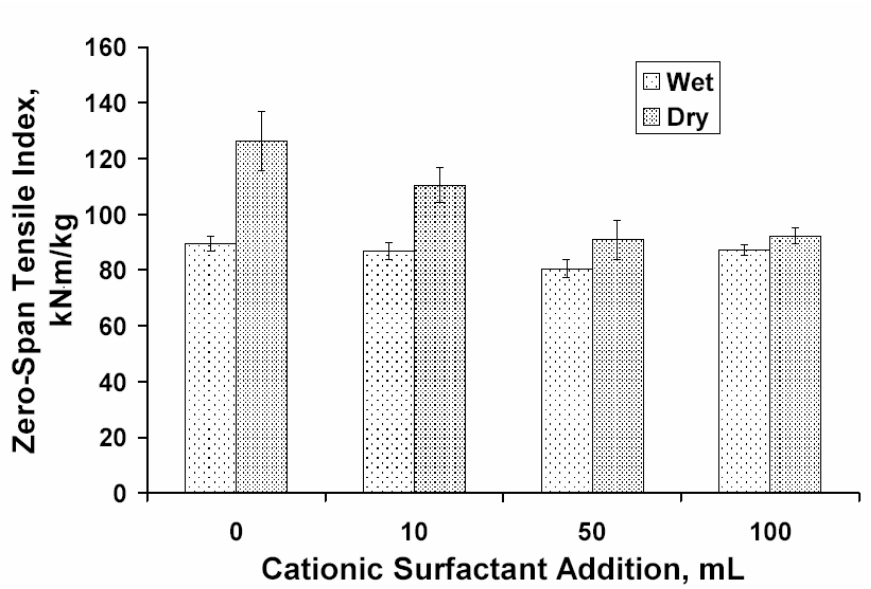


Figure 21. Zero-span tensile index as a function of cationic surfactants (Iribarne 2005).

The relationship between zero-span strength and tensile strength is plotted in Figure 22. One way to interpret the data is that initially the ageing treatment decreases tensile index but has little impact on zero-span results, while with acid vapor the effect appears to be the opposite. When evaluated so, at the same fiber strength acid vapor-treated handsheets have higher tensile strength. Again with this figure there is room for alternative interpretation. Both data sets could again be connected with one straight line or even better with an S-shaped line

Should one assume that there is indeed a difference between the treatments, both of these findings could be attributed to the different degrees of homogeneity/heterogeneity between treatments. Acid vapor produces fewer but more significant defects in the fibers, which cause the mean fiber strength to drop. In fiber networks intact fibers can compensate for this loss by carrying more load. On the other hand, ageing treatment may weaken the fibers homogeneously, which has a smaller but more uniform effect on fiber strength, but also weakens the fiber locations which in acid vapor treatment would have been left unharmed and able to help distribute the load. Data points from Kärenlampi and Yu (1997) have been added to further illustrate the relationship between fiber strength and tensile index.

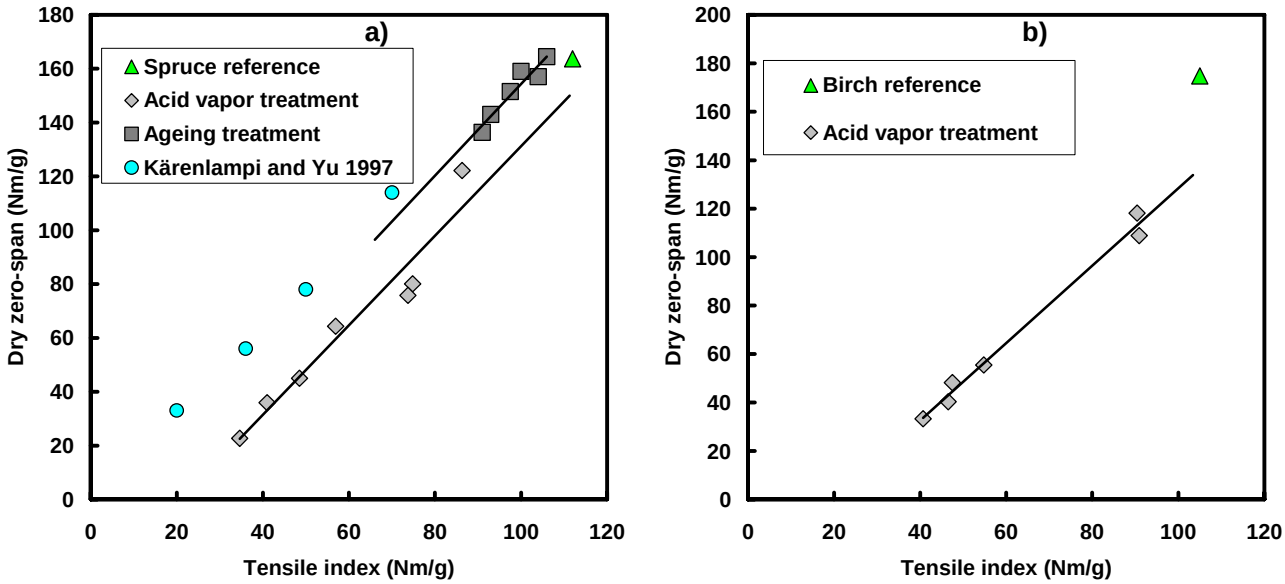


Figure 22. Tensile index of spruce a) and birch b) handsheets vs. dry zero-span measurements. Acid vapor degraded data from Kärenlampi and Yu (1997) added for further illustration of the relationship.

To sum up, though we admit that there is room for interpretation, there exist three indicators that acid vapor treatment is more heterogeneous than ageing treatment:

1. Dry zero-span strength at the same viscosity seem higher for aged handsheets.

2. At the same dry zero-span strength, acid vapor treatment yields higher wet zero-span strength. We hypothesize that hydrogen bonds reinforce aged fibers more effectively than they do acid vapor treated fibers, and their removal during wetting causes the larger drop in wet zero-span.

3. When evaluated at the same fiber strength, dry zero-span vs. ordinary tensile strength reveals that acid vapor treated handsheets have higher tensile strength. The fiber network is able to compensate for the few larger local fiber defects, but not for the numerous smaller defects, which in combination cause network failure at lower tensions.

9.2 Fiber degradation and z-directional fiber strength

Scott-Bond is used as a measure of fiber bonding and Z-directional strength, even though it actually measures energy. According to Seth and Page (1988), acid vapor degradation affects only fiber strength and not inter-fiber bonding. They base the claim on the Page-equation (Page 1969). If the Page equation is applied to our data, assuming that only fiber strength, bonding and tensile index can change, the claim that acid vapor treatment has no effect on bonding is not valid. However, Figure 23a below indicates that no change in inter-fiber bonding or Z-directional fiber strength occurred above viscosities of 400 ml/g for spruce and 700 ml/g for birch. Therefore either the Page-equation is not applicable here, or else one of its parameters changes, probably fiber length (or rather effective fiber length). Figure 22 above showed a linear relationship between tensile index and dry zero-span strength. The effect of bonding for zero-span strength is next to non-existent (Seth 2001). It can therefore be concluded that the degradation treatments do not influence bonding above the viscosity (degradation) levels mentioned. Furthermore, if the degradation treatments do influence bonding below the level mentioned, the effect on tensile index cannot be observed because the fibers are already so weak that inter-fiber bond-related failure does not occur.

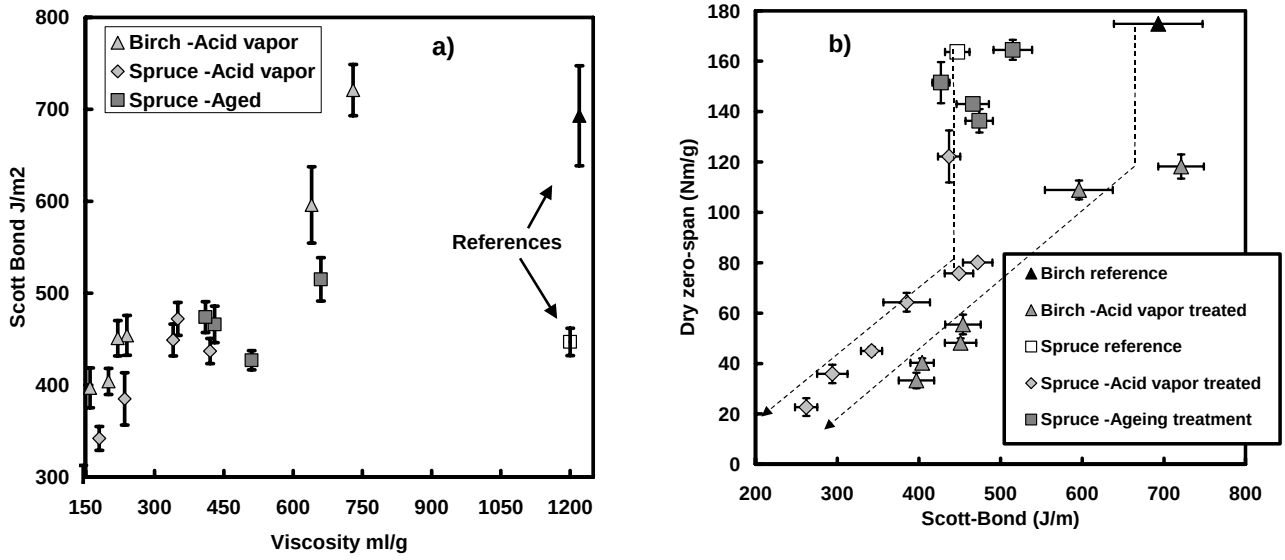


Figure 23. Scott-Bond vs. viscosity a) and Scott-Bond vs. dry zero-span measurement b) for degraded handsheets. Error bars for 95% confidence interval of the mean.

Figure 23b shows how axial fiber strength is compromised much earlier than Z-directional fiber strength or bonding as depolymerization advances. Spruce fibers require the viscosity to drop below 400 ml/g before any difference can be detected in the Scott-Bond values. At this level of degradation, the fibers are probably critically weakened in the Z-direction. For birch fibers the same happens at a viscosity of 700 ml/g. If fiber bonding is not affected by the degradation treatments, these differences can probably be attributed to differences in fiber ultrastructure.

9.3 Degradation of hemicelluloses and fiber strength

The contribution of hemicelluloses to fiber strength is not clear. As discussed previously in this text, some researchers have found hemicelluloses to influence fiber strength, where some have only stated their significance to fiber swelling and fiber ability to form inter-fiber bonds. Despite the short chain length of hemicelluloses compared to cellulose, they may be thought to reinforce the cellulose fibrils via the mechanism depicted in Figure 24.

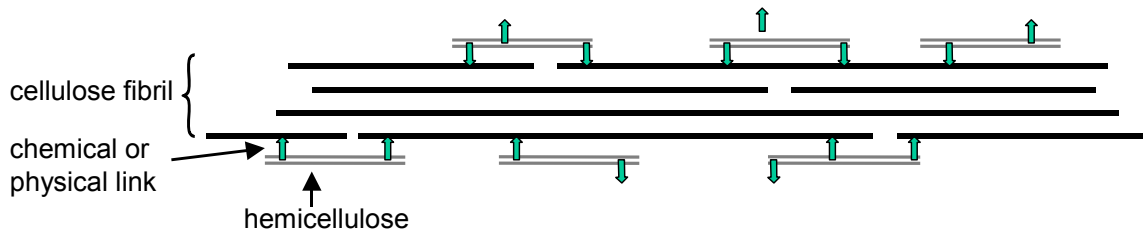


Figure 24. Possible reinforcement of cellulose fibrils by hemicelluloses.

Viscosity reflects the average length of the fiber polymer chains, particularly cellulose. Thus, a viscosity drop indicates depolymerization of cellulose and thus correlates with fiber strength other things equal. Under acidic conditions, certain hemicellulose components are particularly susceptible to hydrolysis. These reactions thus coincide with cellulose depolymerization and may contribute to

fiber strength indirectly. Typical acid-labile hemicellulose components are the arabinose substituents of softwood xylan (Sjöström 1993).

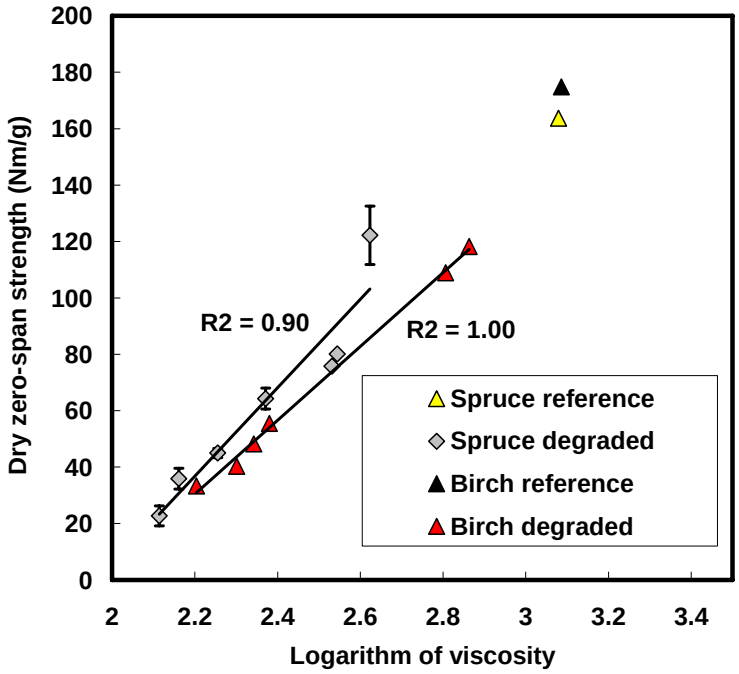


Figure 25. Dry zero-span strengths vs. logarithm of viscosity for spruce and birch. Error bars for 95% confidence interval of the mean.

Figure 25 shows plots of dry zero-span vs. viscosity for both spruce and birch handsheets. It can be concluded from this figure that the correlation between viscosity and zero-span strength is practically the same for the two wood species. No clear initial fast strength loss is observed in either case, which would indicate the existence of acid-labile reinforcing components in one of the wood species. Thus we are bound to agree with Zou et al. (1996a), that acid-induced fiber strength loss is primarily due to cellulose degradation.

10 EXPERIMENTS CONSIDERING ZERO-SPAN STRENGTH (PUBLICATIONS I,IV,V)

10.1 Effect of fiber deformations and damage (Publications IV,V)

Figure 26 show the number of fiber kinks and fiber curl present in the differently treated bleached and unbleached pulps from publications IV and V. The results show that the extent of fiber deformation is slightly higher for the bleached REF-bl pulp than for the unbleached REF pulp. Otherwise the bleached pulps exhibit less fiber deformation than the unbleached pulps.

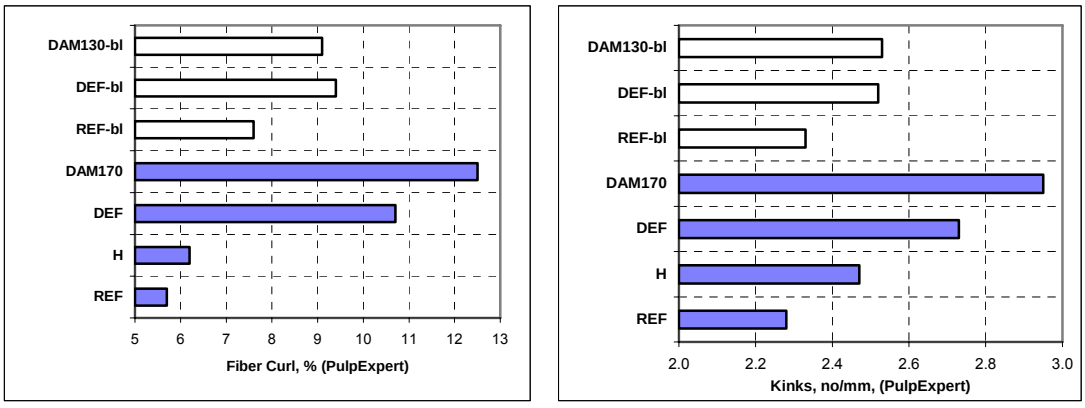


Figure 26. Fiber curl a) and kinks b) of pulps used in publications IV and V. REF=unbleached, PFI 2000; H=unbleached, deformed, PFI 2000; DEF=unbleached, PFI 2000, deformed; DAM= damaged in cooking at 170°C, unbleached, PFI 2000; REF-bl=bleached, PFI 3000; DEF-bl=bleached, PFI 3000, deformed; DAM130-bl=damaged in cooking at 130°C, bleached, PFI 3000.

Seth and Chan (1999) and Mohlin et al. (1996) have argued that fiber strength should be measured from straight, well-beaten fibers (3000-4000 PFI revs) to obtain the real fiber strength using the zero-span measurement. The argument is based on the assumption that if fibers are not straight, they do not carry load in the measurement, see Figure 27a. Mohlin et al. (1996) observed that the deformations that abruptly change the direction of the fiber axis have larger influence on the zero-span measurement than more even deviation from straightness (see *curl* in Figure 11). In our opinion these locations, kinks, are

damaged locations where the structure and thus the strength of the fiber have been compromised. The straightness itself is maybe not the point.

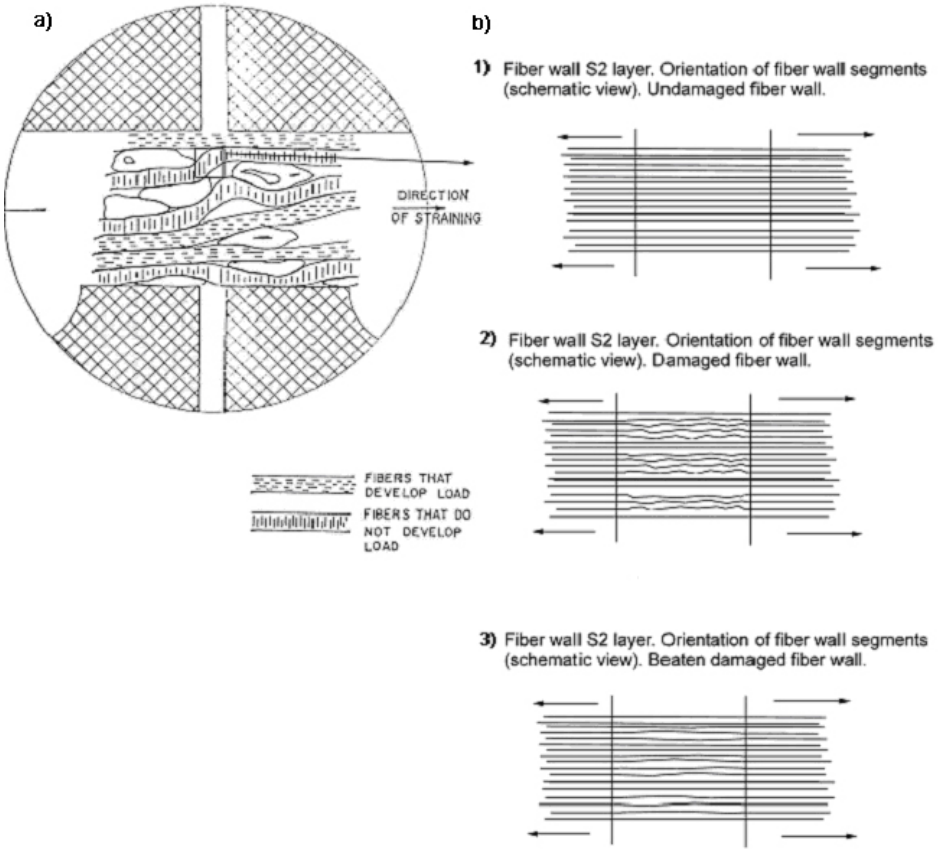


Figure 27. a) One hypothesis of the effect of curl on the zero-span fiber strength (Mohlin and Alfredson 1990, Mohlin et al. 1996). Only straight fibers carry load. b) The new hypothesis: all fibers carry load. Fiber wall segments carrying load in three different cases is illustrated: 1) Undamaged fiber wall stress transfer. 2) Damaged fiber wall stress transfer, 3) Beaten damaged fiber wall stress transfer (publication V).

As can be observed from Figure 28, with unbleached pulp there is very little difference in the wet zero-span of REF and DEF, even though fiber curl as measured with PulpExpert had doubled in value. Statistically there is no difference between the values. With bleached pulp the curl has not increased so dramatically in the homogenization treatment, but there is still a clear difference between REF-bl and DEF-bl. There the difference between the test points in wet zero-span is more likely due to slight damage experienced by the fiber in homogenization treatment, than due to fiber curl.

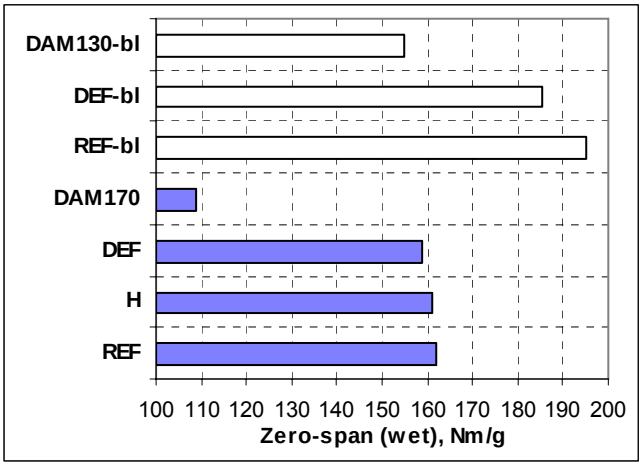


Figure 28. Wet zero-span results of handsheets from publications IV and V. REF=unbleached, PFI 2000; H=unbleached, deformed, PFI 2000; DEF=unbleached, PFI 2000, deformed; DAM= damaged in cooking at 170°C, unbleached, PFI 2000; REF-bl=bleached, PFI 3000; DEF-bl=bleached, PFI 3000, deformed; DAM130-bl=damaged in cooking at 130°C, bleached, PFI 3000.

Our results from publications IV and V suggest that fiber curl does not affect zero-span results or fiber strength in general. Corollary to this would be that the actual span in the zero-span measurement is so short that whether fibers are curled on not is irrelevant to the received measurement value. The situation of course changes when the span length is increased. Accuracy of the hypothesis presented in Figure 27a can be thus questioned. However, it is possible that our result is due to the nature of our fibers and the nature of the zero-span test. It is not known in what order the fibers break in the zero-span test and what proportion of them carries the load.

A theory was put forward in publication V, that it is the disoriented fiber wall components, fibrils, that are the cause for the apparent effect of fiber curl in zero-span measurements. When a fiber wall is damaged, fibrils are disoriented and intra-fiber stress-transfer is disturbed. In beating, which also straightens fibers, the fibrils are again oriented in a favorable way.

What was troublesome in the results was the apparent lack of the so called Jentzen-effect (Jentzen 1964) in our handsheets. According to Jentzen fibers dried under tension become stronger than freely dried fibers, because there occurs favorable orientation of the disoriented fibrils as well as decrease in MFA.

Our handsheets were normally plate dried and therefore one could expect straight fibers to be under higher tension and activate more than curly fibers, in a way to experience more Jentzen-effect. Slack curly segments are in much smaller tension than straight segments. Especially with unbleached fibers the lack of Jentzen-effect was apparent. Explanation follows. First, the deformation treatment of the gently cooked fibers likely does not cause much misalignment of fibrils, especially with unbleached fibers. Thus there are few disoriented fibrils to orient. Secondly, according to Kim et al. (1975), only fibers with high MFA are strengthened by the decrease in MFA when dried under tension. With Norway Spruce, the average MFA is low unless wood from the growth rings 5 and below counting from the pith constitute a very significant portion of the raw material (see 3.4 Fibrillar angle).

As Figure 29 shows, there is little or no difference between the wet and dry zero-span measurements for the bleached DAM-bl, DEF-bl and REF-bl pulps. Mohlin et al. (2003) have shown that the wet zero-span measurement is more susceptible to visible fiber defects than dry zero-span. These defects make it possible for water to break hydrogen bonds within fibers, thus reducing wet zero-span fiber strength. In our case the fact that there was no difference between the measurements, could be because the fiber surface is more or less unchanged while the fiber wall structure is weakened by mechanical action. Figure 29 also shows that even though our fibers were very well bonded, wetting them did very little to the measured values. This issue was already discussed in 9.1 Degradation modes and axial fiber strength.

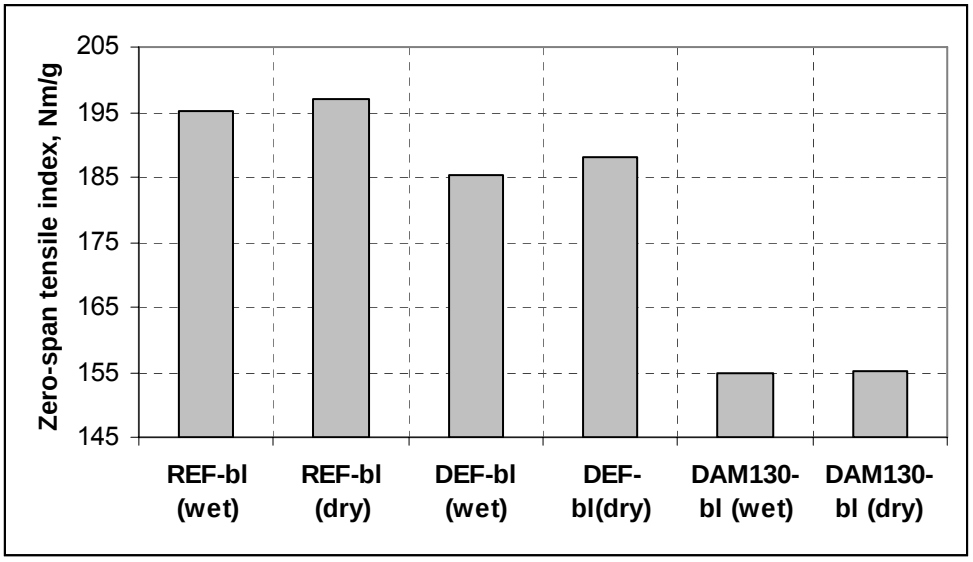


Figure 29. Wet and dry zero-span strengths from publication IV. REF-bl=bleached, PFI 3000; DEF-bl=bleached, PFI 3000, deformed; DAM130-bl=damaged in cooking at 130°C, bleached, PFI 3000.

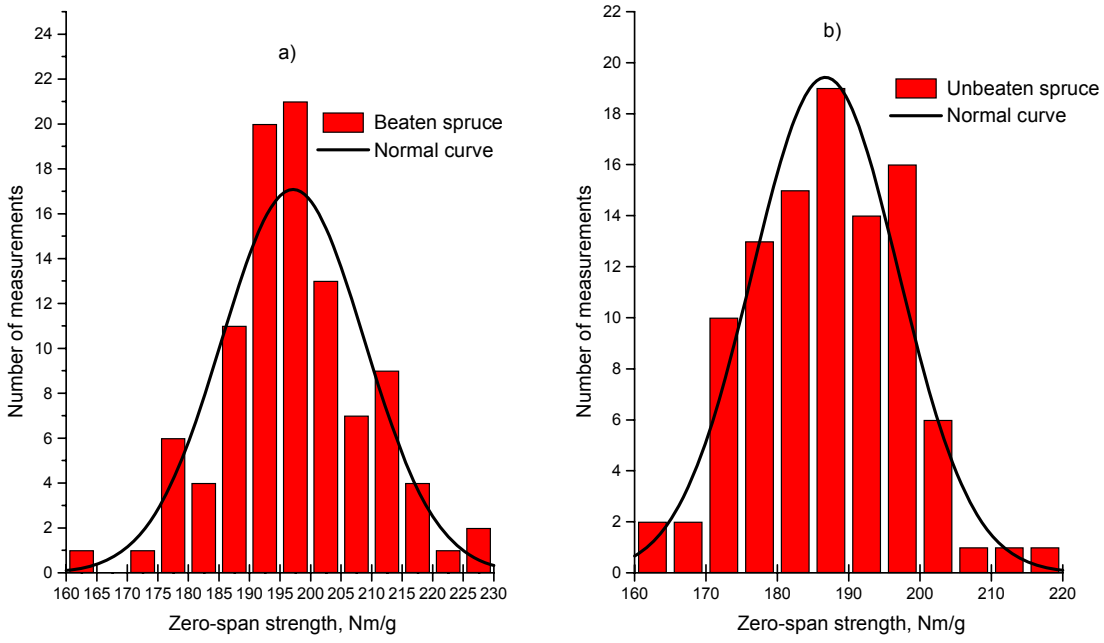
10.2 Statistics of zero-span strength (Publication I)

Zero-span measurements are often used as an indication of pulp strength, and even as a representative value of single fiber strength. The effect of fiber deformations and morphology on the measurement of zero-span strength has been widely studied, but not their effect on the variation in the measurement. In the following, we study that variation in detail. We show how the variation is affected by fiber curl and damage, by refining and raw material and also by sheet thickness and measurement span length. One hundred repetitions were measured at each test point to get a reliable estimate of the variation. Table 2 presents the samples used in this study.

Table 2. Pulp designations and treatment procedures.

Sample name	Treatment in cooking	Treatment procedure
Spruce-B	No treatment	Bleaching→Beating 3000 PFI revs
Spruce-U	No treatment	Bleaching (Unbeaten)
Spruce-DAM	Damaged @130°C	Bleaching→Beating 3000 PFI revs
Spruce-DEF	No treatment	Bleaching→Beating 3000 PFI revs→Deformation
Birch-B	No treatment	Bleaching→Beating 3000 PFI revs
Birch-U **Mill-XX**	No treatment Mill pulp	Bleaching (Unbeaten) Mill bleaching→Beating 3000 PFI revs (XX=different basis weights

Figure 30 and Figure 31 show the experimental distributions of all the zero-span measurements point. All the curves can be seen to be similar to the bell-shaped curve of the normal distribution. We tested this with the χ^2-test as described in publication I. The normality assumption was accepted with all experimental distributions except one at the risk level p=0.05, Table 3. Zero-span measurements with laboratory pulp handsheets had coefficients of variation ranging from 5.29% to 5.93%, thus the difference between variations was small. An increase in span length led to an increase in variation. In the mill pulp series, in which basis weight was varied, the coefficient of variation decreased as a function of increased basis weight.



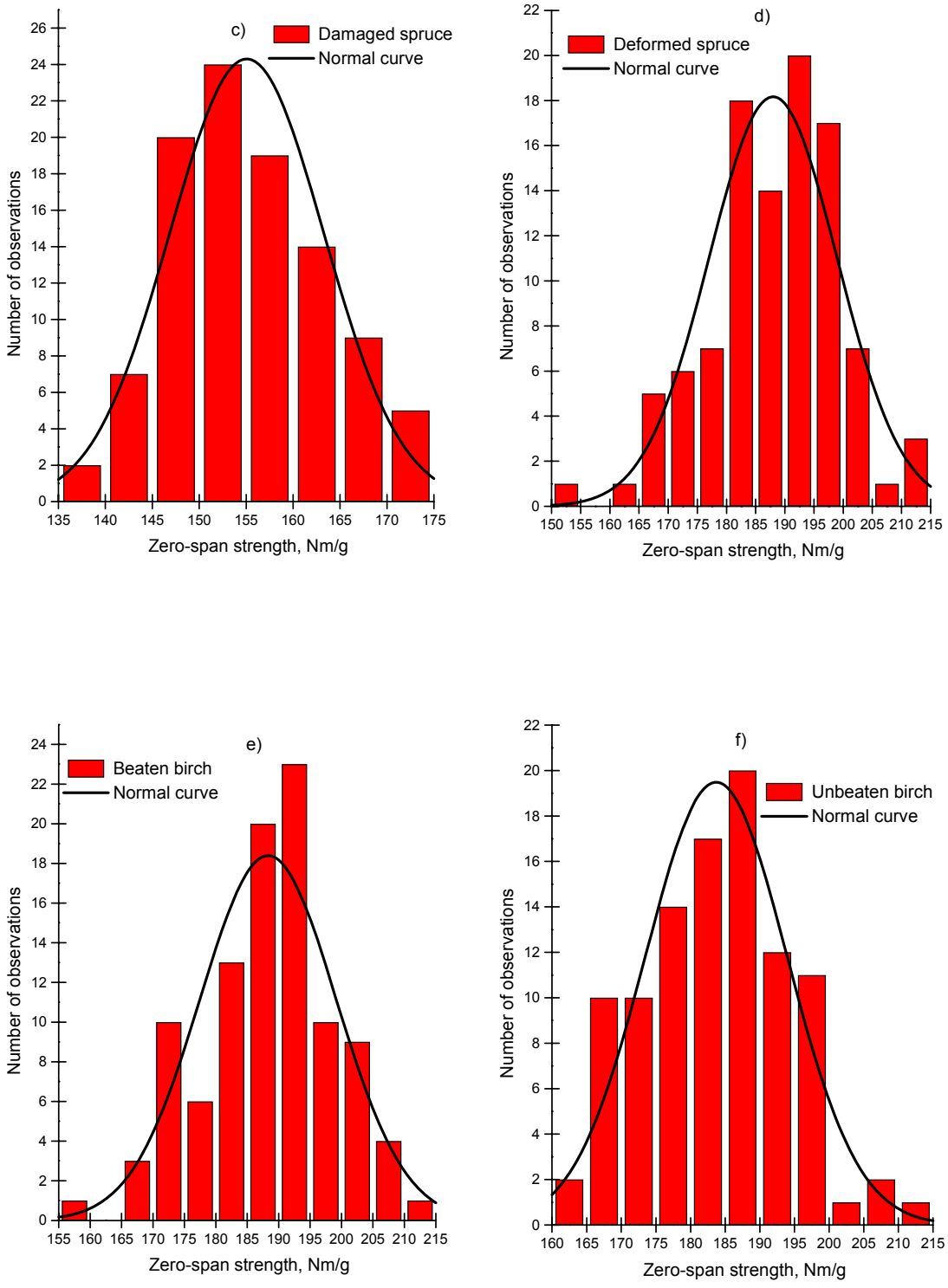


Figure 30. Measured zero-span distributions for laboratory pulp handsheets. 100 individual measurements per distribution. The fitted curve has the mean and variance calculated directly from the measurements.

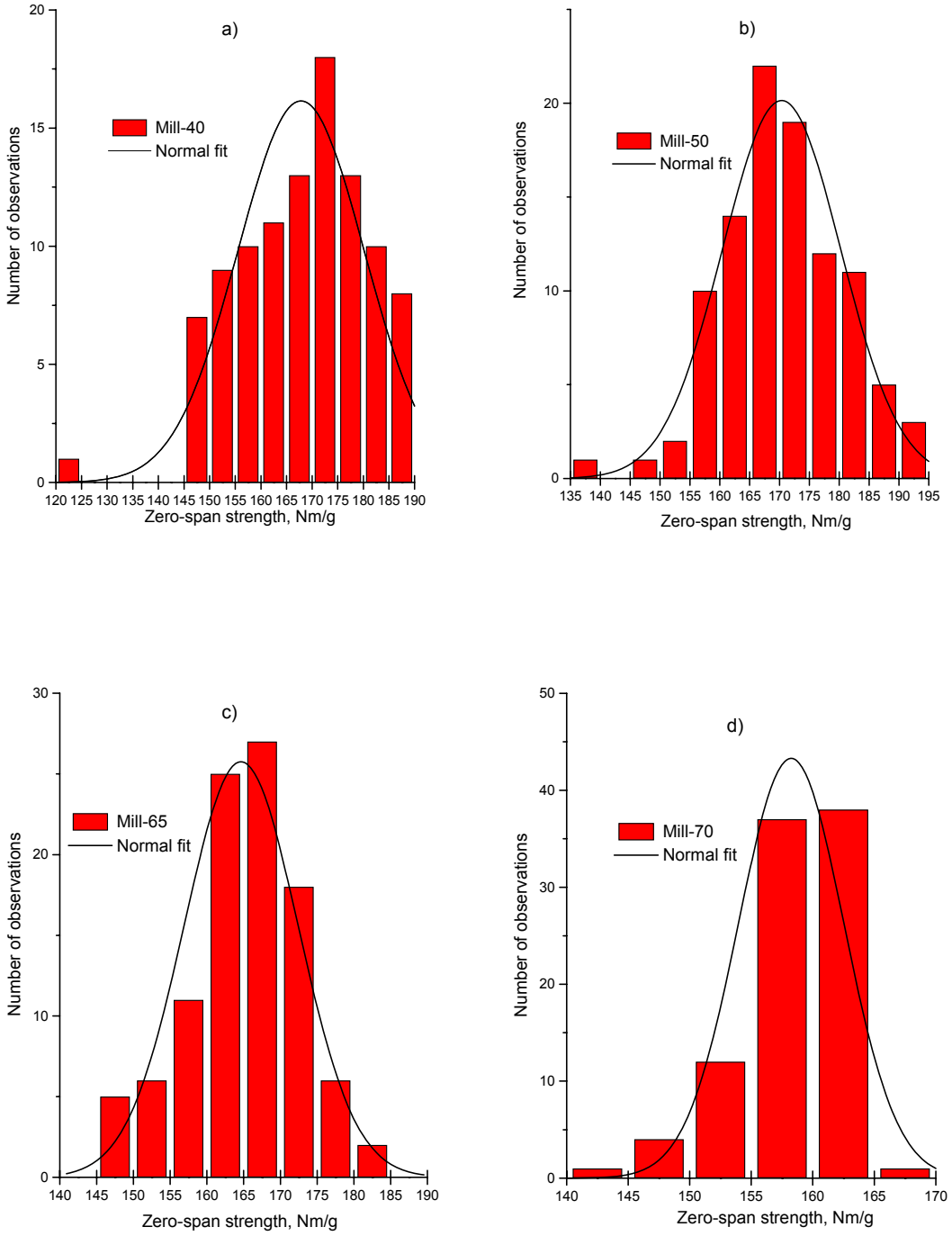


Figure 31. Measured zero-span distributions for mill pulp handsheets with different basis weights. 100 individual measurements per distribution, except Mill-70, where 93 measurements were performed. The fitted curve has the mean and variance calculated directly from the measurements.

Table 3. Calculated parameters for zero-span distributions. Zero-span strength in Nm/g.

	Spruce-B	Spruce-U	Spruce-DAM	Spruce-DEF	Birch-B	Birch-U	Spruce-B Span 0.3mm	Spruce-U Span 0.3mm	Spruce-B Span 0.6mm	Spruce-U Span 0.6mm
Normal										
Mean	197.1	186.7	155.1	188.0	188.3	183.7	203.7	178.2	195.7	155.3
SD	11.7	10.3	8.2	11.0	10.8	10.2	14.0	13.7	14.0	15.1
Variance	136.5	105.4	67.4	120.5	117.7	104.8	197.1	188.1	195.2	229.0
COV	5.93%	5.50%	5.29%	5.84%	5.76%	5.57%	6.89%	7.70%	7.14%	9.74%
χ^2	21.6	13.6	8.4	26.8	14.4	10.4	25.6	22.8	10.0	15.2
p-value	0.20	0.70	0.96	0.06	0.64	0.89	0.08	0.16	0.90	0.58
Weibull										
α	21.6	20.3	20.9	19.8	19.8	20.3	16.5	14.7	16.1	11.8
β	200.4	190.6	157.7	192.5	192.6	187.4	208.6	182.8	200.6	161.2
χ^2	47.6	16.4	19.6	17.2	16.0	18.4	29.2	22.8	15.6	27.6
p-value	***0.00***	0.50	0.30	0.44	0.52	0.36	***0.03***	0.16	0.55	***0.05***
	Mill-40	Mill-50	Mill-65	Mill-70						
Normal										
Mean	167.8	170.3	164.7	158.2						
SD	12.3	9.9	7.7	4.3						
Variance	152.5	98.1	60.0	18.4						
COV	7.36%	5.81%	4.70%	2.71%						
χ^2	27.6	17.6	19.6	22.6						
p-value	***0.05***	0.41	0.30	0.16						
Weibull										
α	15.41	19.43	26.71	49.29						
β	172.96	173.80	167.45	160.17						
χ^2	30.2	28.2	19.8	18						
p-value	***0.03***	***0.04***	0.28	0.39						

Our results show that fiber deformations and raw material have little or no effect on the variation in zero-span measurements. If a little bit of speculation is allowed, it might be said the damaging treatment which probably compromises the strength of whole fibers lowers the variation between individual fibers, making them all "equally bad". As the fiber curl, according to publication V, has no effect on the mean measured zero-span strength, neither has it any effect on the variation in the measurement.

When the span length was increased, the variation in the measurements increased. With larger spans, fewer fibers are clamped from both ends. These fibers contribute to load bearing only via inter-fiber bonds. In the work of for example Cowan and Cowdrey (1974) the mean measured strength decreased when the span length was increased. The same occurs here for the unrefined

pulps but not for the refined pulps. Our gently cooked laboratory pulp produces also very strong inter-fiber bonds. However there is an increase in the variation, likely because the structural effects of the handsheets like formation start to contribute. One can also observe that the variation in the handsheets made from unrefined pulp is larger than in those made from refined pulp when longer span lengths are used. This is the same effect that will be discussed below with sheets of different thicknesses; smaller number of fibers carrying the load will lead to larger variation in the zero-span measurement.

Excluding the Mill-40 test point, the zero-span strength measurements obtained seem to follow normal distribution. Even with the Mill-40 test point the normality assumption is only barely rejected. A system with fibers bearing load in parallel and having a strength distribution of their own is expected to follow a normal distribution (see Sornette 1989 and the model derived in publication I for details). According to the model in the publication I, covariance, or the ratio of standard deviation and mean, is expected to scale as

$$COV(\sigma_{fiber}) \propto \frac{c}{\sqrt{n}}, \qquad (7)$$

where n is the number of fibers contributing to load bearing and c is a small constant. This formula has a simple physical interpretation: the square-root part is related to the central limit theory (see for example Milton and Arnold 1995), and the constant c, which is roughly equal to unity, depends on the detailed properties of the geometry (span length and fiber orientation distribution) and the fiber strength distribution, which for pulp fibers is often assumed to be of a Weibull form. However, the values in Table 3 indicate that the strength distributions are typically rather broad, as can also be seen from Figure 30 and Figure 31. The theoretical model in the publication I predicts a somewhat smaller variation. We recognize that the model lacks many features present in the actual zero-span measurement, like the existence of the through-thickness stress profile (Hägglund et al. 2004). Idealistically, if this and any other relevant features could be incorporated into the model, the model could be used to compute the single fiber strength distribution properties from zero-span data.

In Figure 32 we have plotted the basis weights against the coefficients of variation for the mill pulp handsheet series. It is apparent that the variation decreases as basis weight (or thickness) increases. This is qualitatively as predicted by Eq.(7). If we make a first-hand approximation that the number of

fibers *n* contributing to load bearing in the zero-span measurement is linearly proportional to basis weight, some agreement is obtained between Eq.(7) and the experimental results. However, it is evident that the variation decreases much more rapidly than predicted by Eq.(7).

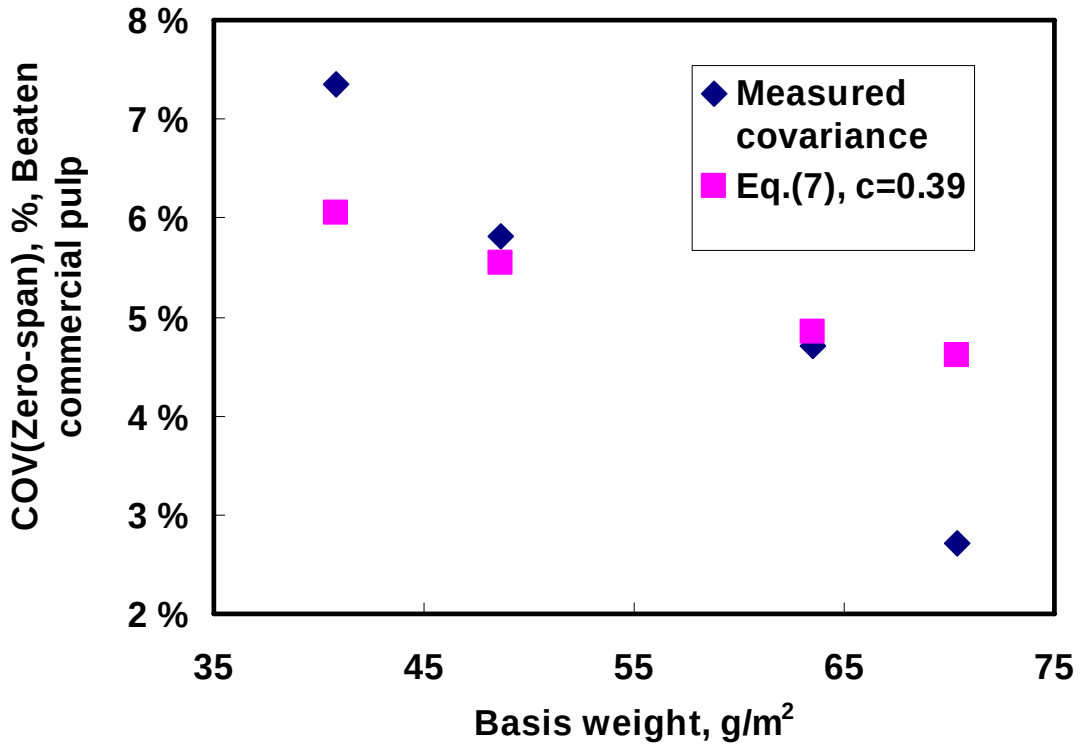


Figure 32. Basis weight vs. coefficient of variation for the mill pulp basis weight series. Respective thicknesses from low to high basis weight are 64, 76, 93 and 99 μm.

Hägglund et al. (2004) point out many problems associated with zero-span strength measurement relating to non-uniform stress profiles. To mitigate this problem they suggest using the thinnest specimens possible for a given span length. We do not argue with this, but point out that when span length increases or thickness decreases, the variation in the measurements increases. Therefore, to differentiate between test points a sufficient number of strips must be measured.

10.3 Connection between fiber strength and zero-span strength (Publication I)

Since zero-span measurement is often used as a representative value of fibers strength, it would be of advantage if the real single fiber strength could be derived from the zero-span strength. However as mentioned, there are non-ideal features in the zero-span measurement. Eq.(8) was derived by Van Den Akker et al. (1958) to relate single fiber strength, s_{fiber} to zero-span strength $s_{zero\text{-}span}$.

$$s_{zero-span} = \frac{3}{8} n s_{fiber} \tag{8}$$

Hardacker (1970) actually got a reasonable agreement between the Eq.(8) and actual single fiber strength measurements. However, as we have shown there is a large variation in single fiber strength between fibers in the same pulp, as there is variation also in fiber thickness. A model derived in the publication I predicts the scale of variation in the zero-span measurement, Eq.(7), but it also gives an estimate of the single fiber strength distribution. In publication I we assumed single fiber strength to be Weibull-distributed, Eq.(1) and found the following equations for the single fiber strength distributions.

$$\alpha = \frac{2k}{LambertW\left(2kp\left(\frac{\sigma^2 n}{s_{zero-span}^{\ 2}}\right)^k\right)} \tag{9}$$

$$\beta = \frac{s_{zero-span}}{\left(\frac{1}{\alpha}\right)^{\frac{1}{\alpha}} e^{\frac{-1}{\alpha}} n} \tag{10}$$

LambertW is Lambert's W function and σ^2 is the variance in the zero-span measurement. The parameters k and p are free and must be determined by simulation or other means. In publication I we have computed values k=1.4 and p=3.0. s_{fiber} can be determined using the equation

$$s_{fiber} = \beta\Gamma\left(1+\frac{1}{\alpha}\right), \qquad (11)$$

where Γ is the Gamma function.

The model is ideal and we do not claim the results given by Eq.(9) and Eq.(10) are exact. The model can and must be improved in the future to account for example stress-profiles in the thickness directions.

11 INFLUENCE OF FIBER PROPERTIES TO SOME NETWORK PROPERTIES (PUBLICATIONS III,IV,V)

11.1 Post-fracture strain (Publication III)

The idea of ”post-fracture strain”, or the strain in the fracture process zone (FPZ) after the initiation of fracture may have some relevance to some desired paper properties. Based on some initial experiments (Wathén et al. 2003), it was concluded that factors like drying shrinkage do not control the post-fracture strain but some other phenomena like the aligning of fibers toward the direction of the applied tension must be decisive. Therefore we prepared handsheets with different fiber orientation levels with the idea that sheets with most fibers oriented toward the direction of the tension would experience the least post-fracture strain. The results from these tests are illustrated in Figure 33, where it is apparent that orientation controls FPZ-strain. We concluded that a major contribution to the strain in the fracture process zone comes from the fibers aligning towards the direction of applied tension.

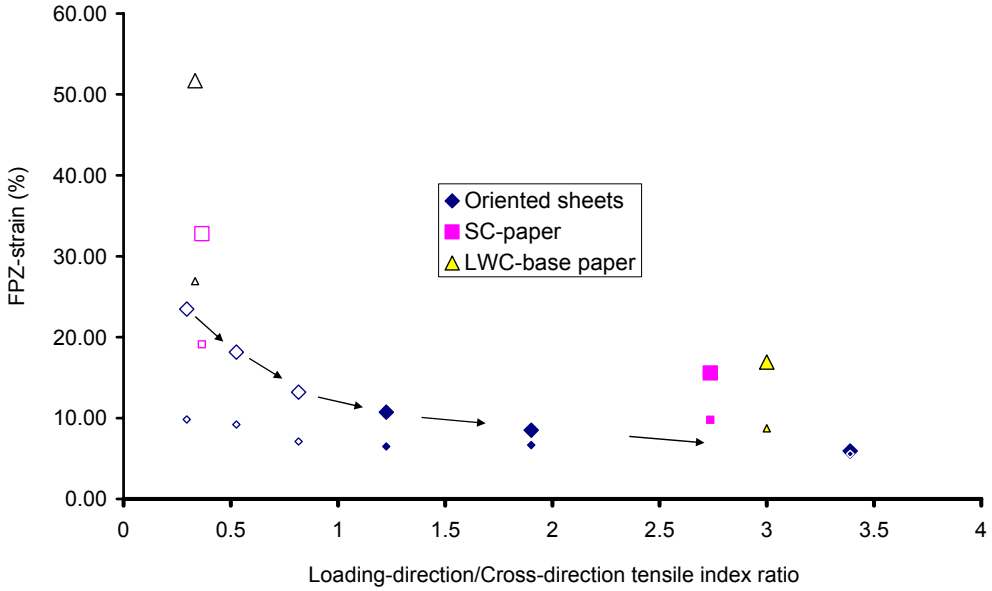


Figure 33. FPZ-strain as a function of fiber orientation measured as the ratio of loading-direction/cross-direction tensile index ratio. Filled symbols for MD direction test, unfilled for CD. Large symbols for FPZ-strain estimated at 10% of the maximum damage, small symbols for FPZ-strain estimated at 50% of maximum damage (see publication III).

In publications I, IV and V we used fibers that were curled or damaged after cooking. In publication III we did not experimentally show how fiber curl or damage affect the FPZ-strain. The relationship between fiber strength, measured using zero-span test, and FPZ-strain has neither been illustrated. Therefore we have plotted the zero-span strength vs. FPZ-strain in Figure 34a) for the sheets we used in publication I and IV, and in Figure 34b) for the sheets used in publication III.

It can be observed that the effect of fiber curl is very small to the FPZ-strain. Fiber damage introduced in the end of the cook has slightly more influence. On the other hand, free drying, that probably introduces microcompressions in the fibers, does have a minor negative influence on the FPZ-strain. Both free drying and damaging in the end of the cook cause a significant drop in fiber strength.

No definitive conclusions can be stated of the influence of fiber strength to FPZ-strain based on the available data. With fibers damaged in the end of the cook there is the problem that damaged and reference fibers form different types of

fiber networks. Fiber curl is expected to influence FPZ-strain similarly to orientation, though that cannot be conclusively proven from the data. Data of freely dried handsheets might suggest that all other things equal, fiber damage might lower the FPZ-strain slightly.

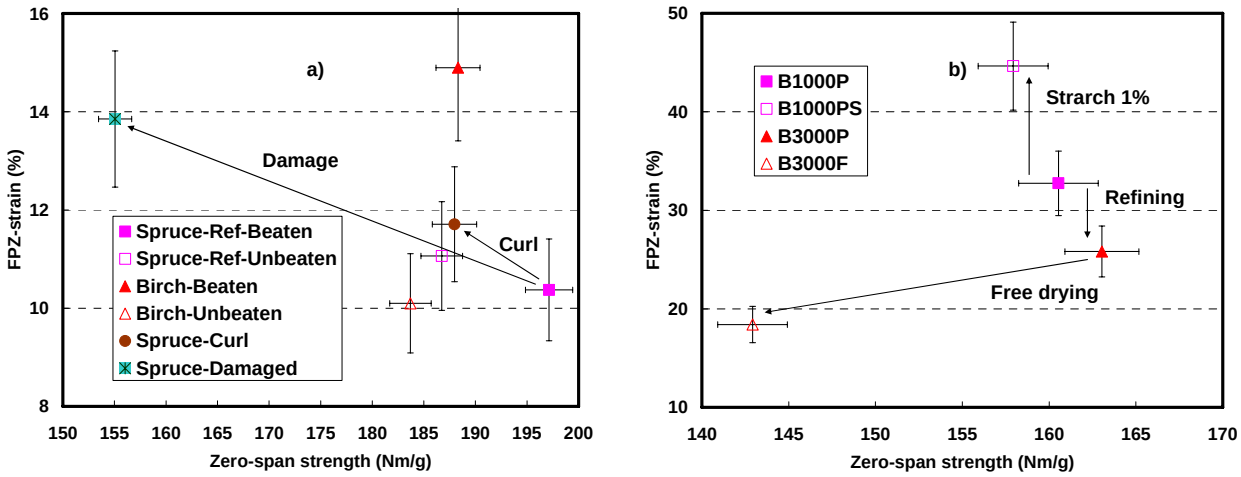


Figure 34. Zero-span strength vs. fracture process zone strain (FPZ-strain). Error for FPZ-strain is estimated to be 10% of the measured value, normal 95% confidence interval is given for the zero-span strength. a) Handsheets studied in publications I and IV. b) Handsheets studied in publication III. The number after B indicates PFI revolutions, P plate drying, F free drying and S the addition of 1% starch.

11.2 Effect of fiber deformations and damage to runnability and end-use properties of paper and paper-board

In this chapter we want to evaluate the role of fiber damage and deformations in real life papermaking, converting and end-use. What possibilities and dangers do they offer? The chapter may seem out of context, but in author's view provides link between theory and reality. Runnability and end-use properties are as important, and maybe even more relevant, paper properties as for example tensile strength.

Runnability can be defined as the problem-free running of a paper web of the desired quality on paper machines, converting machines and printing presses. It may be possible to use deformed fibers to improve runnability. For problem-free running, the essential properties of paper webs are tensile stiffness and its behavior on moistening, web uniformity (i.e. the absence of weak spots) and defect resistance. With deformed fibers, tensile stiffness is often compromised. This is not usually good. There may be compensating effects however. Since deformed fibers distribute load effectively, fracture energy increases, as we (see publication IV) and others have shown. If the drop in tensile stiffness is not too drastic, the defect resistance of the paper web may actually improve. It can also be speculated that some CD profile-related runnability problems might be mitigated when the relative difference between the center and edge positions is lowered. If the converting process is run with constant speed differences instead of adjusting for proper web tensions, the greater breaking strain provided by the deformed fibers will help. Web uniformity is to a large extent defined by the paper machine construction and its operator, though short fibers naturally help in achieving good formation. Structural weak points in paper are either reinforced or weakened by deformed fibers.

Curly fibers lead to higher tear strength, see Figure 35b. This has also been observed by other authors (Page et al. 1985a, Fellers et al. 2001). The increase of tear-index as a function of fiber curl was also observed here, see. Curly fibers distribute damage to wider area and a larger number of bonds are broken. Energy may also bee consumed in deforming the fiber in the process. Our results also show that damaging fibers leads to lower tear-index. This agrees with the results of for example Kärenlampi and Yu (1997) and Kettunen (2000). As such our measurements do not bring anything new to this subject. However tear strength is still used to predict web runnability. In theory fiber deformations could be applied to improve tear-strength for improved runnability. However, Uesaka et al. (2001) have demonstrated that tear strength does not predict runnability at printing presses, see Figure 35a. We think they are right.

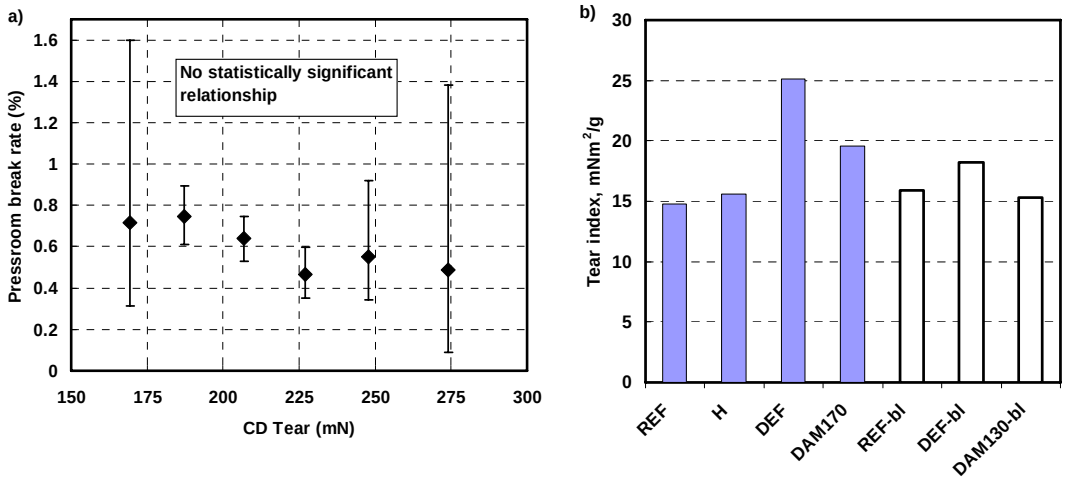


Figure 35. a) Tear-strength vs. printing press runnability (Uesaka et al. 2001). b) Tear index of pulps from publication IV at 2000 PFI for REF, H, DEF and DAM170 and at 3000 PFI for REF-bl, DEF-bl and DAM130-bl.

Based on fracture mechanics calculations, curly fibers give a paper web higher critical elongation, i.e. breaking strain of a web with a defect (Fellers et al. 2001). On the other hand, the same study shows that critical force (breaking tension) also decreases. Nominal tensile index and nominal stretch measure these properties. We have measured these for the curled fibers from publications IV and V, which support the above mentioned calculations, Figure 36.

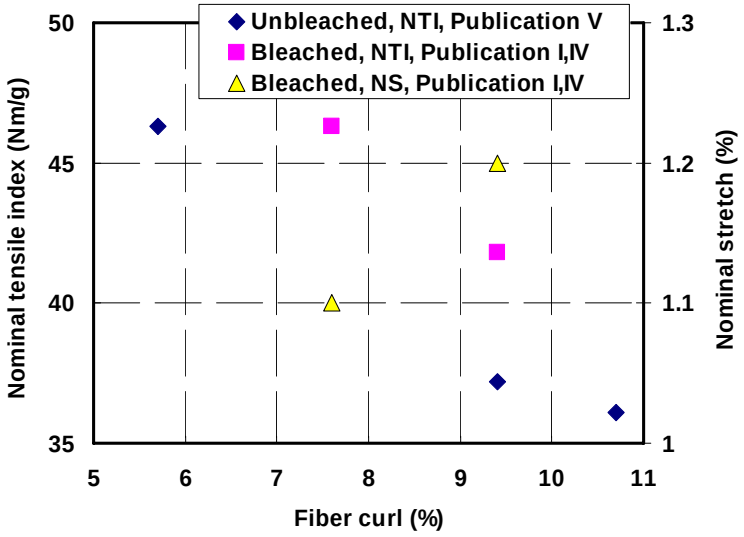


Figure 36. Fiber curl vs. defect resistance of web measured with nominal tensile index (NTI) and nominal stretch (NS) for some pulp handsheets used in publications I, IV and V.

Whether fracture mechanics can give accurate estimations of breaking tensions on the printing press is not clear (Eriksson et al. 1999), but qualitatively it addresses the relevant phenomena. Eriksson et al. (1999) studied ten different commercial kraft reinforcement pulps critical elongation and force. They observed practically no difference between the pulps. The pulps must have some difference between them in terms of damage and deformations, but any difference is obscured by other phenomena.

According to Page et al. (1985a), the fiber orientation of machine-made papers may be diminished by the use of curly fibers. Curly fibers affect the water removal properties of pulp (Page et al. 1985a). The curlier the fibers are, the smaller the resistance to drainage is. This was also seen to a degree in our results from publication V, Figure 37.

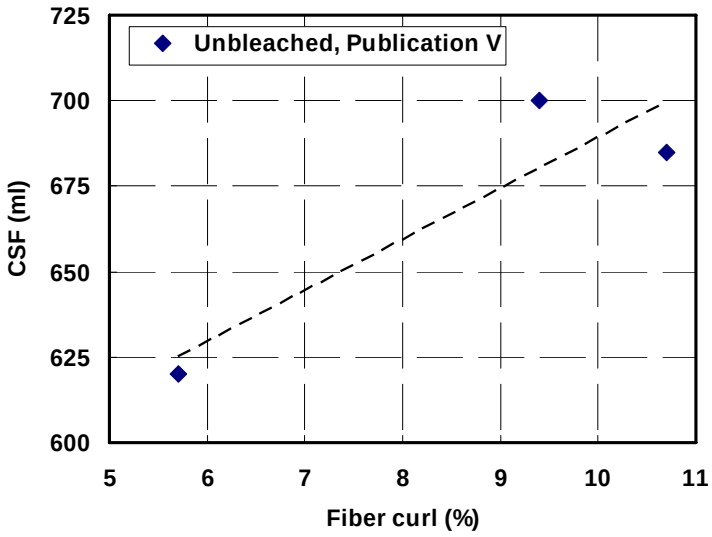


Figure 37. The development of CSF as a function of fiber curl for unbleached Norway spruce pulp (publication V).

In many applications of boardmaking it is important that in-plane properties are closer to one another than for example in printing papers, since CD bending stiffness is a critical property (Kiviranta 2000). This might be achieved through the proper use of curly fibers. Curly fibers also give a higher breaking strain, which is very beneficial to the top layer of cartonboard during creasing (Kiviranta 2000).

Much of the competitive edge enjoyed by paper over other media is due to the sensory satisfaction it gives the user. This, of course, depends on the tactile properties of the paper product: for example, what it feels like to riffle through the pages of a magazine. This is a relatively new area of study that definitely needs to be pursued if paper is to keep its place as an information platform. Deformed fibers can also be exploited in this area. Vihavainen (2004) showed there is a strong statistical connection between instrumentally measured resistance to bending and how a person experiences the rigidity of papers. The same relationship was also found for roughness felt by people in relation to air permeance and roughness measured using instruments. Bending resistance depends on bulk and tensile stiffness, of which the latter is affected directly by fiber deformations. Deformed and damaged fibers may give potential for higher bulk. Forsell et al. (2004) also found a connection between measured paper properties and those experienced by persons.

12 CONCLUSIONS

Measuring fiber strength is challenging due to the small dimensions and heterogeneity of the fibers in any pulp. There are three ways to measure fiber strength. One is to measure the strength of an individual fiber with a suitable tensile tester, another is to embed a group of fibers in resin and measure the breaking strain (SFF-test), and the third is the zero-span strength test. The zero-span test really gives the strength of the pulp, not a single fiber, and suffers from many non-ideal features like stress profiles. However, it is commonly available and easy to use, and gives an indication of the average strength of pulp fibers, which is why it was employed here as a measurement of fiber strength.

We showed zero-span strength measurements to follow a normal distribution. This was expected based on the Central Limit Theorem and also from the model derived in publication I. The variation in zero-span strength was found to increase as functions of decreasing thickness and increasing span length. The former was predicted by the model. The reason for the latter is that the properties of the fiber network start to show in the measurement. As with any measurement with significant variation, it is important to measure enough test strips to confirm the difference between two test points. The model presented in publication I needs further development. For example, the z-directional stress profile should be added. It would also be interesting to know what really happens in the test in terms of the order of fiber failure. When do the first fibers start to fail, where are those fibers located in the test span and is the test result dominated by some type of fibers? It might be possible to find answers using acoustic emission measurements and/or by using a small proportion of colored fibers in the handsheets.

Contrary to some earlier studies, it is suggested here that fiber curl itself maybe does not affect the zero-span measurement results. In some earlier publications it was reported that when fibers were refined, they were straightened and the measured zero-span strength was increased. Thus it was concluded that the straightening of fibers caused the increase in the measurement values. A theory is put forward that the reason may be the favorable organization of fibrils occurring during beating. The higher activation of straight fibers, considered in the text to resemble the Jentzen effect, had no observable effect on the fiber strength as measured in the zero-span test. Because of their high strength, our fibers probably do not have many misaligned fibrils and are made of raw material

that typically has, on average, a low fibrillar angle. There are thus no fibrils to be aligned or very little potential for the microfibrillar angle to decrease during drying, which would cause an increase in strength.

Industrially made pulps are generally weaker than laboratory pulps made from the same raw material. This is due to the mechanical damage they suffer in the fiber line. Fiber strength may also degrade chemically. Chemical degradation may be homogeneous or heterogeneous, the latter being more serious. In relation to degradation studies, it may be that the key words are more and less in what comes to homo-/heterogeneity. In this study, acid vapor-induced degradation was found to cause more heterogeneous degradation of fibers compared to ageing treatment at elevated temperature and humidity, although the data may be open to a different interpretation. The degradation in both treatments occurs via the same mechanism – hydrolysis – but the difference is attributed to initial fast reaction of acid vapors at fiber defect sites. Z-directional fiber strength is less sensitive to fiber degradation than axial fiber strength. Neither treatment was observed to affect inter-fiber bonding.

It would be useful to repeat the degradation tests performed here with a more careful choice of treatment times to obtain less ambiguous data. More information can also be obtained if the amount of degradation is evaluated using SEC in addition to viscosity. It would also be useful to study the effects of degradation by applying different span-lengths in zero-/short-span testing to study the differences between the degradation treatments.

Fiber properties have a significant effect on the fracture properties of paper. Higher fiber curl means higher fracture energy, tear-strength and breaking strain, but lower tensile stiffness index and breaking tension of a paper web. Once the fracture process of paper has initiated, strains deviating from the ordinary breaking strain occur in the fracture process zone. The most significant contribution to these strains comes from the fibers orienting towards the direction of the tension. Some small contribution may come from the straightening of curly fibers, but this is marginal. Fiber strength could not be connected with the strains in the fracture process zone. It would be interesting to visualize the mechanism occurring in the fracture process zone. This could be achieved using the appropriate camera and colored fibers.

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