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Strength of individual fibres and fibre to fibre joints - influence of the pulp type, environmental conditions and the degree of refining

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AFFIDAVIT

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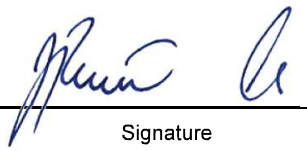
01.08.2017.	
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Abstract

The key to understanding properties of paper lies in understanding the properties of its constituent elements. Among those properties, strength plays a pivotal role in determining the ultimate strength of paper. If either the bond or the fibre strength equals zero, the material fails. Even though much is known about properties of individual fibres and joints, some questions still remain unanswered. Within the scope of this thesis, we have sought to decrease this knowledge gap by investigating properties of individual fibres and joints, namely, their strength and how it changes depending on three parameters: the type of pulp, environmental conditions and the degree of refining. The strength of three commercial pulps has been determined in regards to the pulp type (hardwood or softwood), cooking process (sulphite or kraft), environmental conditions (samples tested at 30, 50 and 80% RH) and the degree of refining (3 refining degrees using a PFI mill). To determine the time necessary for the fibres and joints to reach an equilibrium in specific environmental conditions, DVS measurements were performed on two kraft pulps (hardwood and softwood). The breaking load of individual fibres and fibre to fibre joints has been investigated, after 2 hours of conditioning in the set RH, by using a modified tensile tester. In case of individual fibres, the cross sectional area was determined after the testing by using a microtome, while the optically bonded area of joints was determined by using polarisation light microscopy (PLM). In order to get a better insight into the behaviour of refined joints, investigations using the environmental scanning electron microscopy (ESEM) have been performed. By understanding how fibres and joints will behave depending on their processing parameters and varying environmental conditions, one hopes to gain a better understanding of the behaviour of paper. Furthermore, a wide array of tests conducted using the same pulp will provide a solid base for future numerical modelling trials.

Keywords: hardwood, softwood, individual fibres, fibre to fibre joints, strength, RH, refining

Kurzfassung

Der Schlüssel zum Verständnis der Eigenschaften des Papiers liegt im Verständnis der Eigenschaften seiner Bestandteile. Unter diesen Eigenschaften spielt die Festigkeit von Fasern eine entscheidende Rolle bei der Bestimmung der endgültigen Bruchkraft des Papiers. Wenn entweder die Bindung oder die Einzelfaser Festigkeit gleich Null ist, versagt das Material. Obwohl viel über Eigenschaften von einzelnen Fasern und Faser-Faser Bindungen bekannt ist, bleiben einige Fragen noch unbeantwortet. Im Rahmen dieser Arbeit haben wir versucht, diese Wissenslücken zumindest zu verringern, indem wir die Eigenschaften einzelner Fasern und Bindungen untersuchen. Nämlich ihre Festigkeit und wie sie sich diese in Abhängigkeit von drei Parametern (Zellstoff-Typ, Umweltbedingungen und der Mahlgrad) ändert. Die Festigkeit von drei kommerziellen Zellstoffen wurde in Bezug auf den Zellstoff-Typ (Laubholz oder Nadelholz), Kochverfahren (Sulfit oder Kraft), Umweltbedingungen (Proben getestet bei 30, 50 und 80% RH) und Mahlgrad (3 Mahlgrade mit einer PFI-Mühle) untersucht. Um die Zeit zu bestimmen, die für die Fasern und Binudngen notwendig ist, um ein Gleichgewicht unter bestimmten Umgebungsbedingungen zu erreichen, wurden DVS-Messungen an zwei Kraftzellstoffen (Laubholz und Nadelholz) durchgeführt. Die Untersuchung einzelner Fasern und Faser-Faser Bindungen wurde, nach 2 Stunden Konditionierung unter den festgelegten Bedingungen, unter Verwendung eines modifizierten Zugprüfgerätes untersucht. Bei einzelnen Fasern wurde die Querschnittsfläche nach dem Testen unter Verwendung eines Mikrotoms bestimmt, während die optisch gebundene Fläche von Faser-Faser Bindungen unter Verwendung der Polarisationslichtmikroskopie (PLM) bestimmt wurde. Um einen besseren Einblick in das Verhalten von Bindungen aus gemahlenen Zelstoffen zu erhalten, wurden Untersuchungen mit der Environmental Scanning Electron Microscopy (ESEM) durchgeführt. Durch das Verständnis, wie sich Fasern und Bindungen in Abhängigkeit von ihren Verarbeitungsparametern und unterschiedlichen Umgebungsbedingungen verhalten, hofft man, ein besseres Verständnis des Verhaltens von Papier zu gewinnen. Darüber hinaus liefert eine breite Palette von Tests, die unter Verwendung der gleichen Zellstoffe durchgeführt wurden, eine gute Basis für zukünftige numerische Modellierungsversuche.

Schlüsselwörter: Laubholz, Nadelholz, Individuelle Fasern, Faser-Faser Bindungen, Festigkeit, RH, Mahlung

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Marina Jajcinovic
Graz, August, 2017

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Chapter 1

Introduction

1.1 DokIn'Holz Project

This thesis was performed under the scope of the "Doktoratsinitiative DokIn'Holz, - Mehrwertstoff mit Zukunft", comprised out of twelve research topics under a common goal of covering the entire value added chain of forest-wood-paper, connected by the common theme of sustainable resource utilisation. The research topic, named "Experimental determination and numerical modelling of the strength of individual fibres and fibre to fibre bonds in paper" was carried out by two universities (Vienna University of Technology - Institute for Mechanics of Materials and Structures, and Graz University of Technology - Institute of Paper, Pulp and Fibre Technology), Austrian Economics Chamber and two industrial partners, Mondi Frantschach GmbH and Sappi Austria Vertriebs-GmbH & CO KG. The topic was divided into two parts - one part dealing with experimental testing (TU Graz) with a purpose of gaining deeper understanding of the basic properties of fibres and joints and, at the same time, providing a uniform and complete platform of values for the numerical modelling and model verification (TU Wien). By mechanical testing of individual fibres, fibre to fibre joints and sheets (refined, non-refined, classified and non classified, wet pressed and standard made) a wide scope of factors that play a role in paper strength has been investigated. The work presented in this thesis deals only with a the experimental work, namely, investigations of the mechanical properties of individual fibres and fibre to fibre joints by means of experimental testing in respect to the :

- type of pulp
- environmental conditions
- influence of refining

1.2 Scope of the thesis

The strength of paper depends mainly on the strength of the individual fibres and fibre to fibre joints (Page, 1969). Since its creation, this statement has been the guiding principle of a large number of studies dealing with the properties of individual fibres and fibre to fibre joints. The properties of these individual fibres and joints would depend, among many others, on the type of the wood, morphology of the fibres and production treatments the fibres have been subjected to. Last but not least, their properties will also depend on the environmental conditions the fibres and joints will be exposed to during production and usage life. The thesis sets out to investigate the influence of these three factors on the strength of individual fibres and joints.
The first factor addressed is the type of fibres. Wood for the pulp and paper industry is divided into two main groups - hardwood (deciduous tree species) and softwood (coniferous tree species). This main differentiation comes from the differences in the usage of the fibres. Softwoods are characterised as long strong fibres which improve sheet strength, runnability on a paper machine, extensibility, air permeability, etc. Hardwood fibres on the other hand are short fibres which are mainly used for printing papers and as addition to improve formation, bulk and opacity, i.e. optical properties (Shackford, 2003). In a fibre network, longer and more collapsed fibres such as softwoods are capable of creating more bonds along its length and therefore help create a stronger network, i.e. paper web. However, softwood fibres also give sheets of higher density, lower opacity, and all in all a sheet of lower formation and optical properties when compared to hardwood sheets. Therefore, these fibres are mainly used for papers where the strength is the predominantly desired property, i.e. sack papers. Hardwoods on the other hand, have a greater variety of constituent elements but the main ones, libriform fibres, are short fibres with thick walls and relatively small lumens. Being short and coarse hinders the possibility of forming numerous bonds and better-interlinked networks, but does improve the formation and optical properties of paper. Due to this good formation, high opacity and bulk, these fibres are mostly used in writing and printing paper. As can be seen from above, differences between hardwood and softwood pulp are well known and it is not uncommon that blends of both will be used to obtain the optimum results. However, differences on a smaller scale, namely the differences in mechanical properties of single fibres and joints have not been in the focus of previous research.
The second factor was the influence of humidity on the mechanical properties of fibres and joints. Natural materials such as cellulose are highly sensitive changes in environmental conditions, such as temperature and especially humidity. Besides morphological changes such as swelling and/or shrinking, the mechanical properties of fibres and fibre to fibre joints change as well. During their production and life cycle, cellulose fibres are exposed to a wide range of temperature and humidity conditions - from a fully saturated state in an undisturbed polymer matrix (i.e. live tree), through

drying phase where a partial loss of free water occurs, cooking in acidic conditions, refining (where the free and bound water are restored), to sheet formation, drainage and drying. Later on, in usage, they are expected to bear load and hold structural form in a variety of environmental conditions, many of which differ greatly from laboratory conditions in which the paper and the constituent fibres are normally tested. Besides morphology of the fibres changing with each step, irreversibility of some of them also influences the change in mechanical properties such as bending stiffness, E-modulus and fibre strength. This difference between the wet state and the dry state has been in the focus in the 60ies and 70ies of the 20th century but the findings are somewhat contradictory. Some studies have shown that the mechanical properties, mainly strength of individual fibres, will increase (Wardrop (1951),Leopold and Thorpe (1968)) upon exposure to high RH or water. Others have shown that the strength of fibres decreases due to the increased water content/humidity (Klauditz et al. (1947), Russell et al. (1964), Kallmes and Perez 1966). In case of fibre to fibre joints, the influence of elevated or decreased humidity on joints has never been directly investigated.

Third factor influencing the mechanical properties of fibres and joints is the degree of refining. Refining is a mechanical treatment used in the paper industry to enhance the strength of paper. By subjecting the fibres to compressive, tensile and shear forces, higher degree of swelling, loosening of the cell wall, straightening and curlating, internal and external delamination and overall higher flexibility and conformability of fibres can be obtained Page (1989). Since it is a mechanical action, complete delamination, shortening of fibres and production of fines are also present. The produced fines (particles that can pass through a 76 µm mesh) help improve the formation and strength of paper but at the same time, also hinder the dewatering process. On a single fibre level, a beaten fibre would be expected to have lower strength than the unbeaten one. During refining, the layers in the cell wall (to a greater or lesser extent) delaminate or break off, decreasing the cohesion of the cell wall. However, this disruption is said to allow the fibre to reach better cell wall cohesion and better macro and microfibril orientation (Alexander et al. (1968), McIntosh (1968)). These changes contribute to an increase in strength of refined fibres. However, the increase is not indefinite and after a certain point, the strength is expected to decrease rapidly due to significantly high delamination of the cell wall. When it comes to fibre to fibre joints, one would expect an increase in joint strength due to a larger area in contact. However, only one study reported a significant increase in joint strength (Magnusson et al., 2013) while others reported slight or no increase on a single joint level. The influence of refining on sheet strength is well known, but when it comes to individual fibres and joints, the conclusions are not as straightforward.

1.3 Outline

The thesis is divided into five main parts: Introduction, Background, Materials and methods, Results and discussion and Conclusion and outlook. Each of the sections is, for the purpose of easier following, divided into three parts based on the topic they address.

Chapter 1 *Introduction* - the motivation for the work is stated and the three main objectives are identified based on how they influence the properties of fibres and joints

- influence of wood type
- influence of humidity
- influence of refining

Chapter 2 *Background* - some of the basic information about wood fibres are given and an overview of previous research divided into three sections according to the topic of interest is provided.

Chapter 3 *Materials and methods* - gives information about the used pulps, testing setups and testing methods developed for each research topic.

Chapter 4 *Results and discussion* - presents the results obtained in this study. Discussion offers a comparison with previous research (where available) and possible explanations.

Chapter 5 *Conclusion and outlook* - states the most important conclusions and understanding gained from the investigations. Some of the major issues that occured during testing are highlighted and suggestions for improvement are offered. Possible ideas for future evaluations are proposed.

1.4 List of publications

Peer Reviewed Articles

1. Jajcinovic, M., Fischer, W.J., Hirn, U. and Bauer, W. (2016). Strength of individual hardwood fibres and fibre to fibre joints. Cellulose, 23: 2049 – 2060

Contribution to conference proceedings

1. Jajcinovic, M., Fischer, W.J. , Hirn, U. and Bauer, W. (2016). Influence of different relative humidity on the strength of individual hardwood and softwood fibres and joints. In: Progress in Paper Physics Seminar, p. 174 – 179, Darmstadt, Germany.

2. Jajcinovic, M., Fischer, W.J. , Hirn, U. and Bauer, W. (2015). Mechanical properties of individual fibres and fibre to fibre joints - Influence of varying relative

humidity. In: European Doctoral students conference 2016 - An International Network on Cellulose Fibre Technology, p. 79 – 82, Stockholm, Sweden

3. Jajcinovic, M., Saketi, P., Fischer, W.J., Bauer, W. and Kallio, P. (2015). Determining the breaking load of individual fibre-fiber joints by means of different testing devices. In: COST action FP1105, Understanding wood cell wall structure, biopolymer interaction and composition: implications for current products and new materials: Sixth workshop, p. 17 – 19, San Sebastian, Spain

4. Jajcinovic, M., Fischer, W.J. and Bauer, W. (2015). Investigating mechanical properties of softwood fibre to fibre joints. In: 11th Minisymposium Verfahrenstechnik, p. 186 – 190, Vienna, Austria

5. Jajcinovic, M., Fischer, W.J., Hirn, U. and Bauer, W. (2015). Investigating mechanical properties of softwood fibre to fibre joints. In: Cellulose materials doctoral students summer conference 2015, p. 137 – 140, Autrans, France

6. Jajcinovic, M., Fischer, W.J. , Hirn, U. and Bauer, W. (2015). Mechanical properties of hardwood fibres and fibre to fibre bonds. In: 18th ISWFPC International Symposium on Wood, Fiber and Pulping Chemistry, p. 11 – 14, Vienna, Austria

7. Fischer, W. J., Jajcinovic, M., Hirn, U., Bauer, W. (2015). Mechanical properties of individual cellulose fibres and fibre to fibre bonds. In Book of Abstracts ?Polysaccharides and polysaccharide-based advanced materials: from science to industry?, 4th EPNOE International Polysaccharide Conference, p. 59, October 18 - 22, Warsaw, Poland.

8. Fischer, W.J., Lorbach, C., Jajcinovic, M., Hirn, U. and Bauer, W. (2014). Measured and calculated bending stiffness of individual fibres. In: Progress in Paper-Physics Seminar, p. NA-NA, Raleigh, North Carolina, USA

Presentation

1. Fischer, W. J., Jajcinovic, M., Hirn, U., Bauer, W. , Schennach, R. (2014). Investigating individual fibers and fiber to fiber joints. In PowerBonds Dissemination Seminar, München, Germany

2. Zankel, A., Nachtnebel, M., Jajcinovic, M. and Fischer, W.J. (2016). New investigation methods of fibres and cellulose materials by conventional and environmental scanning electron microscopy. In Die Österreichische Papierfachtagung, Graz, Austria

Chapter 2

Background

2.1 Wood fibres

Wood, or more precisely, the tissue system of wood consists out of multiple elements specialised for mechanical support, water transport and nutrient storage. The most important and abundant ones are the parenchyma cells (storage and water transport), libriform fibres (mech. support), tracheids and vessel elements (water transport and mech. support) (Ilvessalo Pfäffli, 1995). Depending on the species, hardwoods, alongside these four elements, can have multiple other forms, each designed for a specific purpose. Figure 2.1 shows the characteristic elements of wood.

Softwoods have a relatively clean structure with tracheids dominating in proportion and barely any vessels or libriform fibres. The absence of vessel elements is due to the morphology of the crown and vegetation period (less need of rapid water transport due to needles and shorter growth season). Due to this absence, tracheids serve both the purpose of giving the tree its structural rigidity but also having conductive purposes. Because of this conductive purpose, springwood tracheids are often perforated with bordered pits while the summerwood tracheids have mainly smaller slit like pores. These pores play a significant role in both pulping processes and mechanical properties of wood. In pulping, they represent an access point for pulping liquor while in the delignified form they represent a weak spot in the cell wall.

Hardwoods, having a higher degree of organisation, have two main elements serving each its own purpose - vessel elements for water transport and libriform fibres for mechanical support (Ilvessalo Pfäffli, 1995). For this reason, libriform fibres will have less, if any, small scattered pores in the pit membranes and all the water transport will occur mainly through the vessel elements (Rydholm (1965), Parham and Gray (1982), Barnett (2004)).

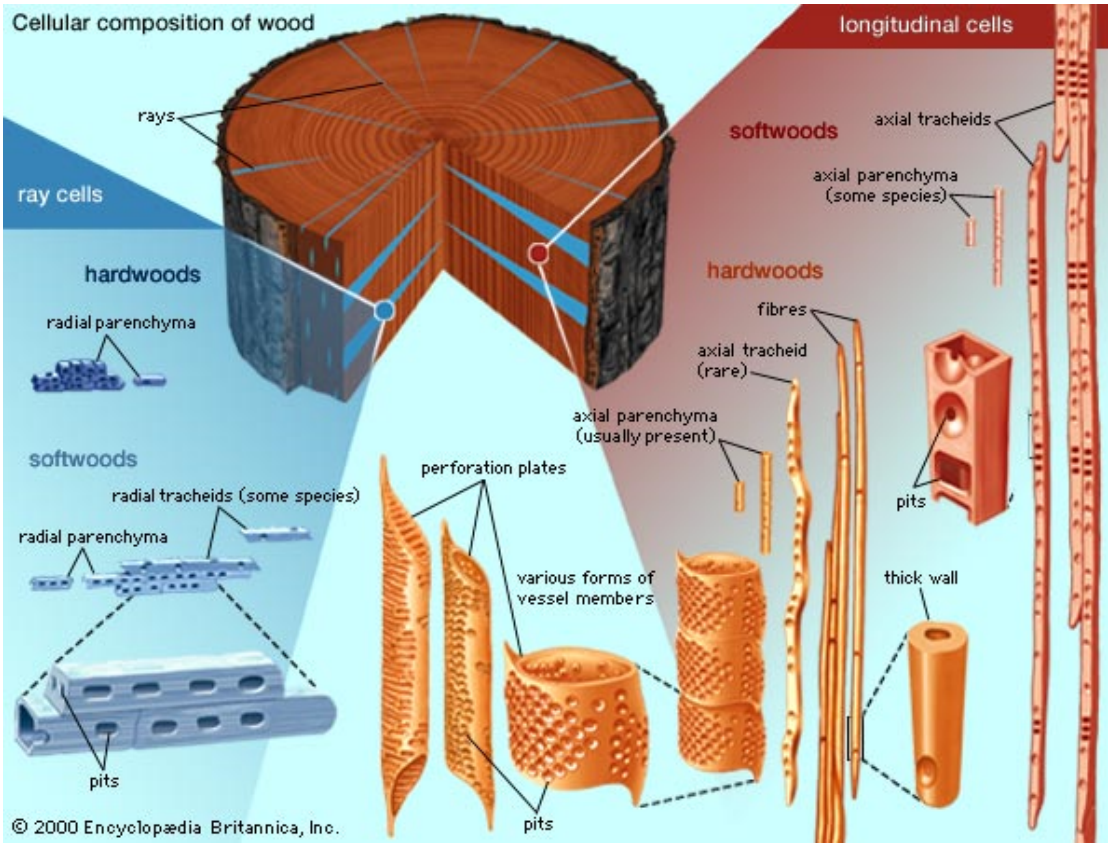


Figure 2.1 Wood fibres, Encyclopaedia Britannica (2017)

The tracheids and libriform fibres, being the most abundant in both species are of special interest in papermaking and have therefore been studied most extensively.

2.1.1 Fibre structure

Regardless of their origin, both tracheids and libriform fibres (from here on referred to simply as fibres) are embedded into a matrix called the middle lamella. The fibres are "freed" out of the matrix during the cooking process which dissolves the majority of the compounds it is comprised of (lignin and hemicelluloses). Each fibre consists out of a primary wall and three main layers - S1, S2 and S3, shown in Figure 2.2.

All three layers are composed out of cellulosic microfibrils embedded in a polysaccharide matrix and lignin (to a lesser extent) (Donaldson, 2008). The cellulosic chains are relatively brittle giving the fibre its strength in the axial direction, while the surrounding matrix provides flexibility. The angle at which they are helically wound against the longitudinal fibre axis is called the microfibril angle (MFA) and it can vary from large angles in the S1 and S3 layer (transversely oriented) to very low angles observed in the S2 (axially oriented) (Donaldson (2008), Barnett (2004)). In the tree, the MFA decreases from pith to bark (Lichtenegger et al. (1999)), and the MFA angels

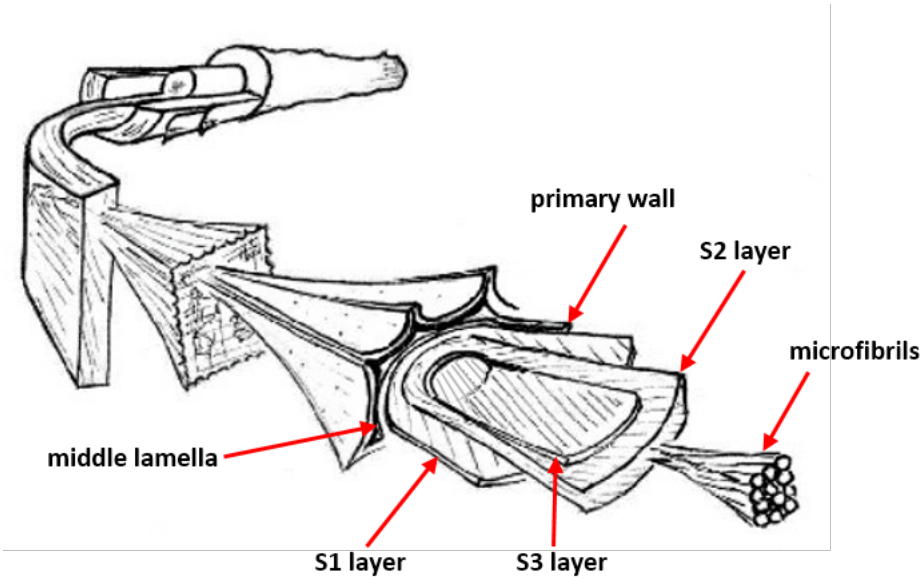


Figure 2.2 Schematics of wood fibre (redrawn according to Eichhorn (2011)

of the S2 layers are generally lower in hardwoods than in softwoods. Since the S2 layer is the thickest layer making up about 80% of the fibre wall area, the orientation angle of the microfibrils in this layer will play the predominant role by influencing the E-modulus, bending stiffness and ultimately, the strength of the fibre. The higher the fibril angle, the lower the fibre strength will be (Page et al., 1972).

2.1.2 Papermaking properties of fibres

According to CEPI report (CEPI Confederation of European Paper Industries, 2013) in European paper industry, 70% of total wood consumption are softwoods, with hardwoods contributing to only 30% of total wood consumption. This discrepancy has been attributed to the availability of the raw material and suitability for the paper production. With hardwoods, it is common to find a greater variety of species within one logging site that require completely different processing methods. Different species also mean different properties and not all of them are suitable for papermaking. Hardwoods generally have higher density, making the wood less penetrable by pulping liquids and a greater variety of elements, which are not all desirable in papermaking. All of these factors played a significant role in the consumption, and even though much of the processing problems (logging, transport and cooking) have been solved, the composition and size of fibres still renders hardwoods as a less used type of wood in papermaking in Europe. Most commonly used types of hardwoods are birch, beech, poplar and eucalyptus, whereas the most common softwoods are spruce, fir and pine. Table 2.1 shows the mean length and width of some of the most commonly used fibres in paper industry.

Table 2.1 Mean fibre length and width of hardwood and softwood fibres (Sirviö, 2008)

	mean fibre length l_f [mm]	mean fibre width w_f [µm]
eucalyptus	1.1	20
birch	1.3	25
beech	1.2	21
spruce	3.5	27
pine	2.8-7.2	37-47

l_f ... length weighted average
w_f ... width weighted average

Softwoods mainly have a mean fibre length of 2-6 mm and the lumen and cell wall, or fibre diameter, vary based on the earlywood/latewood division. Earlywood fibres have thin walls and wide lumens while the latewood fibres have thicker cell walls and smaller lumens. Because of this difference, the earlywood fibres tend to collapse easily and form ribbon-like or flat pulp fibres. The summerwood fibres tend to collapse less and to some extent keep their tubular form. This difference also plays a role in papermaking since the more flat or ribbon-like fibres tend to conform better and form larger bonds with adjacent fibres (Sirviö, 2008). Longer fibres enable creation of multiple bonds along the length of the fibre and therefore produce sheets of greater strength. Precisely this ability of forming large and multiple bonds makes softwood pulps a perfect choice when it comes to papers where strength is the dominant property. Hardwood fibres on the other hand are generally small, their length varying between 0.7 and 1.5 mm (Ilvessalo Pfäffli, 1995). The width of cell walls and lumens varies between species and climate in which they have grown. Since there is a large variation in hardwood species and the properties of fibres, only one of the most widely used hardwoods will be discussed - the eucalyptus fibres. In tropical wood species such as eucalyptus, the differences between earlywood and latewood are not as pronounced as in case of softwoods, simply due to the all year around growth period. Constant growth conditions also render tropical species of hardwood (especially eucalyptus) to have more uniform length and thickness than softwoods. In papermaking, these fibres will not be used to achieve high strength of paper since their short length; thick walls and small lumen inhibit creating of multiple bonds. However, precisely the properties making them less usable for high strength papers make them prefect to achieve good formation, opacity and bulk. For those reasons, hardwood fibres are mainly used for paper where optical properties and bulk are of major importance. Standard division of papermaking fibres would state that softwoods give strong paper, while hardwood fibres give paper of good optical properties. However, it is not uncommon that mixtures of both hardwoods and softwood are used when the optimum is to be achieved. Softwoods will improve runability on the paper ma-

chine and strength (act as a reinforcement agent) while hardwoods will be added to improve formation, bulk and opacity (Shackford, 2003).

2.2 Fibre and joint testing background

If one is to gain a better understanding of the behaviour of paper, one needs to understand what governs the strength of fibres and joints. Most of the earlier studies have dealt with investigations of softwood fibres and joints since they were the more commonly used type of pulp, and, because of their larger size, more suitable for individual fibre and joint testing. Lower consumption in the industry and smaller size of hardwood fibres have rendered this pulp type less desirable and more tedious to test, and in the end, to be somewhat overlooked when talking about individual fibre and joint properties. In this chapter, the focus will be on the knowledge gained from previous studies, rather than on the developed methods. A more detailed description of the indirect and direct methods developed for individual fibre and joint testing can be found in the thesis of Fischer (2013).

2.2.1 Individual fibre tensile testing

Testing devices

There are two possible ways of determining the fibre strength. One is by using direct methods where an individual fibre is tested, and the second one is to use indirect testing methods, namely, the zero span test. Up until today, several direct testing methods have been developed and used for determining the tensile strength of individual fibres. The devices used for testing were in the beginning special or modified types of scales such as "Hebelwaagen" (Klauditz et al., 1947), and the Westphal balance (Wardrop, 1951), tensile testers such as the ones used for paper testing (Klauditz et al., 1947), special load elongation testers (Van Den Akker et al., 1958) or even standard universal testing machines (Kersavage, 1973). Further development and desire to investigate the properties of individual fibres led to more elaborate devices to be developed such as the Instron Tensile Tester (Kellogg and Wangaard (1964), Page et al. (1972), Conn and Batchelor (1999)). Some researchers went even further in developing their own testing devices (Kompella and Lambros (2002), Burgert et al. (2003), Saketi and Kallio (2011), Fischer et al. (2012)). Figure 2.3 and Figure 2.4 show some of the designs for individual fibre tensile testing.

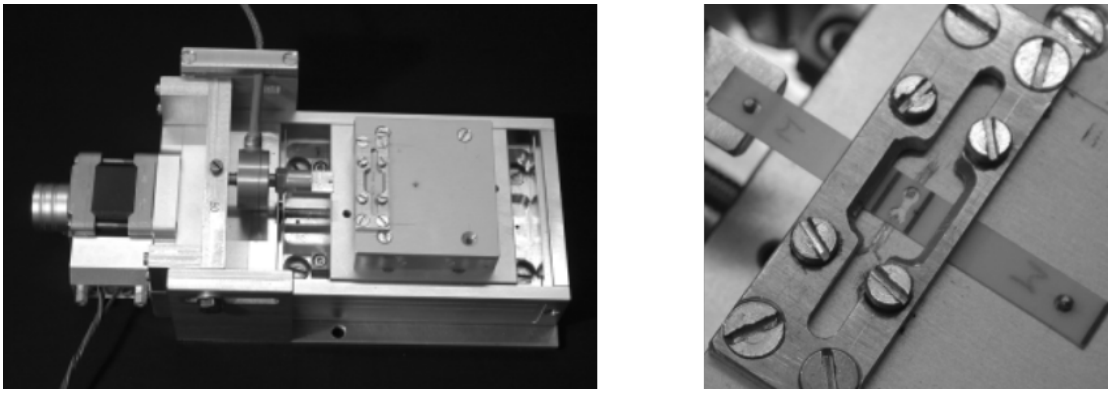


Figure 2.3 Custom built tensile tester developed by Burgert et al. (2003)

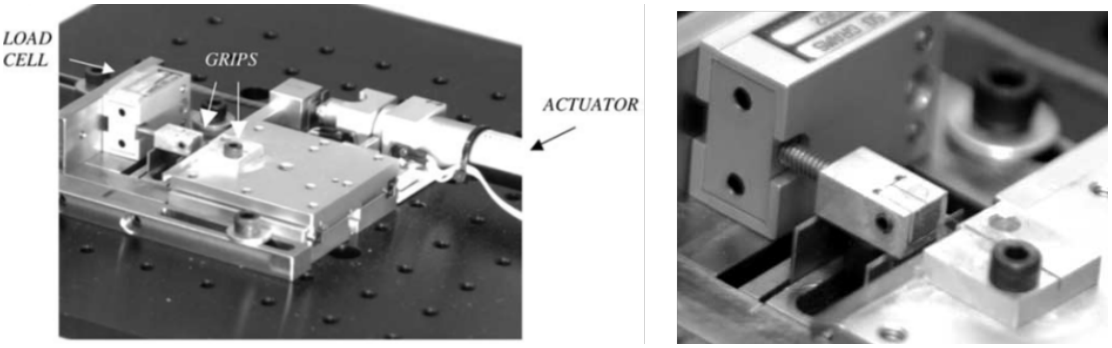
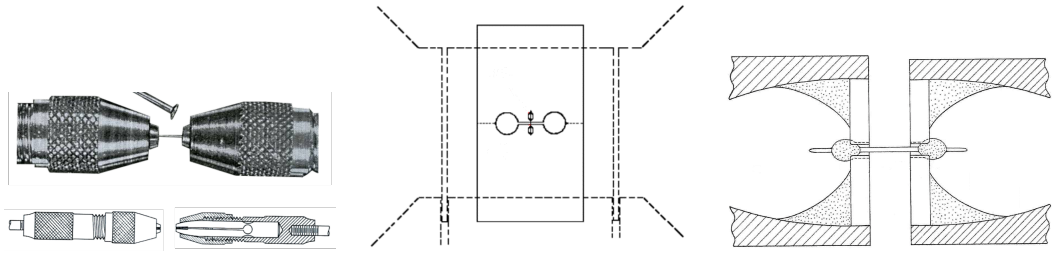


Figure 2.4 Custom built tensile tester developed by Kompella and Lambros (2002)

Fibre fixation methods

The principle of all tensile tests is the same: a fibre is placed over a span and strained in one direction until failure occurs. Regardless of the type of device used for testing, they all have one thing in common - special need of fibre fixation. Fibres are either collapsed ribbons or cylindrical tubes in shape, and can be considered relatively sensitive to manual handling. Therefore, a need of fixation that would not interfere with the properties of fibres was needed. Jayne (1959) used specially designed lightweight grippers with the inside covered with an abrasive paper. The purpose of the paper was to provide enough holding ability so the fibre would not slip out, while at the same time eliminating the contact of the fibre with the sharp metal edges of the gripper. With this setup, the pressure on the grippers had to be carefully adjusted as not to damage the fibre prior to testing. Wardrop (1951), Van Den Akker et al. (1958), Russell et al. (1964), Leopold and McIntosh (1961), Leopold and Thorpe (1968) , Burgert et al. (2003) used specially designed sample holders on which the fibres were glued using different types of adhesives. In this fixation process, the choice of glue played a very important role. Besides providing substantial holding strength, it had to have low shrinkage factor as not to create stress concentrations in the glue points and suf-

ficient viscosity as not to flow into the fibre or to form a thin layer on the surface of the fibres. Kersavage (1973), Mott et al. (1995) and Peters (2010), used a ball and socket system for testing of individual fibres. In this method, a droplet of epoxy glue is placed at either end of the tracheids. Once the glue has cured, the fibre with the epoxy balls is placed into a socket system of a tensile tester. Examples of the three main fixation principles are shown in Figure 2.5.



(a) mechanical clamping (Jayne, 1959)

(b) Gluing on a sample holder (Van Den Akker et al., 1958)

(c) ball and socket system (Kersavage, 1973)

Figure 2.5 Fixation principles of tensile testing

Each of the fixation methods listed above has its advantages and disadvantages. In mechanical clamping, it is relatively difficult to achieve sufficient clamping pressure without introducing stresses in the fixation region and damaging the fibres (Groom et al., 2002). However, fixation of fibres is faster and less tedious than gluing. With gluing, one must take care to use glues that have enough holding ability, good working time and that do not creep over the fibres. Shrinkage during drying is another point that should be addressed - too much of glue shrinkage might introduce stresses in the glued region (Van Den Akker et al., 1958). However, if done properly, the glue will provide enough holding ability without causing stress concentrations in the fixation points. With the third option, the ball and socket system, besides being time consuming, one must take care not to damage the fibre while handling it with tweezers. Since the epoxy balls are placed on the end of the fibres, this calls for careful manipulation with tweezers precisely in the region that is to be tested. On the positive side, the ball and socket system allows self-alignment of fibres and therefore causes no stresses during fixation.

Determination of the fibre cross sectional area

When determining the strength of fibres, two factors need to be known - the maximum force the fibre can withstand (breaking load) and the cross sectional area of the fibres. The direct tensile testing gives the ultimate load or load at break of individual fibres. On the other hand, to determine the cross sectional area, several different methods, with varying levels of reliability, have been developed.

Microscopy investigations were the first methods used for determination of the cross sectional areas. The principle was that the fibre is placed perpendicularly under the microscope on a rotating manipulator as to enable imaging from different angles (Van Den Akker et al. (1958), Tamolang and Wangaard (1961)). From the images, either the minor or major axis of the "ellipse" are measured, or, the cell wall thickness, width and thickness of the fibres are measured. The cross sectional area is then on calculated using those values. Since fibres are not always perfectly ellipse shaped and the lumen is not considered, some over - or underestimation of the real cross sectional area are possible.
A compacted apparatus measurement method was another procedure used in the effort to obtain the cross sectional area (Page et al. (1972), Hardacker and Brezinski (1973)). In this method, a fragment of fibre is cut after tensile testing and the fibre is placed between two glass plates. The thickness is then measured with a microscope and the width by either image splitting eyepiece or again, microscope. In this method, some underestimations are possible since the fibre cross sectional area was measured after a plastic deformation took place, and again, the lumen is not taken into consideration.
Microtome cutting and microscope analysis presents one of the more accurate measurements methods. It involves embedding of a sample into a polymer matrix that holds the fibre in position during cutting (Van Den Akker et al., 1958). A series of images is obtained from which the fibre cross sectional area can be measured or calculated. In this case, care must be taken that the polymer for embedding does not induce swelling of the fibres.
Another method available for determination of the cross sectional area is Scannning Electron Microscopy (SEM) in combination with digital image analysis (Reme et al. (2002), Chinga et al. (2007)). The fibre samples are aligned, freeze-dried, embedded in resin and cut perpendicularly to the fibre direction. Once cut, the samples are scuffed, polished, carbon coated and digital images recorded using the SEM (Reme et al., 2002). Obtained images are then analysed using digital image analysis. As precise as the method is, there are still several factors that need to be considered, namely, the fact that the fibres need to be almost perfectly aligned in order to avoid over- or underestimations, and, that the threshold values need to be chosen according to grey level histograms in the image when converting the grey scale image into a binary one.
Confocal laser scanning microscopy (CLSM) is an optical method comparable to the microtome and the SEM investigations, with the exception of being non-destructive. In this method, the laser beam passes through a pinhole and focuses only on one point in the focal plane. Only light from this point can pass through a detector pinhole and be detected, whereas any additional light is being eliminated. The scanning mirrors deflect the beam over the whole sample in a raster mode. The method gives information about the 3D structure of the samples by scanning them in xy and xz

planes, and the fibre morphology is created in 3D by stacking the images as shown in Figure 2.6.

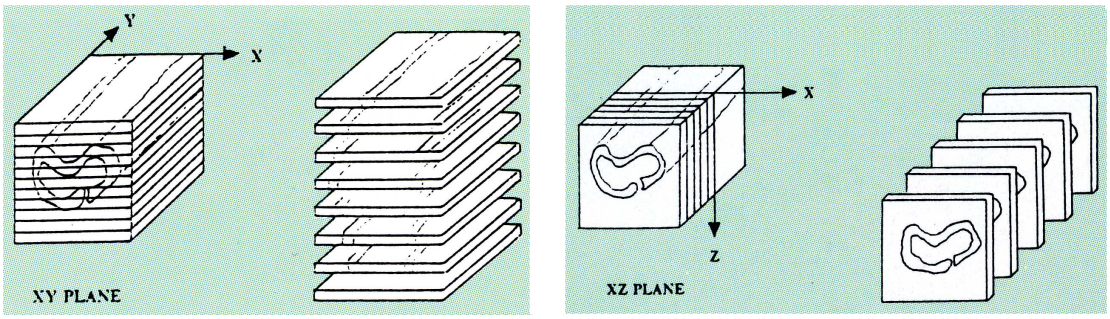


Figure 2.6 CLSM sectioning (Moss et al., 1993)

State of the art in individual fibre tensile testing

There are a number of studies dealing with the investigations of individual fibres but the ones of particular interest for this study are listed below in chronological order. These studies have been selected based solely on the insight they provide into testing of individual fibres.

Van Den Akker et al. (1958) tested individual sweetgum fibres on a custom-built load-elongation tester. The fibres were glued on paper tabs using a glue specially designed for this purpose. The reason for the development of such glue was because they observed that the choice of glue plays a significant role in test results. Using a glue that had high shrinkage coefficient created stress concentrations in the gluing point, leading to an underestimation of the breaking load values. On the other hand, insufficient holding ability resulted in the pull out of the fibres. Another factor that could induce stress concentrations in the fixation points was the misalignment of the fibres. Therefore, glues with high shrinkage coefficient, low holding ability and the misalignment of the fibres in tensile testing should be avoided.

Jayne (1959) investigated the influence of the type of fibre on the fibre strength. He tested earlywood and latewood of Douglas fir, cypress and spruce on an Instron tensile tester where the fibres were fixed in position by using specially designed lightweight grips. The cross sectional area was determined using a calibrated micrometre eyepiece. In the order of magnitude of differences, spruce fibres exhibited only slightly higher strength values in case of latewood fibres. Cypress fibres had more pronounced differences and Douglas fir the most pronounced contrast between the mechanical properties of earlywood and latewood fibres. The differences were attributed to the variation in the elementary molecular structure of the fibres.

Jentzen (1964) investigated the influence of stress applied during drying on the strength of individual springwood and summerwood pine fibres. Individual fibre reference sample was dried under no load, and three subsequent series were dried

under 1, 3 and 5 grams load. He observed that the fibre strength increases when fibres are dried under load. When it comes to differences between earlywood and latewood, the springwood fibres had a higher increase in strength, levelling up (when dried under stress) with the summerwood fibres. The differences, among the discontinuities and possible fibre defects were attributed to the percentage and the orientation of the S2 layer comprising the cell wall (summerwood fibres having larger percentage). When drying under load, the S2 layer in both type of fibres orientated in the similar way, decreasing the differences in the fibre strength.

McIntosh (1968) investigated the influence of refining on fibre strength. They tested bleached and unbleached, springwood and summerwood loblolly pine fibres. Both bleached and unbleached samples were refined to different degrees based on their type (earlywood/ latewood) using a PFI mill. They concluded that refining decreased the breaking load and strength of bleached and unbleached summerwood fibres while the strength of springwood fibres increased. The changes were attributed to the reorganisation and consolidation of the cell wall and the change in the microfibril angle during refining. Similar behaviour was observed by Leopold (1966) (as cited in McIntosh (1968)) with the exception that the observed increase in strength was due to a decrease in fibre cross sectional area.

Leopold and Thorpe (1968) investigated the influence of cooking on the strength of individual fibres. They tested individual sulphite and kraft spruce fibres using an Instron tensile tester and observed higher breaking loads and strength in case of kraft pulp than in case of sulphite pulp. The difference was attributed to the kraft process creating stronger internal cohesion in the fibres than the sulphite one. Hardacker (1970) (as cited in Page et al. (1972)) tested individual fibres over different testing spans and discovered that increasing the testing span reduced the fibre strength. This effect was attributed to the natural defects in the fibres. By increasing the span length, the risk of one or more structural defects to occur along the testing length of the fibre also increases.

Page et al. (1972) investigated the influence of MFA and cross sectional area on fibre strength. They tested earlywood and latewood spruce fibres on an Instron tensile tester paired with a Fibre Load Elongation Recorder (FLER). Following the tests, the cross sectional area of the fibres was determined by compacting the cut-out piece of the fibre between two glass plates. The thickness of the fibre was determined by interference microscopy and the width by image splitting eyepiece. The MFA of the fibres was determined using a mercury reflection technique. They observed that the fibres having the same MFA had similar strengths, regardless of the fibre type (earlywood/latewood) or species (spruce or pine).

Kersavage (1973) investigated the influence of the moisture content on the tensile properties of individual Douglas fir latewood tracheids. The fibres were tested using the ball and socket principle on a universal testing machine (Tinus Olsen) placed in a conditioning chamber. The fibres were conditioned for one week in 1%, 29%, 66%,

83% RH and fully wet state. The maxiumum breaking load of fibres was observed to be at 66% RH with the values decreasing with change to the either end of the RH scale. Optimum of modulus of elasticity was at around 25 to 30% RH.

Alongside testing of individual fibres, which is tedious, time consuming and often yields results of high variability due to the inhomogeneous nature of fibres; indirect methods have been developed in the attempt to facilitate the testing and obtain more uniform results. The most notable one is the zero span tensile test where instead of individual fibres, a paper sheet strip is tested. The principle of testing is similar to any standard tensile test, with the exception that there is no span length between the jaws of the device. With this setup, the force applied to separate the jaws is converted into the load on the sample, i.e. fibres in a sheet strip. The method, as fast as it is, does not give the real fibre strength since the load is divided between thousands of fibres and their properties are affected by fibre defects and misalignments of fibres in the direction of load application (Van Den Akker et al., 1958).

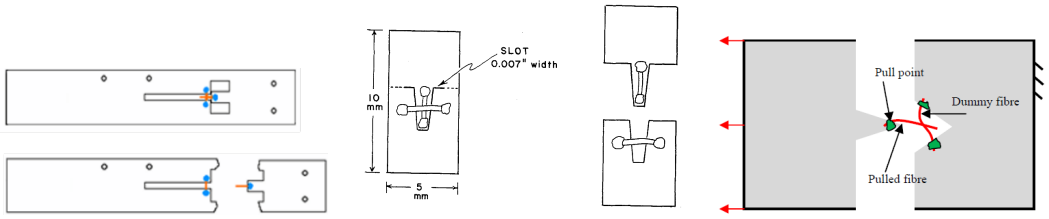
Summary on individual fibre tensile testing

Knowledge gained from the previous studies provides an insight into what influences the breaking load and strength of the fibres. Based on these findings, it is possible to exclude factors which might cause irregularities, unintentional falsification or large variation in results. Among many factors that play a role, the most notable ones would be the influence of the type of a fibre tested, whether it is an earlywood or a latewood fibre. Since previous research states that there are differences in breaking load and strength of earlywood and latewood fibres, dividing the fibres into two principal groups might provide more comprehensive behaviour and less scattering of the values. The fixation method should also be considered since stress concentrations due to the unsuitable choice of glue or misalignment can cause failure of the fibre at lower stress levels due to the non-uniformity of stress distribution. The MFA is considered to play an important role in fibre strength and should, if possible, be accounted for. The influence of testing span should also be taken into consideration since it has been shown that the breaking load of fibres reduces with the span length. Where possible, same span lengths should be used. Last but not least, the cooking process and the subsequent chemical and mechanical treatment will also play a significant role. If a comparison is to be made, same levels of refining should be used and chosen in an increment large enough to expose a change but small enough as not to overlook a potential change.

2.2.2 Fibre to fibre joint testing

Testing methods

Several testing methods were developed over the course of time, which either included controlled joint manufacturing or free joint formation. Controlled joint manufacturing such as a fibre-shive system used by Mcintosh and Leopold (1961), joints of crossing angles of 90° (Stratton and Colson, 1990) or overlap joints used by (Button, 1979) involved placing of fibres in a controlled manner on top of each other in presence of water, and, a subsequent drying under a specified load. Other methods have been developed where the joints were freely formed (Mayhood et al. (1962), Russell et al. (1964), Fischer et al. (2012), Magnusson and Östlund (2011)) and later selected based on the crossing angle and the suitability for testing (size wise). The goal of the latter was to form joints in the same manner as if they would be formed in a sheet. Nevertheless, regardless of how the joints are made, handling them still presents a challenge. Once they are formed, they have to be placed on a sample holder, glued using some sort of an adhesive and subsequently tested. Figure 2.7 shows some of the sample holders used for joint testing.



(a) Fischer et al. (2012) **(b)** Stratton and Colson (1990) **(c)** Magnusson and Östlund (2011)

Figure 2.7 Sample holder used for joint testing

The sample holders are usually made out of polymers (Stratton and Colson (1990), Fischer et al. (2012)) or metal (Magnusson and Östlund, 2011), and based on their design, required additional manipulation (melting of the bridges in case of Fischer et al. (2012)), or gluing of the load application fibre (Magnusson and Östlund, 2011). A different approach of testing was developed by Saketi and Kallio (2011), which included a microrobotic platform enabling the testing of joints without manual handling and gluing. The microrobotic platform and close up of the grippers are shown in Figure 2.8.

In this case, the joint, once it has been identified with a camera, is picked up by microgrippers on one end of the cross fibre and elevated from the surface, then, the other end of the cross fibre is gripped with microgrippers moveable in X,Y and Z direction. The longitudinal fibre is grasped with the third stationary microgripper

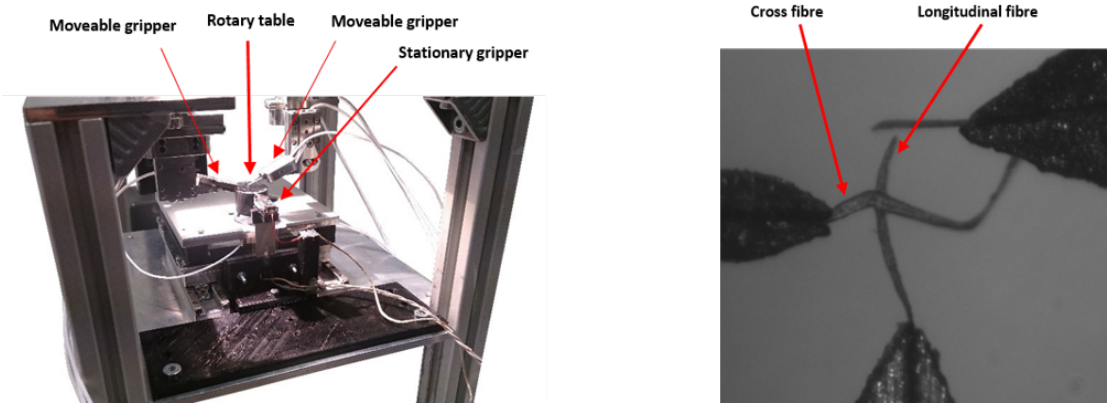


Figure 2.8 Microrobotic platform

equipped with a force sensor. Once the joint is fixated, the microgrippers grasping the cross fibre are pulled away from the stationary gripper until breakage occurs.

Determination of the bonded area

The determination of the bond strength, although less reliable, is easier done with indirect testing methods since the force is already divided by the area it is acting upon. If one is to use direct testing methods to obtain joint strength, besides the breaking load values, the bonded area needs to be determined as well. There are a couple of possible measurements methods such as polarisation light microscopy method (PLM - Page (1969)), dyeing methods such as FRET (Förster Resonance energy transfer - Thomson et al. (2007)) and microtome methods (Asunmaa and Stenberg, 1958). However, only polarisation light microscopy offers quantitative rather than qualitative information about the bonded area that could be used for joint strength calculations (Kappel et al., 2010). Polarisation light microscopy (Page, 1969) is a method based on polarised vertical illumination of the sample. For the measurements, a light microscope with vertical illumination and two polarisers is used. In the first step, the light beam passes through the polariser and is directed towards the sample where it is being reflected towards the analyser. The analyser is positioned at a 90° angle towards the polariser so only modified beams can pass through it. In case of a single fibre, the light beam is reflected from the sample and directed through the analyser making the fibre appear light. In case of two fibres crossing each other, the light cannot pass the analyser and the area appears dark Figure 2.9. The method works the best with fully collapsed earlywood fibres and in case one of the fibres is dyed.

If the joints are made of latewood fibres, or fibres with large differences in the cell wall thickness, it is possible, that the area will not appear dark but light. Kappel et al. (2009) investigated fibre to fibre joints using the PLM method as well as the microtome method and discovered that when fibres of different cell wall thicknesses or latewood

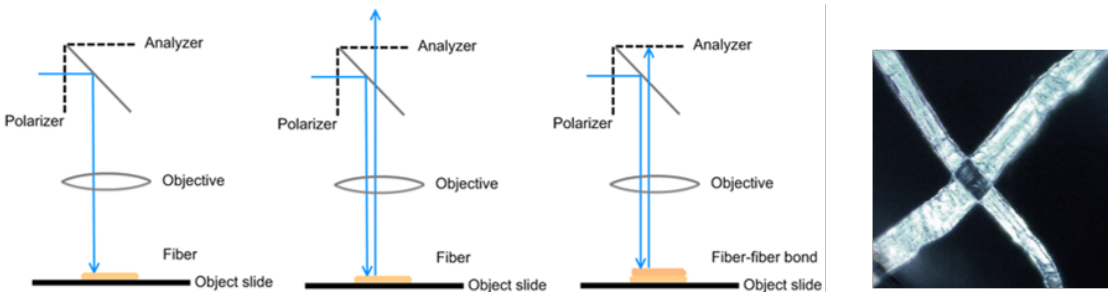
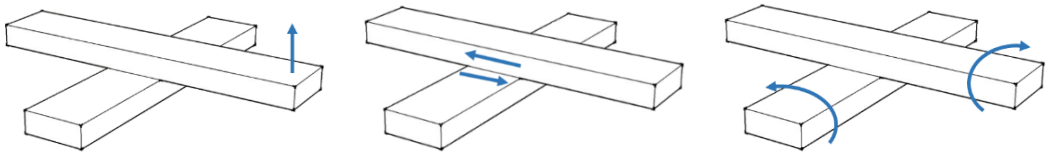


Figure 2.9 Polarisation light microscopy (Kappel et al., 2009)

fibres were in the joints, the area would appear light or unbonded. This was believed to be due to the different light reflectance in case of joints where fibres of unequal thicknesses were bonded. However, these joints, as it was later on discovered with the microtome method, were in fact bonded and the results obtained with the microtome method and the PLM were in good agreement. The advantage of the method is that satisfying results can also be obtained even if non-dyed fibres are used (Kappel et al., 2010) and that it is non-destructive, making it suitable for measurements of the bonded area prior to mechanical testing. However, even though the method gives quantitative analysis of the area in contact, one must keep in mind that the method only gives the area in optical contact and that the degree of contact or the area in molecular contact cannot be determined.

Modes of loading in joint testing

In fracture mechanics, there are three possible ways a crack in a structure might be initiated: by opening the structure, by pulling it apart or by twisting (Perez, 2004). Similar phenomena take place in fibre to fibre joints. Figure 2.10 shows three modes of loading usually encountered in joint testing.



(a) I. peeling mode **(b)** II. shear loading **(c)** III. torsional loading

Figure 2.10 Loading situations in individual fibre to fibre joint testing

In the peeling mode, the load is acting perpendicularly on the joints, causing the "opening" of the joint. In the shearing mode, the force is applied parallel to the bonded area until breaking occurs and in the torsional loading, a torsional moment is created within the joint.

In a sheet, due to the overlapping and interlocking of fibres, it is very hard to discern a specific mode of loading. Mainly, the situation resembles a combination of all of the aforementioned modes. In individual joints, the situation is only a bit clearer, i.e. the force application direction can be controlled. However, the response of the joint cannot be controlled and it is not uncommon that during shear loading, the joint complies with the straining direction and introduces forces acting perpendicularly (i.e. peeling mode). If the crossing angle is not exactly 90°, torsional loading will also have a contribution to the loading situation. Therefore, since an interplay of different modes of loading cannot be excluded, one says that the joints are tested in a predominantly peeling, shearing or torsional loading mode.

State of the art in fbre to fibre joint testing

Mayhood et al. (1962) investigated the influence of cooking process, beating and bleaching on the strength of individual fibre to fibre joints. They tested individual joints of beaten/unbeaten, bleached/unbleached kraft pulp and unbeaten, unbleached sulphite pulp by using a modified chain-weight balance. The unbeaten unbleached kraft pulp exhibited the highest breaking loads, while the untreated sulphite pulp the lowest ones. When it comes to the effects of bleaching and beating, the results showed no significant differences indicating that chemical and mechanical treatments do not play a significant role in the breaking load of individual fibre to fibre joints.
McIntosh (1963) tested tensile and bonding strength of Loblolly pine kraft pulp using a modified analytical balance. The samples for testing were the fibre shive systems with a crossing angle of 90° divided based on their composition type (either summerwood or springwood). Additionally, two individual fibre to fibre joints were tested and the results were in good agreement with the fibre-shive system results. The strength of summerwood joints was around 5.79 MPa and the springwood ones around 1.77 MPa.
Button (1979) tested overlap loblolly hollocelulose joints on an Instron tensile tester paired with a Fibre Load Elongation Recorder (FLER). Due to the overlap of the joints, this method allowed for a very precise loading situation where the influence of the torsional loading was excluded. He concluded that the length of the overlap and structural characteristic of a bond and the fibres forming it played an important role on the joint strength.
Stratton and Colson (1990) investigated the influence of the joint composition on the joints strength. They tested individual springwood and summerwood joints made of loblolly pine with a crossing angle of 90°. Although no significant difference was obtained, the joints made out of summerwood fibre had higher breaking loads and strength than the joints made out of springwood fibres.
Alongside direct methods, indirect methods have also been developed such as the Z-directional tensile test (as cited in Stratton (1991)), the delamination test (Skowronski

and Bichard, 1987), and of course, the Page equation (Page, 1969) where the bond strength is calculated using the values obtained from measurements performed on sheets and individual fibres.
In the delamination tests (Skowronski and Bichard, 1987), the paper strip is sandwiched between two pieces of adhesive tape and mounted in an Instron testing machine equipped with a free rotating wheel. Out of the 6 cm strip, the first 2 cm are delaminated at a constant strain rate to reach stable delamination. The remaining length of the sample is then delaminated and the force recorded. The bond breaking energy is determined only for the second part of the delamination test (4 cm) from the area under the curve. A modification of the delamination test is the peel cohesion test, which has the exception that it is conducted on a flat surface instead on free rotating wheel.
Z-directional tensile (as cited in Koubaa and Koran (1995)) is one of the oldest tests used to determine the strength of fibre to fibre joints. A piece of paper is sandwiched between two double-sided adhesive tapes glued onto the specimen holder. Once glued, the holders are inserted in the testing device. The jaws carrying the upper part of the specimen holder are pulled up and the Z-directional tensile strength is defined as the force required to produce unit area of fracture perpendicular to the paper plane.
Scott bond test (as cited in Koubaa and Koran (1995)) is a dynamic test essentially developed for measuring the internal bond strength of paper and paperboard. The paper sample is sandwiched between the base of the device and aluminium angle (with the aid of double-sided adhesive). A swinging pendulum is then released on the upper part of the aluminium angle causing the sheet to split. Calibrated scale indicates the resistance of the sheet to split in terms of the loss in the potential of the pendulum swing.
Probably the most well-known theory for calculating the bond strength though is to use the Page equation. Even though this equation is made to calculate the strength of paper, it can be used in reverse to obtain the fibre to fibre joint strength. To get the strength of sheets the following factors are necessary: the breaking length, zero span breaking length, fibre cross sectional area, fibre density, fibre-fibre bond strength, fibre perimeter and length and the relative bonded area. Once these values ahve been obtained, and by reversing the equation, the bond strength can be easily calculated although, as proven by Stratton (1991), better results are obtained if fines are removed from the sheets.

Summary on joint testing

The previous studies offer an insight into the factors determining the strength of joints and form guidelines that should be taken into consideration if one is to reach a better understanding of the joint behaviour. Great care must be taken while handling

the joints since they are extremely sensitive to vibrations and might be damaged during mounting. Attention should be paid to the composition of joints if possible, since it has been shown that summerwood joints exhibit higher breaking loads and strength than the springwood ones. When comparing different joint strength values, care should be taken regarding which pulp types are being compared. Kraft pulp not only produces stronger fibres but also stronger fibre to fibre joints. The same care should be taken when dealing with chemically and mechanically treated pulp. If possible, same bleaching sequences and refining degrees should be compared. Last but not least, the loading situation will probably play the most important role. For the real joint shear strength to be measured; the joints should have as clear loading situation as possible and the contribution of peeling and torsional loading should be excluded as much as possible.

2.3 Influence of pulp type on individual fibre and joint properties

Softwood fibres have been extensively studied in the past and the majority of the knowledge about fibres comes precisely from studies dealing with these fibres. Several of those studies have already been covered in the Section 2.2.1 and 2.2.2 and a more detailed description can be found in the thesis of Fischer (2013).

2.3.1 Testing of individual hardwood fibres

When it comes to hardwoods, the literature provides less information about fibre strength, E-modulus or breaking load. There are several studies dealing with the indirect determination of the aforementioned properties but since the focus of this study was the experimental determination, only studies dealing with direct methods will be discussed. As already mentioned in Section 2.2.1, Van Den Akker et al. (1958) tested beaten and unbeaten, unbleached sweetgum kraft pulp on a custom built load elongation tester. The cross sectional area was determined under a hundred-power microscope with a reticle in the eyepiece. The fibre was oriented in such manner that the axis of the fibre was aligned with the rotation axis. Two profiles (minor and major axis) of the ellipse were measured and the cross sectional area calculated. The mean breaking load of the unbeaten, unbleached samples was in the range of 93.2 mN and the calculated strength in the range of 664.9 MPa.
Kellogg and Wangaard (1964) conducted probably one of the most comprehensive studies when it comes to hardwoods. They conducted single fibre tensile tests on six different hardwood species (cooked to different κ numbers) using an Instron Type TT-CL tensile tester. Individual fibres were mechanically clamped at a gauge length of 0.25 mm and load was applied at a rate of 0.002 in/min. After breaking, the fibres were embedded in methyl methacrylate and the cross sectional area determined using

the microtome method. The breaking loads of different hardwoods ranged from 36.07 to 114.04 mN and large differences in the breaking loads and subsequent strength were attributed to large differences in the cross sectional areas of the fibres. Duncker and Nordman (1965) tested unbleached, unbeaten birch kraft pulp of which the individual fibres were glued onto paper tabs over a 0.6 mm test span using Modocoll glue. Tests were conducted using a custom designed apparatus with the ability of measuring breaking load and load elongation curves with the load application rate of 0.1 mm/min. The cross sectional area of fibres was measured on 30 fibres by microscopical measurements and the mean value was used for the fibre strength calculations. For individual fibres, they obtained relatively high breaking load (144.15 mN) and strength values (956.15 MPa). Furthermore, they observed that birch fibres, in comparison to softwood fibres, had strikingly uniform values. Hardacker and Brezinski (1973) investigated the tensile properties of individual fibres of a once-dried bleached mixed hardwood kraft pulp (55% maple). Individual fibres were glued onto metal pins using epoxy adhesive and tested over a span of 0.15 mm at a rate of loading of 0.14 g/sec. The cross sectional area was measured using the compacted apparatus measurement method. The mean breaking load of mixed hardwood fibres obtained was around 39.24 mN and the strength around 623.7 MPa.

2.3.2 Testing of hardwood fibre to fibre joints

In case of hardwoods, there are no direct measurements of the individual fibre to fibre bond strength. Due to the complexity of dealing with such small joints, indirect methods were favoured. To the author's knowledge, there are only two studies dealing with the determination of hardwood joint strength (Koubaa and Koran (1995), and Snowman et al. (1999)). Koubaa and Koran (1995) determined the strength of the individual fibre to fibre joints by using three methods, the z-directional tensile test, delamination test and Scott bond test. The specific bond strength (SBS) was presumed to be the ratio between the internal bond strength (IBS) and the actually joined area. The latter was determined from the relative bonded area (RBA) or apparent density. Since density and the RBA were very close, the RBA was calculated using the density of the cellulose and the sheet apparent density. The obtained values for specific bonding strength varied between 1.23 and 1.7 N/mm^2 but no explanations were provided regarding these, relatively low, values. Snowman et al. (1999) determined the bond strength of oxygen delignified kraft hardwood pulp using the Page Equation of tensile strength (Page, 1969) and the delamination method (Skowronski and Bichard, 1987). The obtained values for the bond strength by using the Page equation were around 12.6 N/mm^2. Relatively high bond strength values were attributed to the higher hemicellulose content in hardwoods than in softwoods. In case of the bond strength determination using the delamination methods, no values were given.

2.4 Influence of relative humidity on the properties of individual fibres and joints

Paper products are expected to bear load and hold structural form in a variety of environmental conditions, many of which differ greatly from laboratory conditions in which the paper and the constituent fibres are usually tested. The parameters such as temperature, moisture and mechanical stresses not only determine the properties of paper during production process, but they continue to influence them later on during usage. How relative air humidity affects the elastic modulus, stiffness and strength of paper is well known (Salmen and Back, 1980). Upon increasing moisture content at higher RH, the paper starts to exhibit a more ductile and elastic behaviour, whereas upon drying, the material becomes more brittle. Softening of the material is attributed to the glass transition temperatures of amorphous cellulose and hemicellulose in the fibre cell walls, which in dry state, varies between 265-230°C. By increasing the relative air humidity, and subsequently, the moisture content (MC), the glass transition temperature of certain polymers, such as hemicellulose, can be lowered to room temperature. Once at this point, the material starts exhibiting more viscous behaviour, leading to the decrease in elastic modulus and strength (Salmen and Back (1980), Salmen (1990)). Figure 2.11 shows the dependence of the softening temperature on the moisture content of lignin, hemicellulose and disordered cellulose. Completly amorphous hemicellulose can reach the glass transition point at 25% MC when exposed to 75% RH, whereas in amorphous cellulose the same effect will take place at moisture contents of around 50% due to the restricting effect of the chrystalline regions.

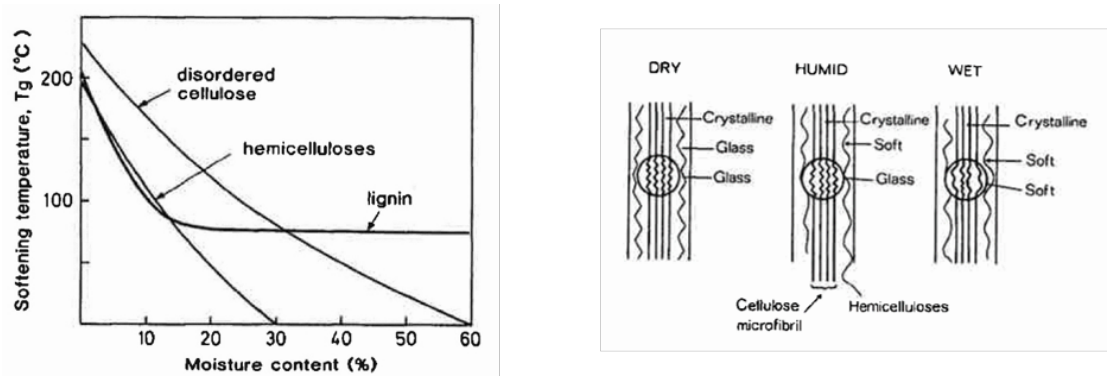


Figure 2.11 Glass transition point of wood polymers and the microstructure of wood in different conditions (Salmen, 1990)

If one is to draw conclusions from the behaviour of paper and individual components, it is right to assume that the E-modulus and strength of the fibres will also decrease upon exposure to water or humid air and increase upon drying. It is at this point, that the data collected from the literature tends to branch off in two different di-

rections. Certain studies have shown that the mechanical properties, mainly strength of individual fibres will increase (Wardrop (1951), Leopold and Thorpe (1968)) upon exposure to high RH or water; whereas others have shown that the strength of fibres decreases when exposed to high relative humidity or water (Kersavage (1973), Klauditz et al. (1947), Russell et al. (1964), Kallmes and Perez (1965)).

2.4.1 Influence of relative humidity on individual fibre properties

As mentioned before, when it comes to individual fibres and the influence of humidity, two premises emerge. The first one states that the strength of fibres increases with increased moisture content. It is believed that during exposure, the water is absorbed into the cell wall of the fibres and this absorbed water acts as a lubricant and helps distribute the stresses more evenly across the fibre cross section. Even stress distribution would in the end, result in an increase of breaking load.
Leopold and Thorpe (1968) tested spruce pulp (kraft, sulfite-bisulfite and acid sulfite cook) in dry and wet state. Fibres were dyed in Victoria blue D dye and glued onto cellulose acetate plastic tabs and glued using duco cement glue. After the duco cement dried, they were reglued using EPON 907 epoxy resin. Prior to testing, the fibres were conditioned for 24 hrs at 22°C and 50% RH. The fibres were tested on an Instron tensile testing machine at a rate of elongation of 0.05 cm/min and a load of 0.5 g in standard laboratory conditions. For the fibres tested wet; a receptacle with distilled water was placed in the test section as to enclose the fibre and the test system. The fibre was immersed in water for 1 min prior to testing and the testing was done while the fibre was in water. Cross sectional area was measured by embedding the fibre in acetone solution of cellulose acetate. Once dried, the sample was cut with a microtome and the obtained cross sectional area measured. For kraft pulps, higher wet breaking load than the dry breaking load was observed. Tensile strength and Young's modulus are not given for wet pulp since obtaining the wet cross sectional area was not possible. In their study, they have observed that summerwood fibres show higher breaking loads in the wet state, but lower ones for springwood fibres. The assumption was that the strength of the fibres depends on mainly two factors - the internal cohesion of the fibre wall and the ability to distribute the stress evenly across the fibre cross sectional area. When water accesses the fibre wall, hydrogen bonds are broken and the loss of these causes plasticisation. Summerwood fibres are considered to have a higher degree of organisation and cell wall cohesion, therefore, the water absorbed increases the ability of the cell wall to distribute the stress more evenly. On the other hand, springwood fibres have lower cell wall cohesion and in this case, the loss of hydrogen bonds causes the decrease in fibre strength.
Hartler et al. (1963) tested spruce fibres mounted on a paper tab over a span of 1 mm using a custom made tensile tester. The paper tabs carrying the fibre were held in position using mechanical clamps. Springwood and summerwood were tested sep-

arately at three different RH-s, 30, 50 and 65% RH. The conditioning time was not specified for any of the test conditions. Maximum strength of fibres was obtained at 65% RH, but no explanations for the observed behaviour were given.
Wardrop (1951) tested individual earlywood tracheids of Pinus radiata using a modified Westphal balance. The fibre was suspended on one end to an adjustable metal rod set in a heavy base and the other end was suspended from the balance arm using a silk thread to which the fibre was glued using dental cement. There is no mention how the wet fibres or water saturated fibres were wetted. In his work, he concluded that the breaking load of wet fibres was higher than the breaking load of dry fibres. The increase in breaking load was attributed to the water present in the intermicellar regions of the wet fibre permitting movement between adjacent cellulose units and achieving more uniform distribution of internal stress.

The second scenario states the decrease in the breaking load due to higher moisture content. In this case, the water absorbed in the fibre increases the spacing between the microfibrils. This increased spacing, allows the microfibrils in the fibre to conform more freely, resulting in higher flexibility of the fibres. However, this higher flexibility also means the loss of cell wall cohesiveness and density, thus, increasing the chance of cellulose chain slippage and failure. Higher flexibility has also as a consequence lower stiffness, lower E-modulus and lower tensile strength.
Klauditz et al. (1947) tested Pinus merkusii tracheids in wet-never dried state, wet (once dried state) and dry state and the testing was done using two devices. One group of the fibres was tested with fibres glued to the paper frame over a span of 1,5 mm using a modified balance. The dry fibres were tested at 20°C and 65% RH (moisture content of 8.2%). In the second testing procedure, the fibres were tested on a tensile tester where the fibres were gripped with special clamps over a span of 1 mm. Additionally, once dried, rewetted and fully wet neverdried fibres were tested, but the study provides no answer as to how this was performed. The highest breaking loads were observed for the dry fibres, with the lowest results obtained for the neverdried-wet fibres. They attributed this behaviour to the effects of the pulping process. During cooking, dissolution of soluble cell wall components (hemicellulose and lignin) leaves voids within the cell wall, making the cellulose grid loosely packed and weak when in hydrated state. During drying, the cell wall densifies, voids close and the fibre becomes stronger. If such densified, dried fibre is rewetted, the strength decreases, but not to the level of a nevedried fibre. Such fibre retains some of the cell wall cohesion due to the hornification. For the same reason, or, the absence of densification as a result of drying, the wet-neverdried fibres exhibited the lowest breaking loads.
Kersavage (1973) tested Douglas fir latewood tracheids with different moisture contents (MC) (0, 6, 12, 18, 30% and in wet state). The moisture content was determined using the oven dry method. To achieve the the specific MC, the fibres were exposed for minimum of one week to 1, 29, 66 and 83% RH using different salts. For the wet

fibres it was assumed that the moisture content of 100% was achieved by placing a small water droplet on the fibre. The fibres were fixed for testing by using epoxy droplets and the ball and socket principle. The measurements of load elongation, modulus of elasticity and breaking load were made on a universal testing machine (Tinus Olsen) with a load cell capable of measuring loads from 0-250 g with an accuracy of ± 0.3 g. The rate of loading was 0.1 mm/min. Temperature and RH were measured using copper constantan thermocouple and an electrical humidity sensor. Cross sectional area was measured by direct observation of the cross sectional area using a Leitz Ortholux microscope. Compared to fibres tested at different moisture conditions, wet fibres exhibited lower breaking loads, tensile strength and E-moduli. The reason for lower wet strength was attributed to the hemicellulose and cellulose in the fibre, which upon wetting or saturation become plastic and weak, resulting in overall weaker bonding between the cellulose structural units. As the tracheid initially dries, the hemicelluloses become less plastic and the bonding between the carbohydrates becomes stronger resulting in higher dry strength. Upon further drying, the hemicellulose and cellulose in particular become more brittle, inflexible and susceptible to microcracks. The breaking loads reach an optimum at around 60 to 70 % RH. During trials, it was also observed that the modulus of elasticity also decreases with wetting. In swollen state, there is less cell wall cohesiveness and the water molecules absorbed act as a lubricant resulting in slippage between the fibrils upon stress.
Russell et al. (1964) tested unbleached bisulphite softwood pulp in dry and wet state using the Instron tensile tester at a loading rate of 0.02 in/min. The goal of the study was not to measure the influence of moisture content on fibre properties but to investigate the influence of wet strength resins on fibre and joint properties. However, values are given for untreated samples as well. All the tests were performed at 22°C and 50% RH whereas the testing of wet fibres was achieved by applying a small droplet of water on the fibre. Fibres were glued onto tabs using Epoxy 907 glue and held in place by specially designed clamps. In single fibre testing a lower elastic modulus and lower failure load were observed in the wet state. However, no explanations for this behaviour were given.

2.4.2 Influence of relative humidity on fibre to fibre joint properties

When it comes to fibre - fibre joints, the literature data is scarce and all the assumptions regarding the influence have to be drawn from studies performed either on individual fibres or on paper sheets. From the two studies dealing with the influence of water on fibre to fibre joints strength, the overall conclusion states that water has a negative or possibly detrimental effect on the joint strength. However, the influence of high or low RH has never been directly investigated.
Russell et al. (1964) tested dry and wet samples of unbleached bisulphite softwood pulp using the Instron tensile tester. Conditions for testing in the wet state were ob-

tained by placing a small droplet of water on individual fibre to fibre joints. The shear load of 0.5 grams in case of dry samples and 0.064 grams in case of wet samples was obtained. Polarisation light microscopy (PLM; Page (1969)) was used to determine the area in optical contact. However, this was only possible for the dry samples. Since it was not possible to determine the optically bonded areas of the wet samples, no joint strength values were given. Nevertheless, a decrease in the breaking load upon exposure to water was observed. Schniewind et al. (1964) conditioned white fir fibre to fibre joints at different RH's (30, 65, 95% RH) for 4 and 24 hrs. However, prior to testing, the samples were conditioned again in laboratory conditions. Joints were tested according to composition (spring-springwood, summer-springwood, summer-summerwood) and the results are given in the Table 2.2.

Table 2.2 Bond shear strength values obtained by Schniewind et al. (1964)

	Bond shear strength after 4 hrs exposure to RH [MPa]			
type of bond	Control 50% RH	30% RH	65% RH	95% RH
summer-summerwood	3.47	2.17	3.99	2.93
spring-springwood	2.56	1.41	1.21	1.43
summer-springwood	3.69	3.38	1.98	3.97

The results obtained in this study show large differences but no definite trends. The explanation for observed decreases were attributed to the differences in longitudinal and transverse shrinkages of fibres in a bond and the change in the size and shape of the bonded area they induce upon exposure to different RH-s. However, since the joints were equilibrated in the laboratory conditions prior to testing, it is unclear whether these differences in the breaking loads can actually be attributed to the influence of different relative humidity.

2.4.3 Summary on testing in varying environmental conditions

In investigations dealing with the influence of moisture on mechanical properties of individual fibre and joints, there are a couple of factors that need to be taken into consideration. The first factor is the determination of the conditioning time. If the effect of different relative humidity on the properties of fibres is to be determined, the fibre needs to be at the equilibrium moisture content at the time of testing. To determine the equilibrium moisture content of a single fibre is nearly impossible but there are two possibilities that provide satisfactory results. Dynamic vapour sorption (DVS) is one method with which the equilibrium moisture content of a pulp sample could be determined. It works on a principle of a mass balance where the de-fibred pulp is put into a chamber and the RH changed in controlled manner. Equilibrium is then detected by comparing the mass of sample with a mathematical asymptote model.

When the difference in mas is less than 1%, the mass is noted. A different approach was used by Ganser et al. (2014) where a fibre was observed using Atomic Force Microscopy (AFM). During conditioning, changes on the surface of the fibre were visible as a result of water sorption. It was believed that the fibre reaches an equilibrium after no further changes are visible on the surface. The importance of testing at the equilibrium lies in the fact that the properties of fibres are greatly dependant on the moisture content. Not knowing the time needed to reach an equilibrium might lead to falsification of results and the extent of changes induced by different moisture contents to go unnoticed.

The second factors is the determination of the cross sectional area. Since individual fibres vary greatly in their size, presenting only breaking load at different relative values might prove to be misleading. If fibres are to be compared to one another, the easiest way this can be done is by calculating the strength of the fibres. However, obtaining the cross sectional area of fibres in swollen or dried state (differing from the one in 50% RH) is complicated. One possibility would be to freeze dry the samples and then use the microtome method to obtain cross sectional area images. The problematic point with this method would be having the conditioning, testing and freeze drying apparatus in one conditioned chamber as to avoid changes in relative humidity and thus the changes in the cross sectional area. Another point would be the plastic deformation of the fibre. Since the cross sectional area can only be determined after failure, once the plastic deformation has already taken place, it is unclear how much the cross sectional area deformed as well. Possibly this was one of the reasons why such methods have never been attempted or successfully performed. Another possible explanation why such attempt were relatively quickly abandoned would be that the increase in volume does not mean the increase of load bearing components. Because of the water sorbed, the water would act as a lubricant and presumably influence the stress distribution, but the amount of cellulose, hemicellulose and lignin, the components that carry the load, would stay the same (d'A Clark, 1978).
The third factor would be the determination of the bonded area of individual fibre-to-fibre joints. To determine the strength of the joint, the bonded surface of the adjacent fibres in a set humidity or in water needs to be obtained. An attempt of determining the change in the bonded area, while changing the moisture content, has been done only in case of Russell et al. (1964) on a separate sample, but no satisfactory results were obtained. Although not discussed in previous studies, all the factors playing a role in individual fibre and joint testing will play a role when testing in different RH-s as well. Here especially, the influence of the pulp type and cooking process will affect fibre and joint behaviour since it is directly linked to the chemical composition of fibres. These cell wall components, especially amorphous celluloses and hemicelluloses will govern the water sorption and consequently, the strength of fibres and joints.

2.5 Influence of refining on individual fibre and joint properties

Refining is a mechanical treatment of pulp in which the fibres are subjected to compression, tensile and shear load (Page, 1989). As such, it is commonly used in the paper industry to increase the strength of paper. The main effects of refining are cutting or shortening of the fibres, production of secondary fines, external and internal delamination. Because of the latter two, the refined fibres have a higher swelling degree and higher flexibility. Depending on the state of the fibres and the refining consistency, effects that also take place are curling or straightening of the fibre, and, inducing or removing kinks, nodes and micro-compressions (Page, 1989). The effects these mechanically modified fibres have on sheet properties are higher strength, better formation and higher density. With higher swelling and flexibility, the fibres have a larger area available for bonding and are able to come into closer contact with each other. The effect refining has on fibre and sheet properties has been extensively studied (Koskenhely (2007), Gharekhani et al. (2015)). The basic summary states that during refining, alongside all of the effects mentioned above, individual fibre also undergo a chemical change, i.e. the redistribution of hemicelluloses from the fibre interior to the surface of the fibre.

2.5.1 Influence of refining on individual fibre properties

When it come to the effect of refining on an individual fibre, one might think that because of the internal and external delamination, the fibre strength would decrease. Contrary to that, researchers reported increasing fibre strength values upon refining (Alexander et al. (1968), McIntosh (1968)).
Alexander et al. (1968) tested unbleached softwood kraft pulps refined in a PFI mill to two levels, 100 and 730 CSF. The results obtained for both summerwood and springwood fibres show an increase in tensile strength up until a certain point, but after that point, the strength decreases upon additional refining. The increase in strength was attributed to a better stress distribution within the fibre. During refining, the fibrils come into a closer contact with each other and show a higher degree of organisation. This densification and orientation of cell wall components results in more uniform stress distribution and higher strength.
McIntosh (1968) tested bleached and unbleached, springwood and summerwood loblolly pine fibres refined to different degrees using a PFI mill. Both bleached and unbleached pulp were refined to different degrees based on the type (earlywood/latewood). They concluded that refining decreased the breaking load and strength of bleached and unbleached summerwood fibres while the strength of springwood fibres increased. The changes were attributed to the reorganisation and consolidation of the cell wall and the change in the microfibril angle during refin-

ing. The same was observed by Leopold (1966) (cited in McIntosh (1968)) who tested springwood and summerwood of loblolly pine and found that while the breaking load of fibres remained the same, the cross sectional area diminished, therefore, increasing the strength of the fibres.
Van Den Akker et al. (1958), to the author's knowledge, is the only study dealing with individual hardwood fibres. During their investigatons, they observed that the breaking load of individual sweetgum fibres increased only slightly with refining but the fibre strength increased due to a decrease in the cross sectional area.

2.5.2 Influence of refining on fibre to fibre joint properties

Since refining increases swelling, flexibility and fibre collapse, one would expect the breaking load and strength of the joints to increase with refining. Contrary to that, majority of the studies found no statistically significant difference (Mayhood et al. (1962), Mohlin (1975), Stratton and Colson (1990)).
Mohlin (1975) investigated joint strength of two high yield and low yield kraft and sulphite pulps refined to 4000 rev. and 2000 rev. respectively. Bond strength was determined by measuring the shear force needed to break the crossing of a fibre and a cellophane strip. The tests were performed in an Alwetron with a strain rate of 0.1 mm/min. Although decreasing bond strength trends upon beating were observed for high yield pulps, and increasing ones for the low yield pulps, no significant differences was obtained. Similar was observed by Stratton and Colson (1990) who tested non-refined and refined fibre to fibre joints made from softwood pulp (pulp was refined in a Valley beater to 570 and 345 ml CSF). The lack of difference between the pulps refined to different levels was attributed to the similar extent of mechanical modification of the fibres. It is believed that the S1 layer of the cell wall was already removed at the lower refining levels and the bonding took place between the S2 layers, same as in the case of the samples refined to higher degree. Had the S1 layer been present, presumably different values would have been obtained. However, comparison with unrefined samples was not possible since the non-refined samples were divided into earlywood and latewood joints. Such division was not possible in case of refined joints and their values (presumably due to a mixture of bonds) fall in between early wood and latewood bond strength values.
Mayhood et al. (1962) tested unbeaten sulphite and unbeaten, mildly beaten and well-beaten softwood kraft pulp (mixture of spruce and pine). The beaten pulps showed an increase in strength when compared to the unbeaten ones but only at 10% level of significance. Even though no more pronounced differences could obtained, they have concluded that severe chemical and mechanical treatment may cause increase in bond strength. The observed high scatter of the values was attributed to the changes in the environmental conditions, manual handling of the specimens and variation between the samples themselves.

Magnusson et al. (2013) conducted the only study where a significant increase in joint strength was obtained. They observed that for a pulp beaten with high-energy input, the joint strength doubles and this was attributed to the increase in external fibrillation of the fibres. Unbleached kraft pulp was refined to different degrees using a laboratory conical refined (Escher Wyss) and individual fibre to fibre joints were tested in two different modes of loading (peeling and shearing). For the pulps refined at higher energy input, the joint strength almost doubled when compared to low energy inputs. Higher joint strength in case of refined samples was attributed to the increase of the amount of external microfibrils.

2.5.3 Summary on the influence of refining on fibre and joint properties

The results from the studies regarding the influence of refining on joints strength are ambiguous and are attributed to different reasons. The first one would be the type of pulp - sulphite having the higher swelling degree and being more prone to crack development than kraft pulp (Page and De Grace, 1967). Sulphite fibres, being weaker would presumably develop faster upon refining than the kraft fibres. The lignin content and bleaching should also be considered since the stiff lignin matrix makes the cell walls more resistant towards mechanical action (Mohlin, 1975). Furthermore, the refiners used differ from one study to another, whether it is ultrasonic refining, PFI mill, Valley beater or a conical refiner (i.e. PFI mill increases the internal fibrillation and swelling whereas the Valley beater tends to cut the pulp to a higher extent and produce more fines (Gharekhani et al., 2015). If comparisons are to be made, the refiners promoting same or similar fibre development should be used. Last but not least, the most important role is the degree and increment of refining. Refining to a very low degree might not be substantial to reveal the differences in the strength of joints and refining to a higher degree might omit the increase in strength obtained at lower levels.

2.6 Motivation of the work

The chapters discussed above provide a large database of knowledge regarding the properties of individual fibres and joints. However, even with all the knowledge of fibre and joint strength and the mechanisms governing it, there is still a lot to be learned about this, on a first glance, very simple material. Lord Kelvin said, "If you cannot measure it, you cannot improve it", and this statement is true in almost every branch of science. The same is definitely true for paper science and investigations dealing with individual fibres and joints, but besides being able to measure, one also needs to understand what lies beneath. This need for understanding and measuring comes from a desire to improve the properties of the existing final products, while at the same time, reduce the energy and the raw material consumption. One way

of achieving this goal is to be able to understand the behaviour of paper and create numerical models capable of simulating it. Exactly at this point, the investigation of fibre and joints properties come to play. They are the smallest constituent of the paper web and if the strength of any equals zero, the paper fails. Due to their physical, morphological and chemical variability, the results obtained by direct testing display high variation, which is only enhanced when using different testing methods and procedures. Therefore, the results obtained are often a combination of the testing method and the samples themselves. Using the knowledge gained from previous studies, it is possible to formulate a testing procedure that would, if not exclude, then at least account for all factors influencing the outcome of the measurements. Hopefully, in this way, the results would have lower variation and offer a more comprehensive understanding of what governs the properties of individual fibres and joints. Once understanding how the fibres and joints behave and measuring their properties, one can hope to improve their properties, and in the end, those of the paper.

Chapter 3

Materials and Methods

All investigations have been made using three industrially produced pulps listed below.

- bleached hardwood kraft pulp (mixture of *E. nitens* and *E. globulus*) - BHK - κ number < 1, dried
- unbleached softwood kraft pulp (mixture of 90% spruce and 10% pine) - UBSK - κ number 42, dried
- bleached softwood sulphite pulp (mixture of spruce and beech) - BSS - κ number 5-7, dried

Length and width of the tested fibres was determined in fully wet state using L& W Fiber Tester plus and are given in Table 3.1.

Table 3.1 Length and width of tested fibres (number in parenthesis represents the standard deviation

	mean fibre length	mean fibre width]
	l_f [mm]	w_f [µm]
BHK	0.779 (0.04)	18.7 (0.1)
UBSK	2.01 (0.10)	28.7 (0)
BSS	1.77 (0)	23.1 (0.07)

l_f ... length weighted average
w_f ... width weighted average

3.1 Mechanical testing

All investigations were performed using the microbond tester, a device for mechanical testing of fibres and joints, developed at Graz University of Technology (Figure 3.1).

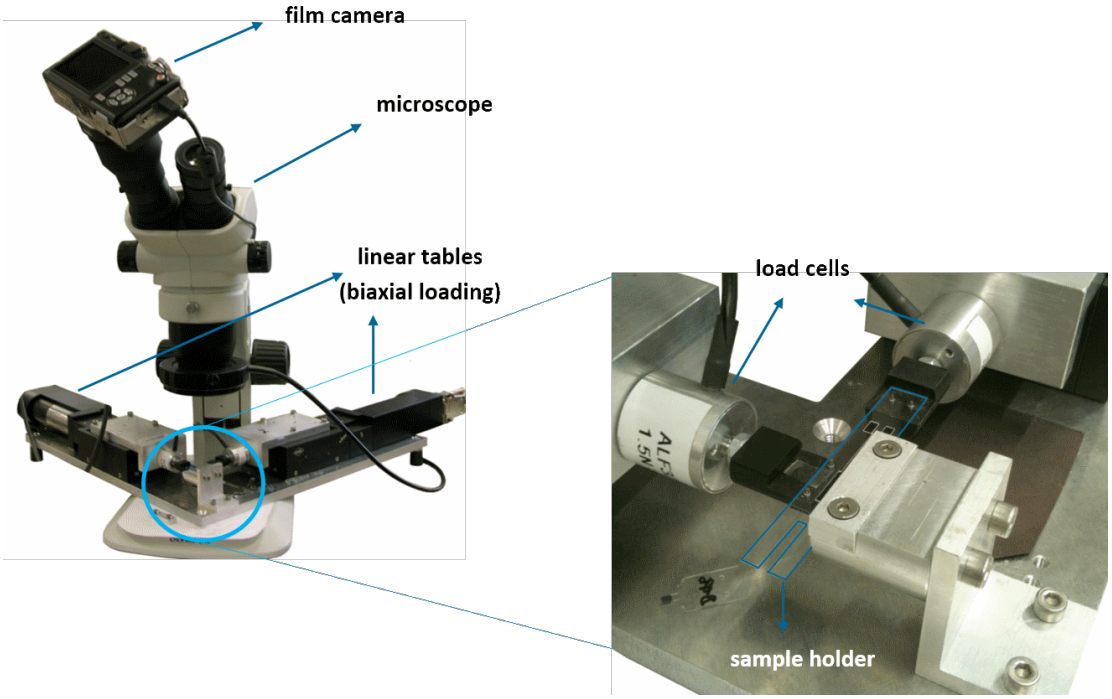


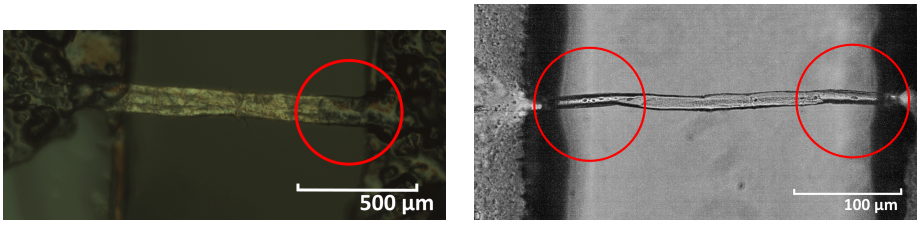
Figure 3.1 Microbond tester (Fischer et al., 2012)

The device consists out of two linear table (LIMES 60-20-HiDS by OWIS GmbH) moveable in x and y direction capable of achieving biaxial loading. Each of the tables is equipped with a load cell (ALTHEN GmbH Mess und Sensortechnik)) with a maximum force of 1.5 N and a resolution of 0.5 mN. The whole setup is placed under a light microscope (Olympus SZ51) equipped with a film camera. With the device, it is possible to perform tensile test, joint testing, bending stiffness measurements, and energy measurements. The recorded videos can subsequently be used to estimate the elongation of single fibres, measure the deflection of a beam in bending stiffness measurements or gain a better insight into the loading situation in joint testing. A detailed description of the device is given in the thesis of Fischer (2013).

3.1.1 Single fibre tensile testing - preparation and testing procedure

Individual fibres for testing were prepared according to the method developed by Kappel et al. (2009). In the preparation method, droplets of thin suspension of fibres are placed on Teflon foils and dried in sheet drier (Rapid Köthen) for one hour. After drying, the samples are conditioned in laboratory conditions for at least 1 hour be-

fore further processing. Individual fibres are identified under a light microscope and transferred to the sample holder using fine tweezers. The fibres are glued using a two component epoxy adhesive (UHU plus Sofortfest) and left to dry for at least 24 hrs prior to testing (manufacturer's specifications specify 12 hours before reaching full gluing strength). After drying, fibres are investigated under polarisation microscope (Leica DMLM) under higher magnification as to exclude fibres with defects, twists or misalignments. Testing of fibres with any of the aforementioned defects could have resulted in stress concentrations and therefore, lead to premature rupture and underestimation of the fibre breaking load. Another factor that might influence the outcome of testing was the glue creeping over the fibre, thus such fibres were excluded from testing. The glue creep over fibre was easily visible under the light microscope or under polarisation as an area of high reflectance and smoothness and an example of such preparation defect is shown in Figure 3.2.

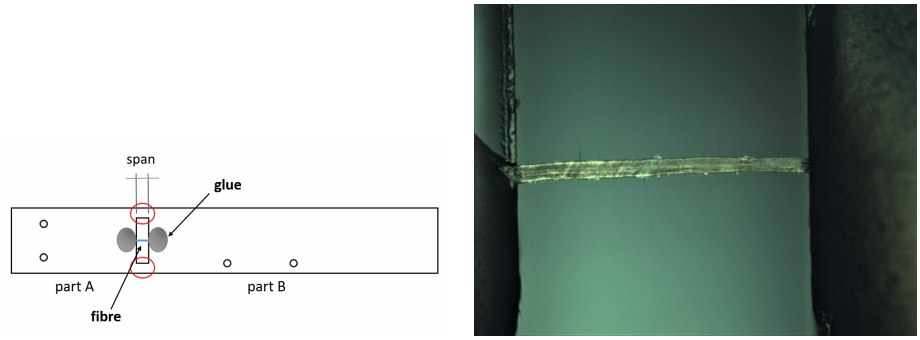


(a) softwood fibre over a span of 1 mm

(b) hardwood fibre over a span of 0.3 mm

Figure 3.2 Glue creep over fibre surface

Sample holder (Figure 3.3) for tensile testing was originally developed by Fischer (2013) but was modified to enable testing of shorter fibres. Testing span in case of softwood fibres was 1 mm and in case of hardwood fibres 0.3 mm.



(a) sample holder

(b) glued SW fibre

Figure 3.3 Sample holder for tensile testing and the mounted fibre

Tensile testing procedure of individual fibres consists out of three main steps described in Figure 3.4. In the first step, the sample holder carrying the fibre is placed onto the bond tester and secured in position. In the second step, the bridges (marked red Figure 3.3) connecting the upper and lower part are melted using a hot wire. In this step, especially in case of hardwood fibres, care must be taken as not to break the fibre prior to testing. Once the bridges have been melted, force is applied at a rate of 1 µm/sec until failure occurs.

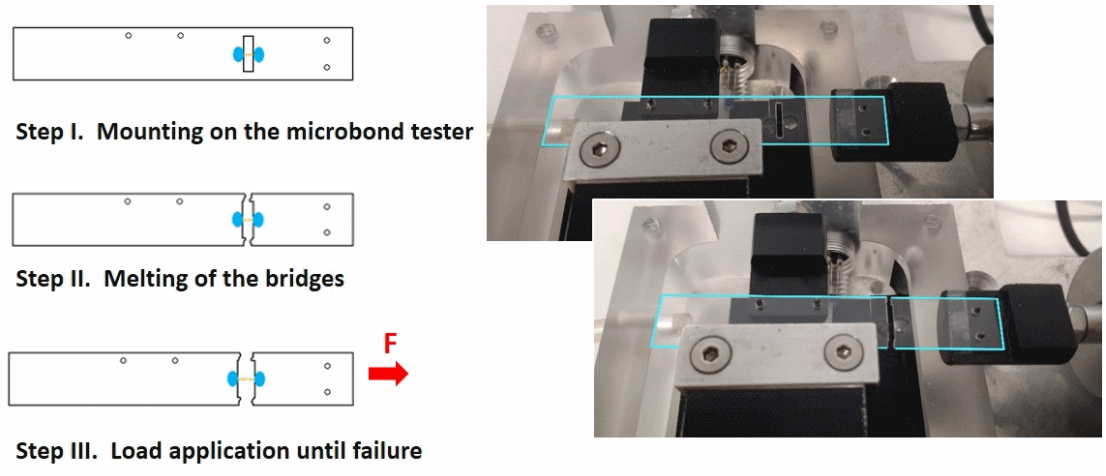


Figure 3.4 Principle of single fibre tensile testing

Testing of the fibre is recorded with a film camera and subsequently used for analysis of failure. In case of any irregularity such as pulling out of fibre from the glue, misalignment or twisting, the results were excluded from the analysis.

3.1.2 Determination of the cross sectional area

Determination of the fibre cross sectional area was done using a microtome. The preparation and measurement method are shown in Figure 3.5 and Figure 3.6.

After the fibres have been tested, the sample holder is removed from the micro bond tester. The fibre with the longer end protruding is removed from the sample holder with the aid of fine tweezers used as a leaver, snapping the glue with the fibre from the sample holder. The fibre (while still in the glue) was then placed onto a paper tab cut to size and glued using nail polish. During the first trials, it was observed that if the two component epoxy came into direct contact with the embedding resin, air bubbles in the contact zone would appear. In that case, distinction between the fibre perimeter and the surrounding resin was not possible. For that reason, it was important to cover the epoxy resin completely in nail polish. After curing, the fibre and the paper tab are embedded in a resin. Once dry, the sample is cut using a microtome in a series of cuts (30 µm in thickness) and after each cut, images are taken. To obtain good results, a minimum length of fibres of 0.4 mm was necessary.

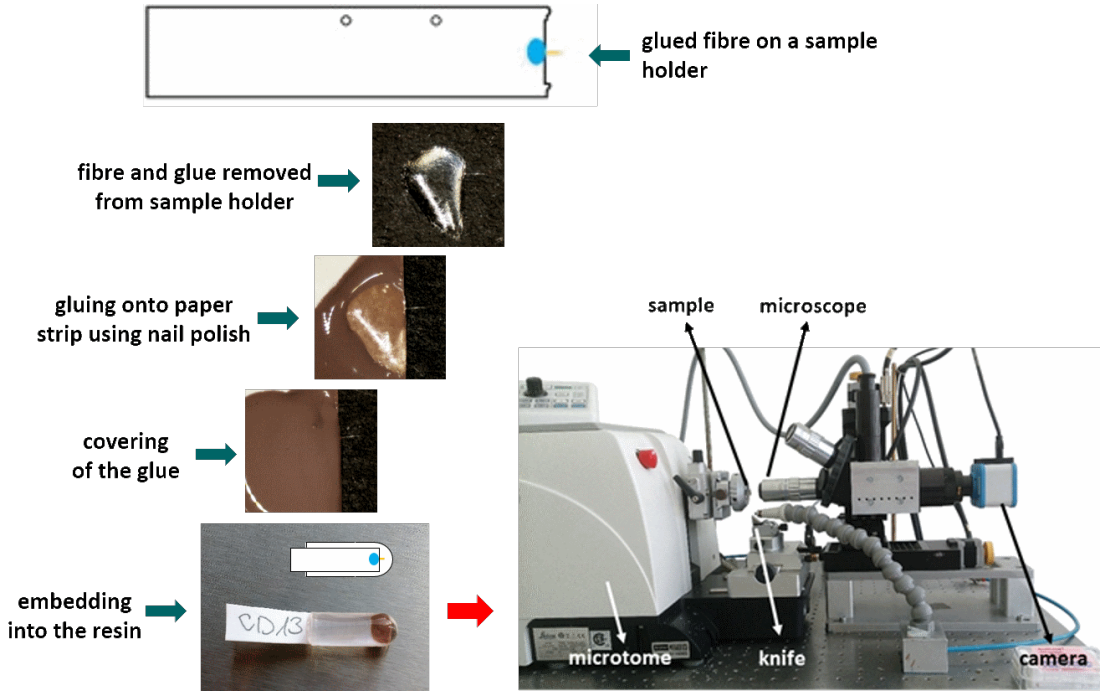


Figure 3.5 Microtome sample preparation

In case the fibres were shorter, the knife would come too close to the fixation point and cutting could not be performed. The epoxy resin and nailpolish used to glue the sample onto a paper tab do not provide a solid enough medium to obtain a good cut. For that reason, it was not possible to determine the cross sectional area of hardwood fibres (testing span of 0.3 mm). The width, thickness and the cross sectional area of those fibres were measured on a bulk sample (Lorbach, 2016).
Since individual fibres after tensile testing were cut and analysed, the initial couple of images containing the rupture zone were excluded. Only images with a complete cross section were analysed. The principle of the fibre morphology determination is shown in Figure 3.6.

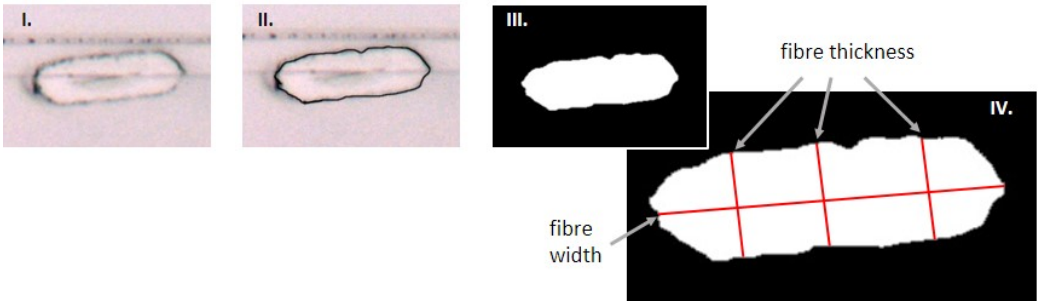


Figure 3.6 Analysis of the cross sectional area: I. original microtome image; II. outline of the fibre cross sectional area; III. image binarisation and cross sec. area determination; IV. width and thickness measurement

After cutting, the fibre cross sectional area was outlined on the original gray scale photo. The image was then binarised (background appears black and fibre cross sectional area appears white, Figure 3.6, step III.) and the cross sectional area calculated using a Matlab routine. In case uncollapsed lumen was visible, that area was excluded from the cross sectional area calculations by treating it the same way as if it were background (appearing black). After determination of the cross sectional area, the same binarised image was used to measure the fibre width and thickness. Several measurement points (lines) per fibre (Figure 3.6, step IV) were measured and the mean length value calculated. This length in pixels was then recalculated using the conversion factor into length in micrometres. The procedure was repeated for all images in the cut (usually 3-8 usable ones) and the mean was calculated.
The width, thickness and the cross sectional area of the fibres obtained by using the microtome method is shown in Table 3.2.

Table 3.2 Width, thickness and the cross sectional area obtained usign the microtome (number in parenthesis represents standard deviation)

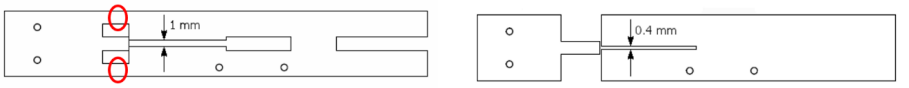
	width	thickness	cross sectional area,
	w, [µm]	t, [µm]	A_{cross}, [µm^2]
BHK*	11.67	3.81	35.12
UBSK	29.45 (1.44)	9.35 (1.60)	271.29 (35.51)
BSS	50.12 (11.74)	5.51 (2.28)	232.5 (77.82)
* ...unpublished data, measured on bulk sample Lorbach (2016)			

In the microtome method used by Lorbach (2016) a bulk sample of fibres provided a background and stitching point with which the tilt angle of the fibre could be determined. With the tilt angle, the projected area of the fibre could be corrected and overestimations avoided. In case of individual fibre measurements however, this was not possible. Since the resin, nor the fibre, provide stitching background and therefore no correction for the tilt angle, it is possible that some overestimations of the thickness, width and cross sectional area might have occurred in case of softwood fibres.

3.1.3 Joint testing - preparation and testing procedure

Same as in the case of individual fibres, fibre to fibre joints were prepared according to the method of Kappel et al. (2009). Droplets of thin suspension were placed on Teflon foils and left to dry in sheet drier for one hour. Afterwards, they were conditioned for at least one hour in laboratory conditions prior to identification under a light microscope. Once the joints have been identified, they were carefully transferred to a sample holder using fine tweezers. Sample holders used for individual softwood and hardwood joint testing are shown in Figure 3.7. An original sample holder developed

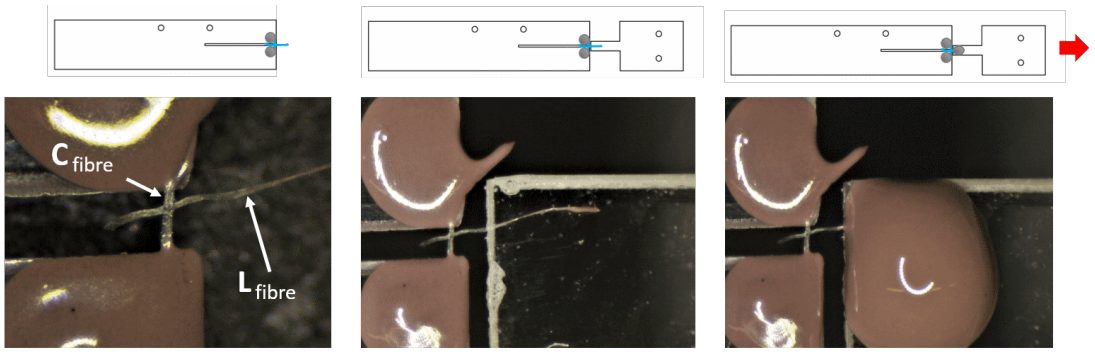
by Fischer (2013) was a one-piece sample holder developed for testing of softwood fibres. The bridges marked red in Figure 3.7 (a) were melted using the hot wire leaving the joint as the only connecting part of the upper and lower part of the sample holder. For testing of the hardwoods, the bridges connecting the two parts had to be removed since the melting of the same tended to destroy the joint prior to testing. The two piece sample holder for testing of hardwoods is shown in Figure 3.7 (b). Furthermore, since the mean length of hardwood fibres was 0.72 mm, the span over which the joint was glued was reduced from 1 mm to 0.4 mm.



(a) softwood one-piece sample holder **(b)** hardwood two-piece sample holder

Figure 3.7 Sample holder used for fibre to fibre joint testing

Smaller span enabled gluing of short hardwood fibres while still providing enough distance between the two gluing points to prevent the glue from running over into each other and covering the joint.
During first trials, the two-piece sample holder was used solely for hardwood joint testing whereas softwoods were tested on a one-piece sample holder. Later on, softwoods were also tested using the two-piece sample holder. Tests conducted on sulphite pulp using both sample holders revealed no statistically significant difference in values, and confirmed that the differences in the design played no role in the measured breaking load of the fibres. Using the two-piece sample holder also enabled the reuse of the sample holder as well as a higher success rate.
Testing procedure using the two-piece sample holder consisted of three steps shown in Figure 3.8.



I. Gluing of the joint via the C fibre

II. Gluing of the L fibre once the sample holder is mounted

III. Load application until failure

Figure 3.8 Fibre to fibre joint testing principle

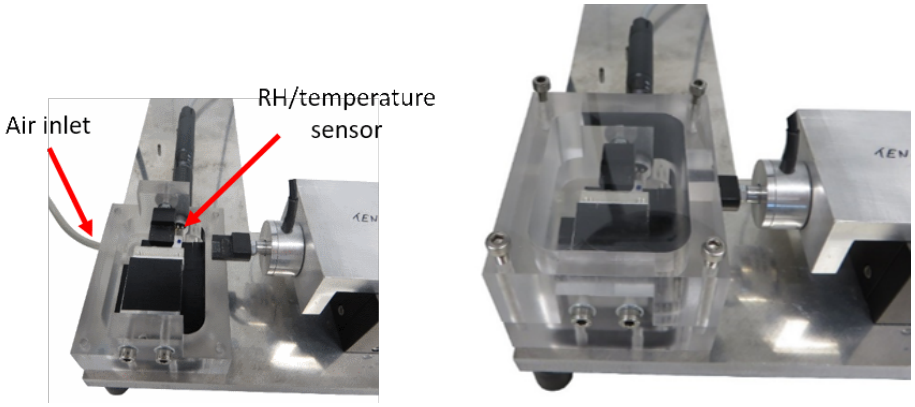
Once the joints has been identified under the light microscope, it is glued onto the lower part of the sample holder using nail polish. After the nail polish has cured, determination of the optically bonded area is performed under polarisation light microscope. Since the microscope is not in a conditioned room, the joints are left to condition in laboratory conditions for 24 hrs prior to testing. After the joints have reconditioned, mechanical testing can proceed. This is done by putting both pieces (upper for load application and lower part carrying the joint) of the sample holder onto the microbond tester. Once both parts are mounted, the L fibre (one used for load application) is glued by applying a droplet of nail polish on the fibre (in case of a one-piece sample holder, the bridges holding the two parts together are melted). Once the nail polish has dried, the force is applied until failure occurs. The entire testing procedure is filmed and subsequently analysed. Joints in which the L-fibre pulled out or the C-fibre broke at one of the fixation points were excluded from the data analysis. Furthermore, the videos gave a better insight into the loading mode and behaviour of joint under stress and have shown that the smaller the gap over which the C-fibre is glued, the less twisting and rotation of the joint can be observed.

3.1.4 Determination of the optically bonded area (OBA)

Optically bonded area of individual fibre to fibre bonds was determined using polarisation light microscopy according to method of Page (1969). In this case, the lower fibre was not dyed as to not interfere and influence the bond strength measurements. All investigations were performed using a polarising microscope Leica DMLM. The images from the microscope were processed in the same manner as the ones obtained from the microtome. The area in optical contact was outlined, binarised and calculated using a Matlab routine.

3.2 Conditioning chamber

For the purpose of testing fibres and joints at a specific relative humidity, a conditioning chamber was developed and constructed as an additional part of the microbond tester. The chamber was custom made out of 10 mm thick acrylic glass with the bottom and three surrounding walls coated with black Teflon foil. The Teflon foil reduced the reflection of the acrylic glass while providing a humidity and temperature inert surface. Close up of the chamber is shown in Figure 3.9.



(a) opened conditioning chamber **(b)** closed conditioning chamber

Figure 3.9 Conditioning chamber with marked air inlet and RH/temperature sensor

The air for the conditioning chamber is conditioned to a desired humidity inside a S503 humidity generator (Michell instruments) shown in Figure 3.10.

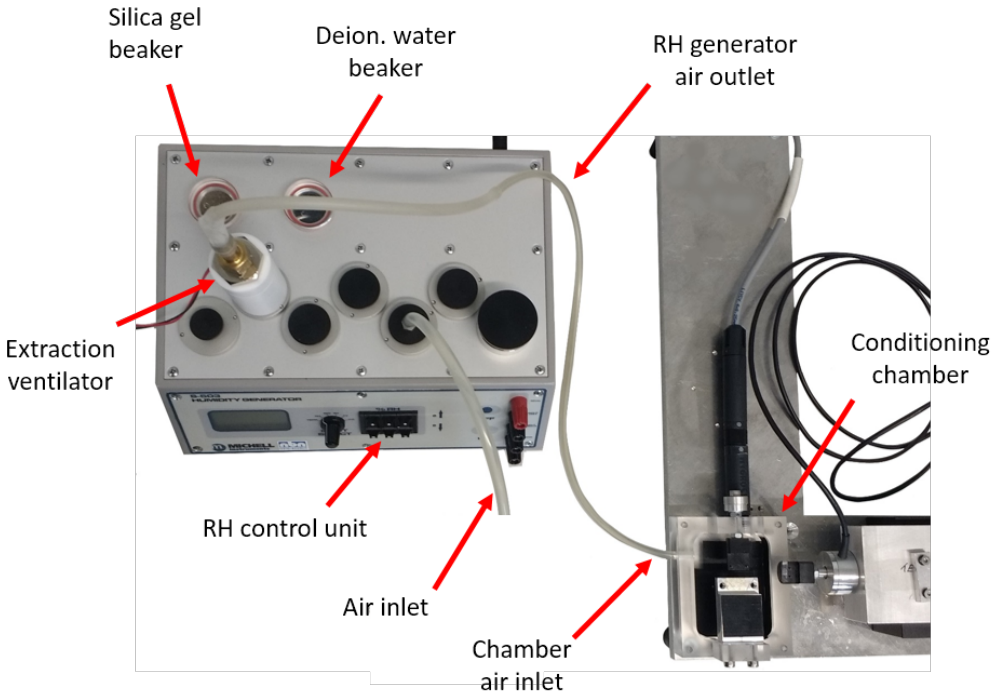


Figure 3.10 Humidity generator and conditioning chamber (top view)

The working principle is the following: Once the generator is running, the desired humidity is set on the RH control unit. The air is sucked in the generator through an air inlet by means of an internal ventilator. The air is then circulated over the silica gel and/or deionised water beaker (depending on whether the desired air is humidified

or dried). Once the starting RH of 50% RH is reached, the extraction ventilator is turned on and the air is blown through the RH generator air outlet through a rubber tube into the conditioning chamber. At this point, the chamber is closed and the humidity and temperature are recorded by means of a RH/temperature sensor (Figure 3.9). Humidity within the chamber could be varied between 25% and 95% RH and target RH could usually be achieved within 3-5 min. In case faster change is needed, the outlet air can be pre-dried or pre-saturated with a silica gel or a water beaker under the air inlet. Complete setup with the RH recording, additional external silica beaker and full testing setup is shown in Figure 3.11.

Figure 3.11 RH chamber testing setup: 1 - conditioning chamber, 2 - video camera, 3 - humidity generator, 4 - RH recording

In case of this study, individual fibres were tested at 30, 50 and 80% RH. In all cases, the starting RH of 50% was kept constant for 5-10 minutes prior to change for two reasons. Firstly, the load cell is highly susceptible to vibrations such as the ones induced by mounting of the sample holder or melting of the bridges. Allowing it to stay in constant conditions for a short period enabled the load cell to calm down. Secondly, in case of joints, this time was needed to allow the nail polish to cure. Once the nail polish was dry and the load cell close to a zero signal (signal of an unloaded cell), change of RH was commenced. At the same time, load cell signal recording was started as well. By recording the signal of the load cell during conditioning time, it was possible to see fibre response to the change in RH as an increase or decrease in tension.

3.2.1 Conditioning stress response

Recording of the load cell signal during conditioning has revealed a "conditioning stress response" of fibres and joints. Changing of the relative humidity is bound to cause changes in the morphology of the fibres due to shrinking or swelling. During

conditioning, it was observed that the fibres and joints had a strong response towards a decrease in humidity. All three groups of fibres have shown a development of the so-called conditioning stresses. Figure 3.12 shows an example of a conditioning stress response of a softwood kraft fibre.

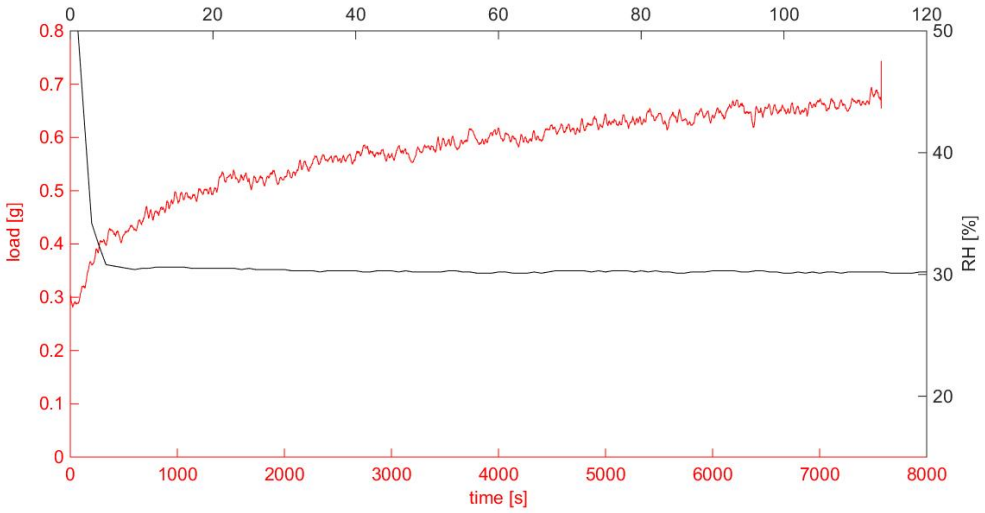


Figure 3.12 Conditioning stress of an individual softwood kraft fibre (reduction of RH)

Red graph represents a load increase corresponding to the decrease in RH (black graph). A similar behaviour was observed with fibre to fibre joints. Figure 3.13 shows a response of a fibre to fibre joint to a decrease in RH.

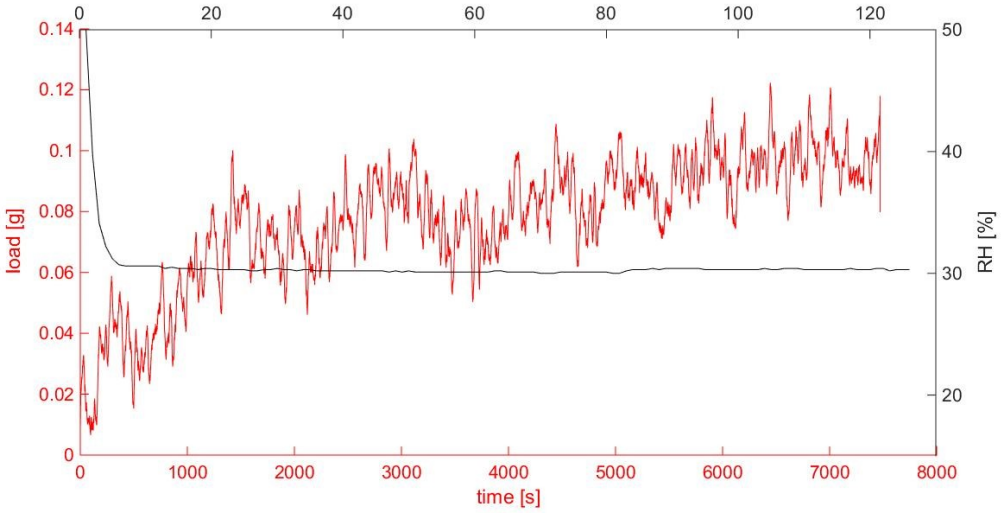


Figure 3.13 Conditioning stress of a fibre to fibre softwood kraft joint (reduction of RH)

Fibres, when left unrestrained will shrink in a curl, twist and bending manner upon drying. Since fibre and joints are glued onto sample holders, they can only

shrink in one plane and this shrinkage is what can be seen as a load increase. Conditioning in such manner might results in strain hardening of the fibres and influence the outcome of the measurements. In case of individual fibres, the shrinking could be amended by releasing the tension of the fibre, simply by pushing the load cell in the opposite direction of load application (i.e. relaxing the fibre). In case of joints, such release was not possible since it would push only the L-fibre backward and damage the joint. For that reason, only fibres could be tested in a non-restrained/relaxed state. This was achieved in following manner: Once the fibre was mounted, kept at 50% RH for 5-10 min, changing of the RH was commenced, simultaneous to the signal recording. The fibre response was the strongest in the beginning so the fibre was initially relaxed until the load cell signal reached the unloaded value. Afterwards, the response was still monitored and the fibre was again relaxed. Per fibre, at least one and at most 5 relaxation cycles were needed.

Softwood kraft fibres, being the strongest of out of all three groups were strong enough to withstand conditioning in restrained/unrelaxed state. For individual hardwood fibres, the drying conditioning stress was so great that the fibre would break prior to testing in the first 10 minutes.For that reason, hardwood fibres could only be tested in the unrestrained state. Twisting nature of the fibre during a decrease in RH from 50 to 30% RH is shown in Figure 3.14.

Figure 3.14 Shrinking of fibre when exposed to reduction of RH from 50 to 30% RH

In case of joints, a similar behaviour can be observed as a rotation of the bond. Figure 3.15 shows s fibre to fibre joint with one fixation point during a RH decrease from 50 to 30% RH.

Figure 3.15 Shrinking of a fibre to fibre joint when exposed to reduction from 50 to 30% RH

After individual fibre tensile testing, the fibres were cut with the microtome method to obtain the cross sectional areas. However, since the microtome sample preparation is done in standard laboratory conditions, and the cutting action of the knife is bound to develop heat, the real size of the fibre cross section in the given hu-

midity is unknown. For that reason, no attempt on the calculation of the fibre strength was made. In case of joints tested in 30% and 80% RH, the optically bonded area was not measured, since there was no possibility to measure it in the set RH.

3.2.2 Conditioning time assessment

To make sure the exposure time was long enough for fibres and joints to reach an equilibrium, dynamic vapour sorption (DVS) measurement have been performed. the pulp used for the measuremnets was soaked, disintegrated, drained and put into oven for drying. Afterwards, bulk pulp was de-fibred with the aid of tweezers and gloves. Isotherms of water vapour sorption were determined with a with a dynamic gravimetric water sorption analyser (DVS Intrinsic, Surface Measurement Systems, Alperton- London, UK). Approximately 40 mg of the pulp was placed in the sample pan and was pre-conditioned at 0% RH for 12 h at 25°C to remove any adsorbed water molecules prior to all three sorption tests. After being conditioned at 0%, the RH was elevated to a desired level of 30, 50 and 80% and kept constant for 12 hours. Equilibrium was detected by comparing the mass of sample with a mathematical asymptote model. When the difference was less than 1%, the mass was noted.

Since the DVS measurements could only be performed on defibred pulp, a scale much larger than individual fibre, additional conditioning time assessment in terms of different exposure times have been performed on individual fibre to fibre joints. A sample of ten UBSK fibre-to-fibre joints have been tested after 2, 4 and 8 hours of exposure to 80% RH.

3.3 Refining

Pulp used in this part of investigations only included softwood kraft and softwood sulphite pulp. Hardwood pulp was not used since the unrefined fibres were already on the limit of a feasible fixation and measurement. Both sulphite (BSS) and kraft pulp (UBSK) were refined at three different levels (3000, 6000 and 9000 rev) using a PFI mill. After each refining cycle, the freeness of the pulp, length, width, thickness and cross sectional area were measured. Length of fibres was measured in fully wet state by using L&W Fibre Tester Plus. Fibre width, thickness and cross sectional area were measured using the microtome according to the method described in section 3.1.2.

The characteristics of the tested pulps are given in Table 3.3.

Table 3.3 Pulp properties before and after refining

pulp type and refining degree	SR	length	width	thickness	A_{cross}
		l_f [mm]	[µm]	[µm]	[µm^2]
BSS_0	13.65	1.77	50.12	5.51	232.5
BSS_3000	21.05	1.23	44.68	6.91	266.64
BSS_6000	35.45	0.76	34.5	7.49	236.16
BSS_9000	59.5	0.65	31.64	6.76	200.5
UBSK_0	13.65*	2.13	29.45	9.35	271.29
UBSK_3000	16.3	1.93	38.45	6.61	225.62
UBSK_6000	22.45	1.75	36.67	6.36	201.23
UBSK_9000	29.55	1.61	41.68	7.23	271.29

* ... Kappel et al. (2009)

The cross sectional area of the refined fibres presented in Table 3.3 should be regarded with caution. During refining, the fibres are mechanically treated which should result in a decrease in the fibre wall area, either due to consolidation of the wall or external delamination. The absence of a decrease and presence of higher cross sectional area at higher refining levels implies that either only the strongest fibres or the fibres that managed to get through the refining process untouched were tested.

In case of individual fibres for tensile testing, special care was taken with regards to which defects should be excluded or included. Refined fibres will be internally and externally delaminated to a greater or lesser extent, especially the ones at extremely high number of revolutions. Due to this, fibres with extreme external delamination such as parts of the wall missing or heavily kinked fibres were excluded. Such defects might results in stress concentrations and results in underestimation of fibre strength. To make sure the fibres were fit for testing, they were examined under a polarisation microscope. From fibre defects, the following ones (shown in Figure 3.16) were acceptable:

- microcompression (visible in all images as light wrinkle areas)
- light external fibrillation
- slip planes
- slight kinks
- curved fibres

Tensile testing of suitable fibres was performed according to the method described in section 3.1.1. In case of joint testing, no exclusion criteria was used. Measurements

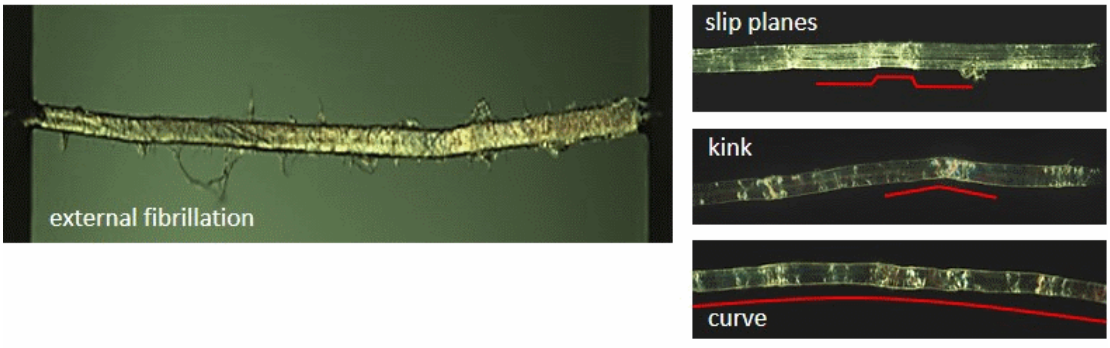


Figure 3.16 Refined fibre defects acceptable for testing

of the optically bonded area were done using the PLM method (Page, 1969) as well as standard light microscopy. In case the joint had a bright surface or appeared to be bonded under polarising light, additional images were taken with standard light. The PLM method gives only the area in which the light cannot pass, whereas the thin, fine web like structures at the edges of the bonds are virtually invisible. By using different filters and standard illumination, it was possible to see a larger bonding structure that might not necessarily carry the main load but might help to redistribute it. To ensure these web like structures were indeed bonded and not free standing structures, additional investigations of the fibre to fibre joints were performed using Scanning Electron Microscopy (SEM) Zeiss Ultra 55 microscope. An example of the obtained images is shown in Figure 3.17.

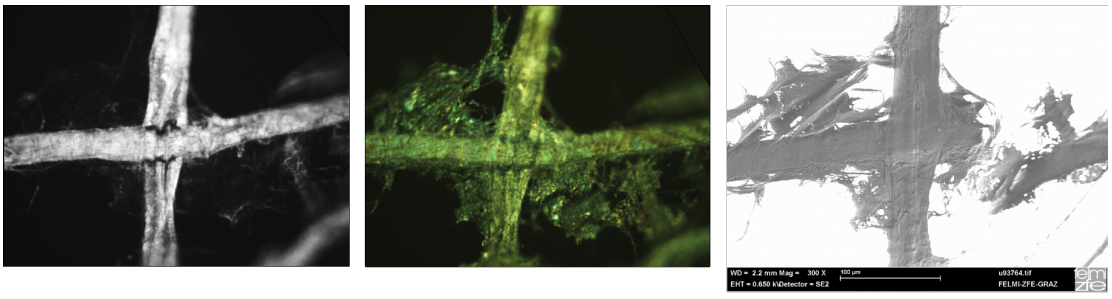


Figure 3.17 Sulphite fibre to fibre joint refiend to 9000 PFI

The SEM was used at low voltage level of 0.65 keV, which enabled stronger interaction of the electron beam with the material. The low voltage SEM is more sensitive towards the topography of the surface than the bulk of material and therefore suitable for investigation of the fine structures observed on the surfaces and edges of the bonds. Figure 3.17 shows the most severe case of external delamination in which the structural integrity of the bond is jeopardised by the failure of the fibre, rather than the bond itself. In these cases, testing of the joints was not possible since they would

fail during mounting. For joint testing, only joints with relatively undamaged fibres (fibre characterised in the same manner as in case of tensile testing) were chosen. Testing of refined joints was performed according to the method described in detail in Section 3.1.3.

Chapter 4

Results and Discussion

The results are divided into three groups, based on the focus of the investigations:

- Influence of the pulp type
- Influence of relative humidity
- Influence of the refining degree

Only the tests where both breaking load and the cross sectional area (in case of fibres) or the optically bonded area (in case of fibre to fibre joints) will be discussed. In cases where only one value has been obtained, either the breaking load or the area, the values have been excluded from the discussion. A complete overwiev of all obtained values is given in the Appendix.

4.1 Influence of the type of the pulp

This section is divided into two parts, the first one dealing with joint properties and the second one dealing with the properties of individual fibres. At the end of each section, the results are compared to previous studies (where possible) and explanations of the observed behaviour given.

4.1.1 Individual fibre to fibre joints

As mentioned in Chapter 3, joints of three pulp types were tested, unbleached softwood kraft (UBSK) pulp, bleached hardwood kraft (BHK) pulp and bleached softwood sulphite (BSS) pulp. The joints were tested using both one-piece and two-piece sample holders. The type of the sample holder used for testing is indicated alongside

the success rate of each tested group (Table 4.1). The numbers in parethesis respresent the samples where only the mechanical testing was succesful but no values for the OBA were obtained. For that reason, only tests where both the mechanical testing and area measuremnets have succesfully been obtained are included in subsequent analysis.

Table 4.1 Statistics of joint testing

Type	successfull no. of test	total no. of samples	sample holder
BHK	6 (17)	48	two-piece
*UBSK**	14	22	one-piece
BSS	12 (15)	21	combined**

* Fischer (2013)
** one-piece and two-piece sample holder used

First trials with hardwood joints tested on a one-piece sample holder had a success rate of only 2% (1 out of 47 joints) and was therefore discarded. For that reason, modifications (explained in detail in Section 3.1.3. were made and the two-piece sample holder was used. To ensure that the change in design did not have an influence on the testing outcome, sulphite softwood (BSS) joints were tested on both one piece and two-piece sample holder and the results are presented in Table 4.2.

Table 4.2 Comparison of joint breaking loads using one- and two-piece sample holder

	no. of tests	breaking load [mN]	stand. dev. [mN]
one-piece	8 (8)	4.88	2.94
two-piece	4 (6)	4.51	2.42

Since there was no statistically significant difference in the breaking loads of joints tested with the one- and two-piece sample holder, the two-piece sample holder was used for all subsequent tests conducted in this study.

The lowest success rate of only 12.5% was obtained in case of hardwoods. Although this has not been measured and confirmed, the HW joints seem to exhibit more brittle behaviour. Even the slightest vibrations during mounting and gluing would damage the joints and render the test unsuccessful. Another reason was that due to their small size, it was not always possible to glue the L fibre sufficiently well onto the sample holder in which case the fibre would pull out of the nail polish. Similar problems would occur if too much of the nail polish was applied, in which case, the nail polish would not cure and reach its maximum holding ability. In those cases, the results obtained from these tests were not included in the analysis. Additionally, some joints broke during the mounting of the sample holder on the microbond tester. In case of the bleached softwood sulphite joints, six samples failed prior to testing, 15

samples were tested successfully but the otpically bonded area was succefully measured for only 12 of them. In case the fibres were not alligned in one plane, the optically bonded area appeared blurred and could not be measured. In case where the joints failed prior to testing, the failures occured due to the incomplete curing of the nailpolish or pulling out of the fibre.
Since there is already an existent database (Fischer, 2013) of unbleached softwood kraft joints, there was no need for additional tests.

Optically bonded area of hardwood and softwood joints

Prior to mechanical testing, optically bonded area of joints was determined using the PLM method (Page, 1969) and the results are presented in Table 4.3.

Table 4.3 Optically bonded area of fibre to fibre joints

type	OBA [μm^2]	stand. dev.
BHK	291.69	118.81
UBSK*	2198.18	1016.27
BSS	1356.38	534.91

* Fischer (2013)

As can be seen, the optically bonded area of hardwood joints (BHK) is roughly 4-8 times smaller than the bonded area of softwoods (BSS and UBSK). This is attributed to two factors - firstly, to the size of the fibres and, secondly, to the collapsibility of HW fibres. Considering that the width of hardwood fibres is almost two times smaller than that of softwood (Chapter 3, Table 3.1), the difference between the OBA is greater than expected. Using the equation for calculating OBA (Kappel et al., 2009) the average calculated bonded area is 350 μm^2. Correction factors used in the study of Kappel et al. (2009) for the change in the crossing angle, width of the fibre and the change in the degree of bonding have only been provided for the unbleached softwood kraft pulp and have therefore been excluded from this calculation. Had the correction factors been provided and used, the calculated OBA might correspond better with the measured one. Additionally, hardwood fibres (eucalyptus in particular) have fibres with thicker cell walls and smaller lumen. Such fibres tend to collapse less (Kibblewhite et al., 1991) and therefore have less area in physical contact. Smaller collapse index was already discovered in investigations of Lorbach (2016) where it was observed that 95% of softwood fibres were fully collapsed whereas in case of eucalyptus, 81% of fibres were collapsed. Thus, the difference in the OBA is attributed to the smaller width and lower collapsibility of hardwood fibres. Softwood sulphite and kraft fibres form joints of similar size which does not come as a surprise based on fact that both pulps are mixtures containing spruce and have similar width and thickness of the fibres.

Breaking load of hardwood and softwood joints

Breaking load of softwood and hardwood joints is given in Table 4.4.

Table 4.4 Breaking load of individual fibre to fibre joints

type	breaking load [mN]	stand. dev. [mN]
BHK	1.58	0.42
UBSK*	6.58	4.45
BSS	5.15	2.61

* Fischer (2013)

First thing that can be seen is the large difference in the breaking load between softwood and hardwood joints. Hardwood joints shows reduction of 70% when compared to BSS pulp and a 76% reduction when compared to UBSK pulp. There are several reasons why hardwoods exhibit lower breaking loads, the first one being the difference in the optically bonded area. Smaller bonded area would mean less surface capable of carrying the load.

Second reason for the smaller breaking load of hardwoods when compared to the unbleached kraft softwood could be attributed to the effect of bleaching. During the kraft cooking process, the decomposition of the fibres starts from the lumen, dissolving the lignin but along the way, also the hemicelluloses (Bachner et al. 1993). Upon further delignification, remaining lignin is dissolved, leaving the cell wall weaker. Even though the removal of the hydrophobic lignin is beneficial for swelling and subsequent bonding, it is also known that the collateral loss of hemicelluloses has a negative impact on the strength of joints. To make sure that the influence of bleaching is not the primary cause of the lower breaking loads, a comparison of the sugar content has been done on the unbleached softwood kraft pulp and the bleached hardwood kraft pulp. The results of the sugar content analysis are given in Table 4.5.

Table 4.5 Monosaccharide compositions of hardwood and softwood

type	arabinose [%]	rhamnose [%]	galactose [%]	glucose [%]	xylose [%]	mannose [%]	total sugars [%]
BHK	0	0	0	79.1	19.5	0	98.6
UBSK	6.8	0	0.4	71.2	7.5	6.3	86.1 [%]

Contrary to expected, hardwoods show 12% higher sugar content than the softwoods, mainly in the amount of xylan which has an important role in fibre to fibre bonding. Therefore, the smaller breaking loads in case of hardwood joints cannot be attributed to the lower hemicellulose (xylan) content but smaller optically bonded area. When it comes to comparison of the UBSK and BSS joints, the difference in the breaking load (although not statistically significant) is attributed to the effect of the

cooking process. During the sulphite cooking process, the decomposition starts from the primary wall or the outside of the fibre and results in higher removal of hemicelluloses than the kraft process (Sixta, 2006). Mayhood et al. (1962) and Schniewind et al. (1964) tested both kraft and sulphite pulp and both obtained lower breaking loads in case of sulphite pulp. The reduction was attributed precisely to the cooking process. During the kraft cooking, the hemicelluloses, which are crucial for fibre of fibre bonding, are precipitated on the surface, thus increasing the strength at bond site. Besides the differences in the cooking process, the sulphite pulp was bleached which lead to and even higher loss of hemicellulose. Therefore, the increase in the breaking loads of softwood kraft pulps is attributed to a more favourable distribution of hemicelluloses, but also to the overall hemicellulose content of the pulp.

A comparison of the breaking loads obtained in previous studies and the current one is shown in Figure 4.1.

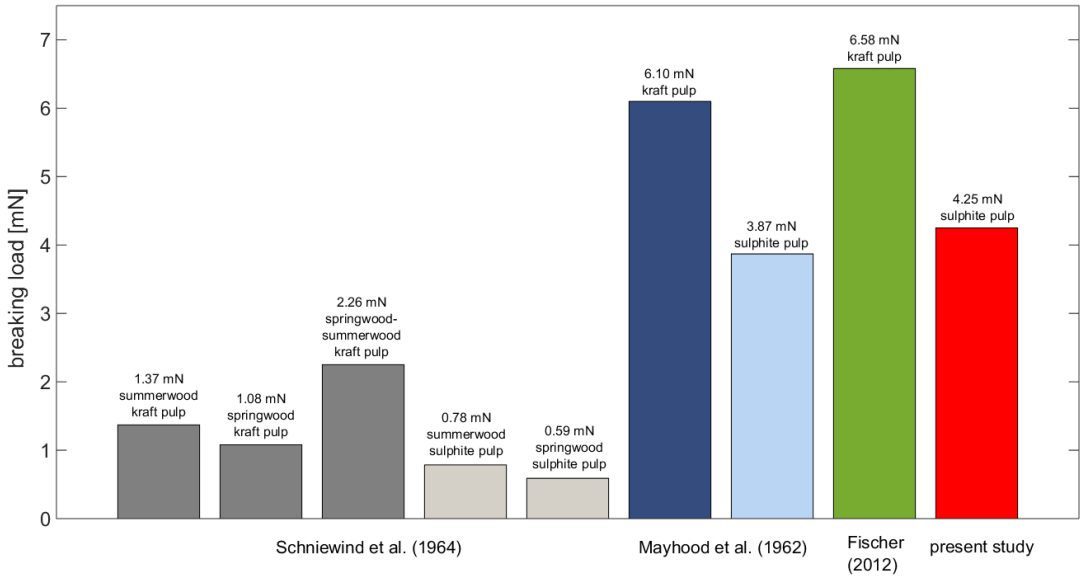


Figure 4.1 Comparison of joint breaking load values obtained in previous studies

The results obtained in this study are in good agreement with the study of Mayhood et al. (1962) where unbeaten, unbleached sulphite and kraft pulps were used. The agreement between the sulphite pulp values is especially interesting since it appears that in this case, the bleaching did not have such a significant influence on the breaking load. When it comes to the values obtained by Schniewind, the differences are more pronounced. In case of the kraft pulp, the values are roughly 3 times lower than the values obtained in the previous studies (Fischer (2013), Mayhood et al. (1962)) and in case of the sulphite pulp, 4 to 5 times lower values were reported. In case of the sulphite pulp though, it has been pointed that only five out of a total number of 72 joints could be tested. Such low success might imply that the even the tested joints

were damaged to some extent prior to testing and furthermore, it poses a question on how reproducible these values actually are.

Figure 4.2 shows the distribution of the breaking load values of the three types of joints tested in the current study and the Table 4.6 gives the results of a t-test which was performed in order to see if the values were statistically significantly different from each other.

The box plots show the median, upper and lower quartile ("box" area which represents a range where 50% of all obtained values lie) and upper and lower whisker representing the values outside of the middle 50% "box". The t-test performed with a confidence level α of 0.05 tells us that the BHK (hardwoods) are statistically different than any of the two softwoods (both UBSK and BSS) (if p-value < α - values statistically significantly different from each other).

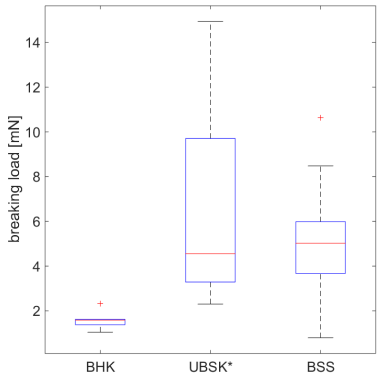


Figure 4.2 Breaking load distribution of individual fibre to fibre joints

comparison	conf. level, α	p-value
BHK - UBSK	0.05	0.0145
BHK - BSS	0.05	0.0048
BSS - UBSK	0.05	0.3378

Table 4.6 t-test results of individual fibre to fibre joints

From the figure, it is apparent that the widest distribution of values is present in case of UBSK joints, followed by BSS and BHK joints. Softwoods such as pine and spruce have pronounced differences between early wood and latewood. Latewood fibres make stronger joints while earlywood fibres form joints of lower strength (Stratton and Colson (1990), Schniewind et al. (1964)). Having both latewood and earlywood in the tested sample might explain the large variation. Eucalyptus on the other hand is a tropical species with less pronounced differences between the earlywood and latewood and this could be a reason for lower variations. Fibres of more uniform size would give joints of more uniform size and properties. Another issue that might play a role is the size and angular orientation of the fibres in the joint. Hardwood fibres and joints are on the limit of feasible testing size and this would imply that in order for the fibres to be glued, the crossing angle of the joints had to be as close to 90 $^\circ$ as possible. Any change in the crossing angle would be taking off from the free length of the fibre. Softwood fibres on the other hand are longer and therefore capable of creating joints that can still be tested even if the crossing angle is less or more than 90 degrees. This joint configuration would contribute to a more

mixed mode of loading. While in hardwoods, the mode of loading is closer to true shear, in softwoods the variation in the crossing angle introduces torsional loading in the joint. The extent of the mode I and mode III interplay in the shear loading (mode II testing) would cause the differences in the distribution of values.

Strength of hardwood and softwood joints

Comparison of the calculated joint strength (force per optically bonded area, F_{OBA}) is shown in Table 4.7. As can be seen, hardwood joints show the highest values (5.32 MPa), followed by sulphite (4.51 MPa) and kraft pulp (3.10 MPa).

Table 4.7 Joint strength values obtained in the current study

type	F_{OBA} [N/mm^2]	stand. dev.
BHK	5.32	1.46
$UBSK^*$	3.10	1.78
BSS	4.51	2.92

* Fischer (2013)

The explanation for the increase in joint strength is the well-known size effect (Button (1979), Uesaka (1984)). The size effect describes a decrease in force per optically bonded area with increasing bond size. The larger the bonded area the more uneven is the stress distribution in the joints will be.
Figure 4.3 shows the stress distribution within a joint plotted against the distance from the edge of the joint: from the figure it is evident that the higest stresses occur at the edge itself and gradually diminish towards the centre of the joint.

When calculating the strength of joints, one assumes uniform stress distribution, whereas in real situations, in case of large joints, the edges will be under stress but the centre of the joint will be exposed to zero or lower stresses and carry very little or practically no load. In case of smaller joints, such as hardwoods in this case, the stress distribution is more uniform and such situation resembles far more the one assumed in the joint strength calcualtions.

However, the results presented here should not be considered as a confirmation of hardwood joints being stronger than softwood since it is difficult to observe a relationship between the optically bonded area and breaking load (Fischer (2013)). The same has been reported in earlier studies dealing with viscose fibres (Weber et al. (2014)) and softwood fibres (Fischer (2013)).

The variability of the strength values is shown in Figure 4.4. Highest variability of values is visible in case of sulphite pulp, followed by softwood kraft and hardwood kraft joints. According to a t-test (confidence level $\alpha = 0.05$) there is a statistically significant difference between hardwood and softwood kraft joint strength (p-value

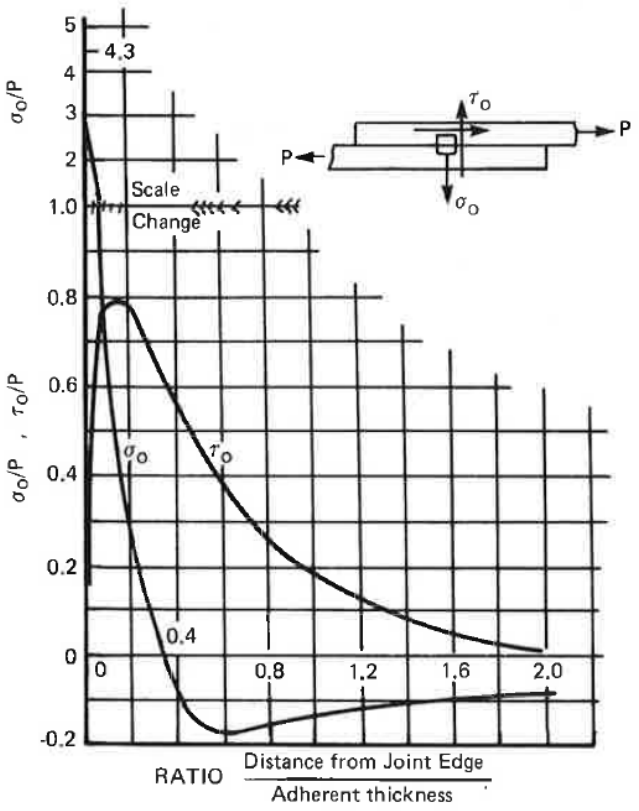


Figure 4.3 Stress distribution depending on the size of the joints, (Uesaka, 1984)

= 0.0447, Table 4.8). However, there is no statistically significant difference between hardwood kraft joints and softwood sulphite joints (p-value = 0.4396, Table 4.8).

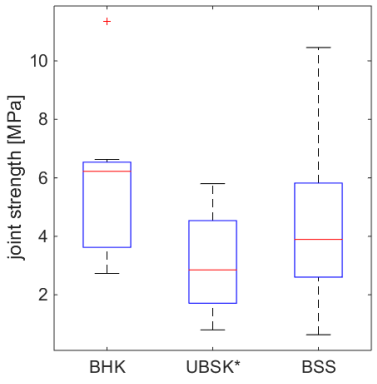


Figure 4.4 Joint strength value distribution

comparison	conf. level, α	p-value
BHK - UBSK	0.05	0.0447
BHK - BSS	0.05	0.4396
BSS - UBSK	0.05	0.2756

Table 4.8 Joint strength comparison t-test results

The relatively large standard deviation in case of the strength values does not come as a surprise since softwoods joints vary in their size and composition more than the hardwood joints and the same trend has already been observed with the breaking

loads and the size of the optically bonded area. Comparison of the hardwood joint strength values could only be done with two studies where the joint strength was determined indirectly. Comparison of the values obtained in the previous studies and the present one are given in Table 4.9.

Table 4.9 Comparison of hardwood joint strength

	F_{OBA} [MPa]	stand. dev.
present study	5.32	1.46
Koubaa and Koran (1995)	1.23 - 1.7	N/A
Snowman et al. (1999)	10.7 - 12.8	N/A

In case of Koubaa and Koran (1995) the Z-directional tensile tests was used for calculating the so-called specific bonding strength. The first issue when comparing the results with those obtained during this study is the mode of loading. In paper fracture mechanics, the Z-directional tensile test corresponds closely to the peeling mode. In this mode, so called mode I, the force is acting perpendicular to the joint surface while in shearing, the force acts parallel to the joint. Peeling tests yield lower values than shearing (Schmied et al. (2012), Magnusson and Östlund (2011)). Secondly, led by the findings of Stratton (1991), Koubaa and Koran (1995) assumed that the measure of relative bonded area (RBA) is the relation between the apparent sheet density and fibre wall density, therefore, calculating the values for the entire bonded area and not for individual fibre to fibre joints. The possible overestimation of the bonded area and breaking loads obtained in mode I might have led to an underestimation of the calculated force per unit bonded area values. In the study of Snowman et al. (1999) the calculated force per unit bonded area values are ten times higher when compared to the values calculated by Koubaa and Koran (1995) and two times higher than directly measured values in the current study. Snowman and co-workers used the Page equation to determine the force per unit bonded area. Due to several factors included in this equation (zero and finite span tensile strength, fibre coarseness, RBA, average fibre perimeter and length, shear bond strength etc.) the results are susceptible to experimental errors. Furthermore, vessels, ray cells and parenchyma cells as well as sheet structure related properties such as z-directional entanglement and fibre interlocking have not been taken into account since it is difficult to determine their effect on the results. Fines are another factor influencing the outcome of the calculations since it is known that fines contribute to the strength of paper (Retulainen et al. (2002)). Stratton (1991) tested classified softwood handsheets (fines were removed) and calculated the "bond shear strength" using the Page's equation. The results were compared to those obtained from a single joint testing and both values were in good agreement, confirming the influence of fines on the calculated force per unit bonded

area. Disregarding the influence of the aforementioned factors might give and explanation for the differences between calculated and directly measured values.

Comparison of kraft and sulphite joint strength values obtained in previous and current study are given in Table 4.10. In the study of Schniewind et al. (1964), they tested softwood kraft and sulphite joints of varying composition and obtained values from 0.2 to 0.98 MPa. In this case, the bonded area of the joints was calculated as the gross overlap area by treating the area as a rectangle and measuring its sides. Due to this, it is possible that the area in contact was overestimated and this, in combination with the lower breaking loads, could account for relatively low joint strength. In case of Mayhood et al. (1962) the bonded area of kraft and sulphite joints was measured using the PLM method (Page, 1969) and the values obtained are in good agreement, despite the sulphite joints exhibiting slightly higher strength values in the present study.

Table 4.10 Joint strength values obtained in the current study

		joint strength [MPa]	
	joint type	kraft	sulphite
Schniewind et al. (1964)	summer-summerwood	0.77	0.31
	spring-springwood	0.36	0.20
	summer-springwood	0.98	-
Mayhood et al. (1962)	-	2.93	2.86
Present study	-	3.10*	4.51

* Fischer (2013)

Same as in the case of hardwood joints, the values obtained in the present study should not be considered as a confirmation that the sulphite fibres form stronger bonds than the kraft ones since it is not possible to correlate the breaking load of the joints to the optically bonded area.

4.1.2 Individual fibre tensile testing

Softwood fibres (UBSK and BSS) were tested over a span of 1 mm whereas the hardwood fibres (BHK) were tested over a span of 0.3 mm and the success rates of the tests are given in table 4.11.

Table 4.11 Success rate of individual fibre tensile testing

Type	successfull no. of test	total no. of samples	testing span [mm]
BHK	8 (16)	21	0.3
UBSK	4 (14)	16	1
BSS	12 (20)	22	1

The lowest success rate was obtained in case of UBSK fibres (25%). Out of 16 samples, 14 were tested successfully but the cross sectional area could only be measured for 4 of them. In case of hardwood fibres, the cross sectional area was measured on a bulk sample (as mentioned in Section 3.1.2). However, out of 21 fibres, 16 were tested successfully out of which, only eight fibres were free of kink and twists. Kinked and twisted fibres were excluded from the breaking load and fibre strength analyses since those defects presumably negatively influenced the fibre mechanical properties. In case of BSS fibres, the highest success rate of 57% was obtained (Table 4.11).

Breaking load of hardwood and softwood fibres

Breaking loads of individual fibres are shown in Table 4.12. Breaking load of BHK fibres is only 17% of the UBSK fibres and 37% of the breaking load obtained for BSS fibres. The reduction in both cases can be attributed to the size of the fibres. Hardwoods have smaller width and thickness corresponding to smaller cross sectional area. Less load bearing material would mean lower breaking loads (Paavilainen, 1991). When comparing hardwoods to the unbleached kraft softwood pulp, another factor that might play a role is the influence of bleaching. Lignin increases the stiffness of materials, and dissolving it alongside some of the hemicelluloses, might lead to a decrease in the breaking load. When comparing the values of the kraft softwood and sulphite softwood pulp, the lower breaking loads are attributed precisely to the cooking process. During pulping, the sulphite process tend to produce fibres of lower strength with more defects due to higher level of fibre degradation during pulping.

Table 4.12 Breaking load of individual fibres

type	breaking load [mN]	stand. dev.
BHK	38.81	16.31
UBSK	221.23	110.32
BSS	101.43	62.01

Table 4.13 shows that both BHK and BSS have statistically significantly lower breaking load values when comapred to UBSK.

Figure 4.5 shows the distribution of breaking load values, with UBSK having the widest distribution, followed by BSS and BHK fibres. The coefficient of variation on the other hand is largest in case of BSS fibres (61%), followed by UBSK fibres (49%) and lastly by BHK pulp (42%).

The reasons for the large variation of values in case of softwoods are presumably due to the differences between earlywood and latewood and the differences in the MFA. In comparison to hardwoods, which have a relatively clean structure (Forgacs, 1961) with fewer irregularities than softwoods, the latter have a higher number and more pronounced pores and pits. Alongside that, the softwood fibres are tested over

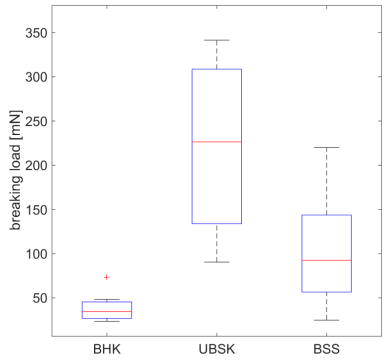


Figure 4.5 Comparison of fibre breaking loads obtained in the current study

comparison	conf. level, α	p-value
BHK - UBSK	0.05	0.000714
BHK - BSS	0.05	0.0132
BSS - UBSK	0.05	0.0181

Table 4.13 Individual fibre breaking load comparison - t-test results

a longer span. Having a greater testing span and more irregularities and weak spots would mean that there is a higher chance of a strength reducing flaw to occur in that region. Therefore, this large coefficient of variation might also come from unaccounted flaws or weak spots in the fibres.

Figure 4.6 shows comparison of the fibre breaking loads obtained in previous studies dealing with hardwoods.

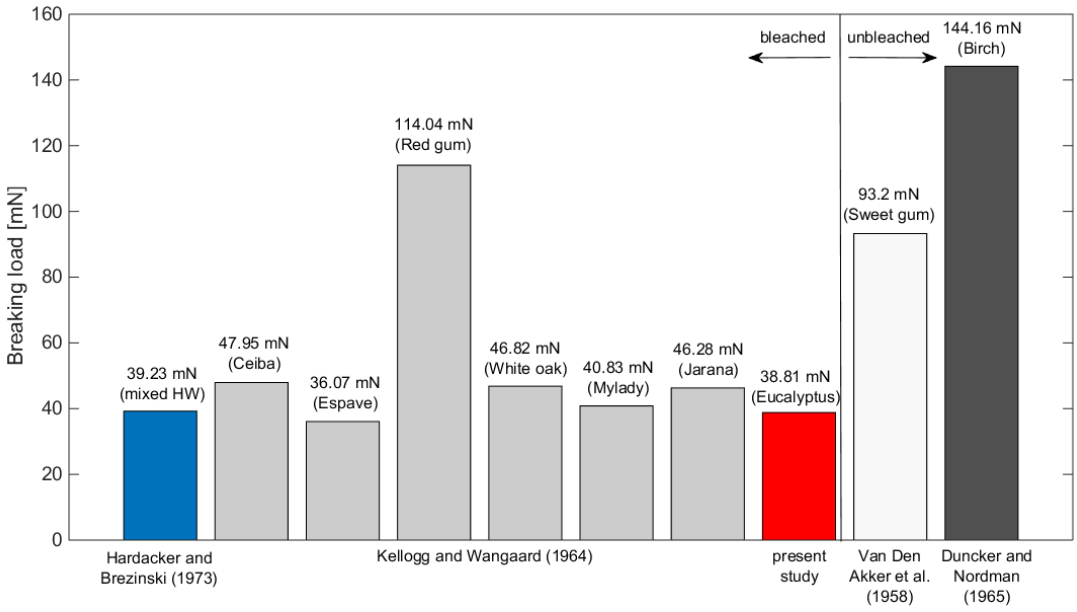


Figure 4.6 Comparison of fibre breaking loads of hardwood fibres

Since all studies dealt with different pulps, loading rates, testing spans and bleaching sequences a selection criterion has been made on the basis of the bleaching and beating sequences. Different loading rates and testing spans have been disregarded. Only the low kappa number pulps used in the study of Kellogg and Wangaard (1964)

and unbeaten, unbleached pulps used in the study of (Van Den Akker et al., 1958) were included in the comparison. The comparison of the values of bleached pulps shows good agreement. Slight differences in the breaking loads of different fibres are attributed to the size of the cross sectional area, cell wall thickness and possible imperfections such as microcompressions, wrinkles or nodes (Page et al., 1972). The increment in the load bearing material results in an increase of the breaking load. Further factors which influence the outcome of tensile testing are the S2 microfibril angle (Page et al., 1972), degree of crystallinity and the degree of polymerization (Paavilainen, 1991). Unfortunately, those factors could not be accounted for. Comparing the values of the current study, bleached eucalyptus fibres with unbleached sweetgum (93.2 mN) and birch (144.16 mN), a higher reduction in the breaking load can be observed. As already known, the degradation and removal of lignin weakens the cell wall and also dissolves hemicellulose which has a crucial effect on tensile strength (Spiegelberg, 1966).

Pulps used in the study of Kellogg and Wangaard (1964) were bleached to different degrees (permanganate numbers/lignin content) and cannot be directly compared to unbleached or fully bleached fibres since they lie somewhere in between. Nevertheless, they observed a correlation between fibre strength and permanganate number (i.e. lignin content). In each of 6 types of pulp tested, the removal or degradation of lignin was followed by a reduction of breaking load. Therefore, the reduction of strength between bleached and unbleached hardwoods is, besides the size of the cross sectional area, attributed also to the effect of bleaching.

Comparison with previous studies dealing with differences in breaking load between softwood kraft and sulphite pulps is shown in Figure 4.7

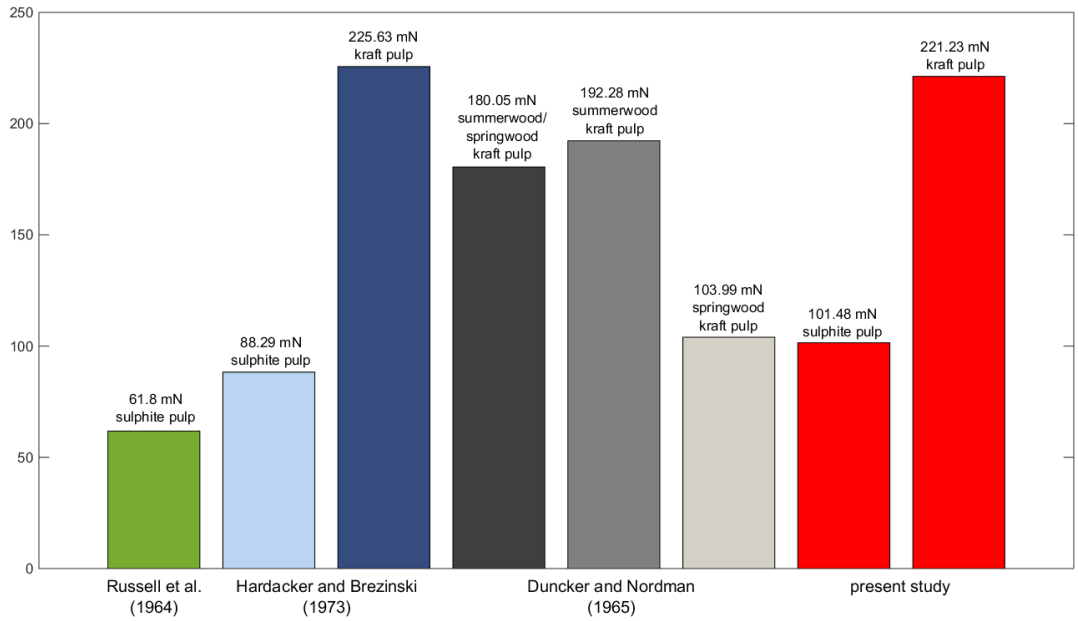


Figure 4.7 Comparison of softwood fibre breaking loads

Russell et al. (1964) tested unbeaten and unbleached bisulphite softwood pulp on an Instron tensile tester and obtained breaking loads of 61.8 mN for individual fibres. Hardacker and Brezinski (1973) tested unbeaten unbleached softwood kraft (southern pine) and bleached sulphite (western hemlock) pulp and obtained values of 225.63 and 88.29 mN respectively. These values are in surprisingly good agreement with the values obtained in the present study. Duncker and Nordman (1965) tested laboratory cooked softwood kraft pulp on a custom-built tensile tester. The fibres were tested in three groups, combined springwood and summerwood fibres, separate group of only springwood fibres and the third group of only summerwood fibres. The breaking load values obtained for the summerwood fibres (192.28 mN) are in good agreement with the ones obtained in the current study. However, the breaking load values obtained for springwood fibres exhibited significantly lower values (103.99 mN). The difference was attributed to a more complete development of the S2 layer in the summerwood fibres than the one of the springwood fibres. The mean breaking load of 180.05 mN for the combined group (springwood and summerwood) was not considered representative of the whole fibre population since obviously more latewood fibres were selected and tested. In case of the present study, no selection based on the type of the fibre was made. However, considering relatively high breaking load values, it is possible that a higher number of latewood fibres than springwood fibres was tested.

Cross sectional area of hardwood and softwood fibres

Cross sectional areas of the tested fibres are shown in Table 4.14. By far, the smallest cross sectional area belongs to BHK fibres with only 35.12 μm^2, followed by BSS (232.50 μm^2) and UBSK (271.29 μm^2).

Table 4.14 Cross sectional area of individual fibres used for tensile testing

Type	$A_{cross}[\mu m^2]$	stand dev.
BHK^*	35.12	-
UBSK	271.29	41.00
BSS	232.50	77.82

* unpublished data, Lorbach (2016)

Cross sectional area of the hardwood fibres was obtained by cutting a randomly selected group of fibres, meaning that small and large fibres, and possibly ray cells were cut and the mean values calculated. Therefore, it is possible that some underestimation of the real cross sectional area occurred. For sulphite and kraft softwood pulp, only fibres tested in the tensile tests have been cut and the area analysed. However, even in this case it is possible that some overestimations occurred. When cutting a single fibre, it is not possible to determine the cutting angle in the fibre so that in case of a tilted fibre, the area appears larger than it actually is. Even though similar fibres were tested (spruce and pine) a difference in the size of the cross sectional area can be observed. The reason for these differences is rather unknown. Some possibile explanations include the diferences in the cooking process (sulphite process being more agressive towards the fibres), the effect of bleaching (further loss of lignin and hemicelluloses), differences in the wood from which the fibres were pulped or simply random selection resulting in smaller fibres being tested.

Strength of hardwood and softwood fibres

Using the cross sectional area of the fibres (A_{cross}) and the breaking load values, it was possible to calculate the breaking stress and the mean strength values are given in Table 4.15.

Table 4.15 Individual fibre strength obtained in the current study

Type	F_{break} [MPa]	stand dev.
BHK	1105.07	464.29
UBSK	801.95	333.68
BSS	454.59	217.63

The highest fibre strength of 1105.07 MPa was obtained in case of hardwood kraft pulp (BHK), which is not surprising considering that these fibres have the smallest

cross sectional area. Sulphite fibres (BSS) show the lowest values when it comes to breaking stress (454.59 MPa) and in this case, the reduction in strength, when compared to the UBSK and BHK, is attributed to the lower breaking loads rather than the higher cross sectional area. Sulphite cooking alongside the bleaching process creates a fibre of lower cell wall cohesion (Stone and Scallan (1968)) whereas the kraft process yields fibres with greater cell wall cohesion. Higher cohesion within the cell wall would lead to a better stress distribution and ultimately give fibres of higher strength.
The distribution of the values is shown in Figure 4.8. From the figure it can be seen that the softwood kraft fibres exhibit the widest distribution of values , followed by sulphite softwood pulp and lastly, hardwood kraft.

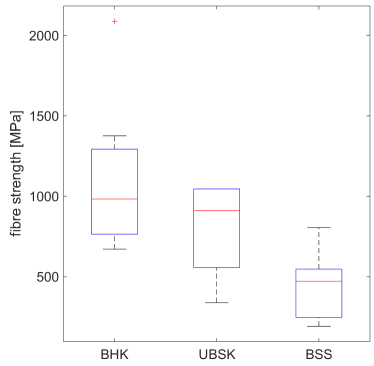


Figure 4.8 Fibre strength distribution

comparison	conf. level, α	p-value
BHK - UBSK	0.05	0.2757
BHK - BSS	0.05	0.0012
BSS - UBSK	0.05	0.0379

Table 4.16 Fibre strength comparison - t-test results

These distributions are a result of the variation in the cross sectional areas and the breaking loads, so it does not come as a surprise that the same trend is observed in the strength values distribution. The differences in the size of the fibres, degree of crystallinity, MFA, possible cell wall irregularities and the presence of pores and weak spots all have an influence on the stress distribution and fibre strength.

Comparison of the hardwood fibre strength values obtained in previous studies with the values obtained in the current study are given in Table 4.17.

Table 4.17 Individual fibre strength

	type	F_{break} [mN]	A_{cross} [μm^2]	F_{break} [N/mm^2]
Duncker and Nordman (1965)	birch	144.15	150	961.07
Hardacker and Brezinski (1973)	mixed HW	39.23	64	612.92
Van Den Akker et al. (1958)	sweet gum	93.20	178	523.39
present study	eucalyptus	38.81	35.12	1105.07

When it comes to analysis of the fibre strength, the results obtained by Duncker and Nordman (1965) are in good agreement with the results obtained in the current study. A discrepancy in the case of Hardacker and Brezinski (1973) is attributed

to the type of pulp tested. With a pulp mixture containing 55% maple, the exact cell wall thickness and the cross sectional area of tested fibres could not be clearly determined. The discrepancy in the case of Van Den Akker et al. (1958) is attributed to method used to measure the cross sectional area. The lumen of the fibre was not excluded from the cross sectional area and therefore the true cross sectional area is unknown. Lumen provides no load bearing material and inclusion of the same might result in an underestimation of the breaking stress. In case of fibres tested in the current study, the lumen, if present, was excluded from the cross sectional area. Another possible factor mentioned to influence the tensile strength is the testing span. Kellogg and Wangaard (1964) used 0.25 mm, Duncker and Nordman (1965) used 0.6 mm, Hardacker and Brezinski (1973) used a test span of 0.15 mm and in the present study a testing span of 0.3 mm was used. Considering the similarity of the results of the aforementioned studies (previous figure regarding comparison of HW) and also taking into account that different wood species were investigated, it appears that the variations in the testing span do not have such strong effect on hardwoods as they have on softwoods. Comparison of the softwood fibre strength values with the ones obtained in the previous studies dealing with softwoods are given in Figure 4.9

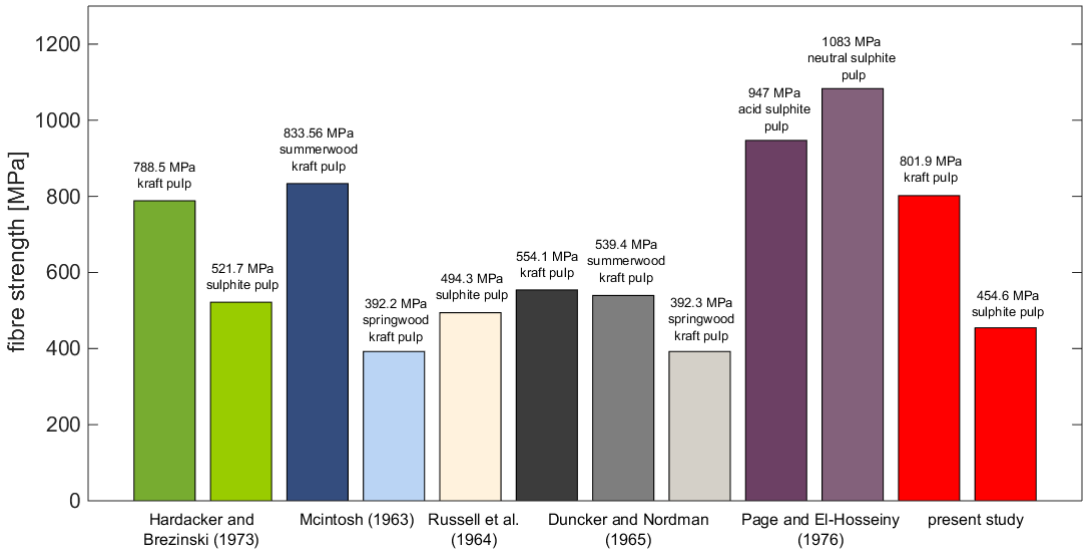


Figure 4.9 Comparison of strength values for softwood fibres

Kraft pulp results are in good agreement with the results obtained by Hardacker and Brezinski (1973) and the summerwood fibre values of McIntosh (1963), which might indicate that in the present study and the one of Hardacker and Brezinski (1973), the random choice of fibres actually did result in higher number of summerwood fibres being tested. McIntosh (1963) tested springwood and summerwood bleached kraft pulp (loblolly pine) and obtained relatively high values of 833.6 MPa for summerwood fibres and 392.2 for springwood fibres. Duncker and Nordman

(1965) obtained somewhat lower values for kraft pulp but in this case, this was attributed to possible overestimation of the cross sectional area. The width and thickness of the fibres was measured using a microscope and the cross sectional area calculated under the assumption that the cross sectional area was a rectangle. This assumption might have led to a higher cross sectional area and consequently lower strength. In case of sulphite pulps, Russell et al. (1964) tested unbeaten, unbleached softwood bisulphite and obtained values of 494.3 MPa which is very close to the values obtained in the current study.
Page and El-Hosseiny (1976) tested acid sulphite (63% yield) and neutral sulphite (56% yield) softwood pulp fibres (springwood only) and obtained values of 947 and 1083 MPa respectively. These values are approximately two times higher than the previously reported ones; or the ones obtained in the current study. The possible explanations for the exceptionally high strength values could be attributed to carefully prepared samples in which great care was taken as not to damage the fibres during disintegration. Another factor playing a role was the fibril angle, which in this case varied between 0 and 10°. Since the fibres are strongest if the microfibrils are parallel to the fibre axis, the low MFA might account for the high fibre strength.

4.2 Influence of relative humidity

4.2.1 Conditioning time assessment

Isotherms of water vapour desorption/sorption were determined with a with a dynamic gravimetric water sorption analyser (DVS Intrinsic, Surface Measurement Systems, Alperton-London, UK). Approximately 40 mg of the pulp was placed in the sample pan and was pre-conditioned at 0 % relative humidity (RH) for 12 h at 25°C to remove any adsorbed water molecules. Subsequently, the RH was increased to 30% for 12 h, decreased to 0% for 12 h again, increased to 50% for 12 h, decreased to 0% for 12 h, increased to 80% for 12 h and finally decreased to 0% for 12 h. The amount of water absorbed was calculated from the difference of the sample between 0% RH and the according RH value. Equilibrium was detected by comparing the mass of sample with a mathematical asymptote model. When the difference was less than 1%, the mass was noted. The moisture content was measured at 3 different humidity levels, 30, 50 and 80% RH. It is believed that the equilibrium was reached when the change in mass was constant. The measurement principle and the results are shown in Figure 4.10 and Table 4.18 , respectively. Time to reach equilibrium is defined as a function of the equilibrated moisture content (EMC) based on the individual sorption/desorption kinetics of the pulp at constant humidity and 25°C.

The time to reach the equilibrium depends on the initial moisture content of the pulp, RH level and the rate of RH increase. According to the DVS, 480 min were required to reach EMC at 30 and 50% RH. At 80% RH constant mass was achieved after

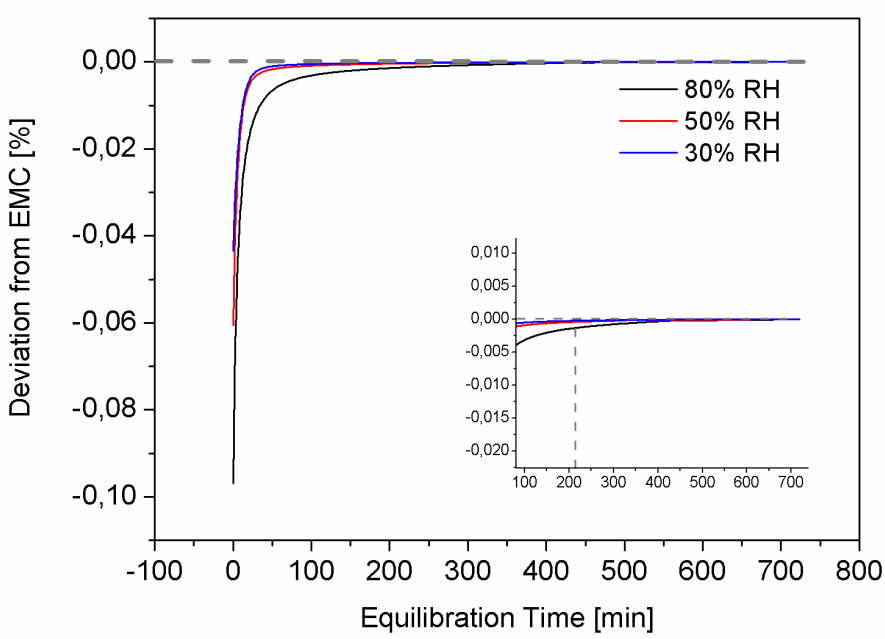


Figure 4.10 Sorption behaviour of softwood kraft pulp

600 minutes. These measurements were performed on the pulp level and therefore it can be concluded that the time to reach the equilibrium at the single fibre scale is much lower. Table 4.18 shows the results obtained from DVS measurements (time needed to reach the EMC and the percentage reached after 120, 240 and 480 min).

Table 4.18 Equilibration time of softwood kraft pulp

		% of EMC after		
RH %	Time to EMC [min]	120 min	240 min	480 min
0-30	480	99.95	99.98	99.99
0-50	500	99.93	99.96	99.99
0-80	600	99.77	99.91	99.98

Based on these results, it was decided to conduct the experiments on UBSK joints after 120 min of equilibration time. To ensure that the time chosen was enough to equilibrate the fibres and joints to the point where further moisture sorption would play no further role, mechanical tests with three set times were performed. Figure 4.11 and Table 4.19 shows comparison of the breaking load values of joints after 120, 240 and 480 min.

Table 4.19 Breaking load of softwood joints after different equilibration times (10 joints tested in each group; number in parenthesis respresents the standard deviation)

	breaking load at 80% RH		
exposure time	120 min	240 min	480 min
UBSK	3.11 (1.31)	4.27 (2.27)	3.21 (1.48)

A t-test with 95% confidence level showed no significantly different values based on different exposure times (Table 4.20).

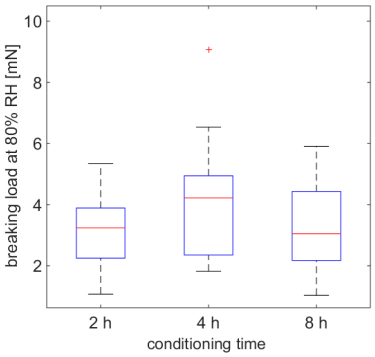


Figure 4.11 Comparison of joints after three different exposure times

comparison	conf. level, α	p-value
2 h - 4 h	0.05	0.181
4 h - 8 h	0.05	0.233
2 h - 8 h	0.05	0.883

Table 4.20 t-test results - joint exposure time

Based on these results, it was concluded that the exposure of 120 min was long enough for the joints as well as fibres to reach an equilibrium where further water sorption would not influence the mechanical properties significantly.

4.2.2 Individual fibre to fibre joint testing - RH

The results of the testing at 50% RH are have been discussed in the previous section (joint breaking load). For the joints tested at 30% RH, UBSK samples had a success rate of 100%, the BHK joints had a 70% and, BSS joints 60% success rate. In case of joints tested at 80% RH, 80% success rate for hardwood kraft pulp, 100% for softwood kraft and 70% for sulphite softwood pulp was obtained.

Table 4.21 Success rate of joint testing at varying RH (number in parenthesis represents the total number of samples)

	breaking load at 80% RH		
type	30%RH	50% RH	80% RH
BHK	7 (10)	6	8 (10)
UBSK	10 (10)	14	10 (10)
BSS	6 (10)	12	7 (10)

It is surprising that all the joints tested at 30% RH experienced the conditioning stress response (discussed in Section 3.2.1) but none broke due to it. This high survival rate is attributed to the higher flexibility of the joints compared to the fibres. Since the L-fibre of the joints was only fixed in one point, it was free to move at the other end, while the C-fibre could bend and compensate to the shrinking direction in the L-fibre. However, even though the joint was partially free to move, one must assume that some changes took place in the joint prior to testing.

Breaking load of fibre to fibre joints

The results of the joint testing are given in Table 4.22. For UBSK pulp, the joints tested at 80% RH show a 52% reduction in breaking load whereas bonds tested at 30% RH show a 35% reduction when compared to 50% RH. However, the only statistically significant difference was found in case of joints tested at 80% RH ($\alpha = 0.05$, p-value = 0.023).

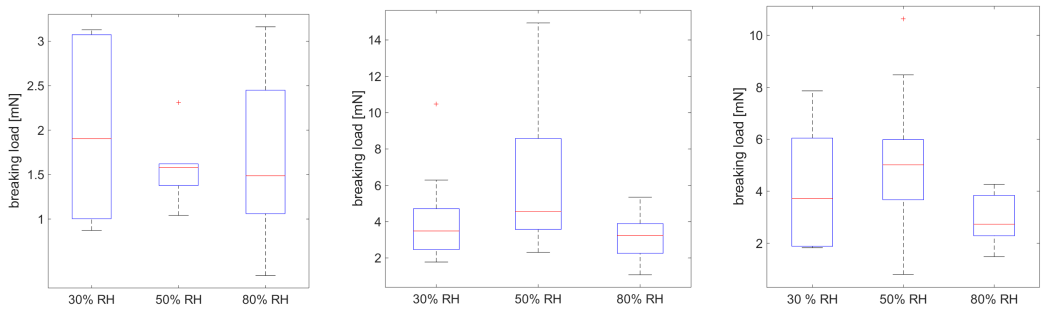
Table 4.22 Breaking load of fibre to fibre joints at varying RH (number in parenthesis represents the standard deviation)

	breaking load [mN]		
type	30%RH	50% RH	80% RH
BHK	1.99 (1.05)	1.58 (0.42)	1.69 (0.94)
UBSK	4.27 (2.67)	6.58 (4.45)*	3.11 (1.31)
BSS	4.15 (2.55)	5.15 (2.61)	2.88 (1.05)

*.... Fischer (2013)

Hardwood kraft (BHK) fibre to fibre joints showed slight difference when comparing the values of joints tested at differnt relative humidities. However, according to a t-test, no statistically significant difference between bonds tested at 30, 50% and 80% RH could be obtained. In case of sulphite softwood joints (BSS), same as in the case of BHK joints, a reduction could be observed but this difference was again not statistically significant.

It is believed that the exposure of 2 hours was sufficient for the hardwood kraft (BHK) and sulphite softwood (BSS) joints to reach an equilibrium since the same amount of time was sufficient for the equilibration of UBHK joints. The distribution of the breaking load values is shown in Figure 4.12.



(a) BHK **(b)** UBSK **(c)** BSS

Figure 4.12 Breaking load values of individual fibre to fibre joints

Table 4.23 t-test analysis of three joint groups

UBSK	α	p-value
30-50% RH	0.05	0.1748
50-80% RH	0.05	0.0230

BHK	α	p-value
30-50% RH	0.05	0.3846
50-80% RH	0.05	0.8034

BSS	α	p-value
30-50% RH	0.05	0.4817
50-80% RH	0.05	0.0616

The explanations for the decrease in the joint breaking loads in case of softwoods are attributed to the increase and decrease of the dried-in stresses and the effect of restrained conditoning. Figure 4.13 shows schematics of what could possibly be happening in a joint during conditioning to lower or higher RH.

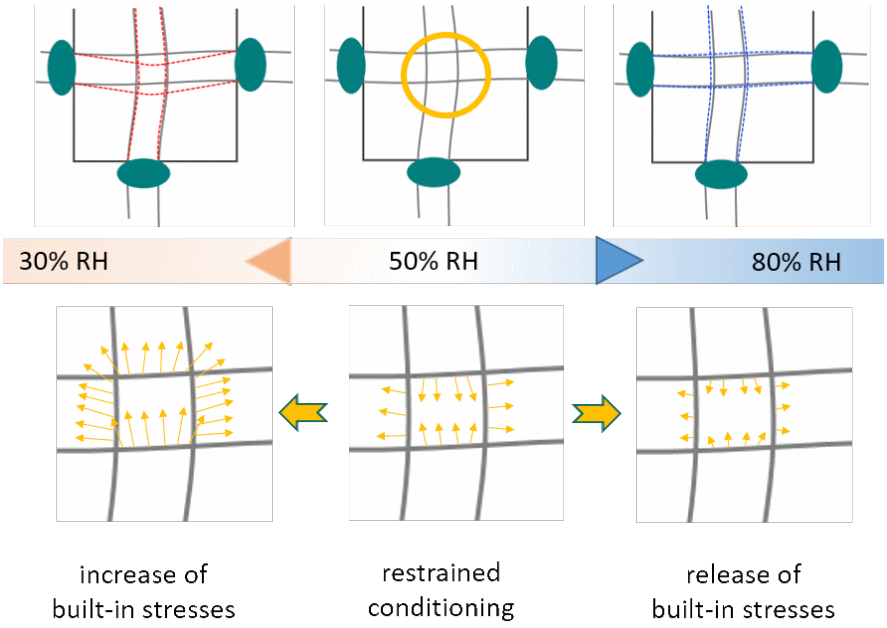


Figure 4.13 Joint behaviour during conditioning

Fibre to fibre joints are fixed in three points during conditioning and testing time which disables the fibre natural behaviour during conditioning to lower or higher RH, namely, it prohobits the twisting, shrinking and swelling.

In case of joints tested at 30% RH, the preexistent dried-in stresses increase even more due to the shrinkage of the fibres in the cross direction, while the shrinkage in the longitudinal direction imposes additional tensile stress on the joint. In such conditions, embrittlement of joints would be expected. As mentioned in Chapter 3, in case of joints, it was not possible to reduce the tensile, or, conditioning stress, but the fact that the joints did not break gives an indication that the embrittlement was avoided through compensation of the crossing fibre bending.

In case of fibres tested at 80% RH, the decrease is attributed to the decrease in the dried in stresses and partial failure of the bond due to swelling. As the moisture is absorbed, the fibres swell and soften, increasing the spacing between the fibres and potentially breaking some of the bonds.

However, it must be kept in mind that the joints were conditioned and tested in reastrained state, and it is quite possible that different results would have been obtained if the joints were conditioned freely prior to testing.

Higher breaking loads at 30% RH in case of hardwood (BHK) joints are believed to be an artefact of the measurement system and method since the same behaviour has not been noticed in any of the other tests.

Comparison with previous studies of Schniewind et al. (1964) and Russell et al. (1964) was not possible since the samples have been tested either fully wet or after reconditioning in standard laboratory conditions. Joint strength calculations were not made since it was not possible to determine the optically bonded area of the joints in the testing conditions.

4.2.3 Individual fibre tensile testing - RH

The analysis of the tensile testing success rate at different RH is given in the Table 4.24.

The highest success rate of 100% was observed in the case of softwood kraft pulp fibres tested at 30% and 80% RH. In case of fibres that were tested at 30% RH under restraint, the success rate was somewhat lower (80%). This was attributed to the effect of restrained conditioning which presumably weakend or damaged the fibres prior to testing, resulting in failures prior to testing. Precisely for this reason, sulphite pulps were tested at 30% RH only in the non-restrained state. The success rate in case of the sulphite pulps was 90% for the fibres tested at 30% RH and, 90% for the fibres tested at 80% RH.

Table 4.24 Analysis of success rate of tensile testing in varying RH (number in parenthesis represents the total number of samples)

	Number of tested samples		
type	30%RH	50% RH	80% RH
BHK	8 (10)	8	6 (10)
UBSK	10 (10)	4	10 (10)
	8* (10)		
BSS	9 (10)	12	9 (10)
*.... tested with pretension			

Hardwood kraft pulps had the lowest success rate of 80% in case of fibre tested at 30% RH and 60% in case of fibres tested at 80% RH. In case of hardwood kraft fibres tested at 30% RH, the testing could only be performed in the unrestrained state (where the fibre was relaxed). Conditioning in the restrained state tended to break the fibre prior to testing. In case of fibres tested at 80% RH, no fibre response was observed and thus, no relaxing was necessary.

Breaking load of fibres at different RH

Table 4.25 shows a comparison of the breaking load of individual softwood and hardwood fibres tested at different RH (30, 50 and 80%).

Table 4.25 Breaking load of fibres at different RH (number in parenthesis represents the standard devation)

	Breaking load [mN]		
	30%RH	50% RH	80% RH
BHK	24.05 (11.81)	38.81 (16.31)	27.39 (14.85)
UBSK	186.72 (97.72)	221.23 (110.32)	193.96 (82.72)
	143.38 (46.78)*		
BSS	86.01 (36.93)	101.43 (62.01)	63.09 (38.13)
*.... tested with pretension			

As can be seen from the Table 4.25, individual fibres tested at 30 and 80% RH of both softwood and hardwood pulps show slightly lower values when compared to fibres tested at 50% RH. In case of softwood kraft fibres (UBSK), the breaking load is around 20% smaller when the fibres were tested either in elevated or decreased humidity.

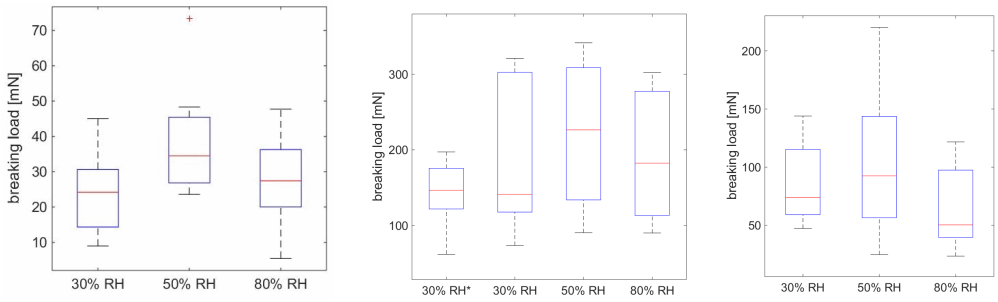
Table 4.26 t-test analysis of three fibre groups

UBSK	α	p-value
30-50% RH	0.05	0.6690
30*-50% RH	0.05	0.1020
50-80% RH	0.05	0.6283
*.... tested with pretension		

BHK	α	p-value
30-50% RH	0.05	0.0571
50-80% RH	0.05	0.2036

BSS	α	p-value
30-50% RH	0.05	0.5408
50-80% RH	0.05	0.1367

In case of hardwood fibres, the same behaviour as in case of non-restrained softwoods can be observed. For fibres tested at 30 and 80% RH, a reduction of 29 and 38% can be seen, respectively, but no significant difference was obtained in either of the cases (Table 4.26. Sulphite fibres (BSS) show a 33% reduction in breaking load when the fibres were tested at 80% RH, and only a 8% decrease when tested at 30% RH. Figure 4.14 shows a comparison and distribution of values of softwood and hardwood fibres.



(a) BHK **(b)** UBSK **(c)** BSS

Figure 4.14 Breaking laod of individual fibres

Additionally, Table 4.25 shows a slight decrease in standard deviation when the fibres are tested at either high or low RH. Jentzen (1964) observed that when fibres are dried under load, the standard deviation decreases but unfortunately, no explanation for this behaviour was found. However, the data from the current study suggest that similar effect might be taking place with fibres tested at 30% RH (especially pronounced with fibres tested under restraint).

Comparison of the values obtained in the current study with the ones obtained in previous studies is shown in Figure 4.15. The softwood (UBSK and BSS) values obtained in the current study are similar to the most comprehensive study performed by Kersavage (1973), showing a maximum at 60% RH and a decrease when moving towards higher or lower RH.

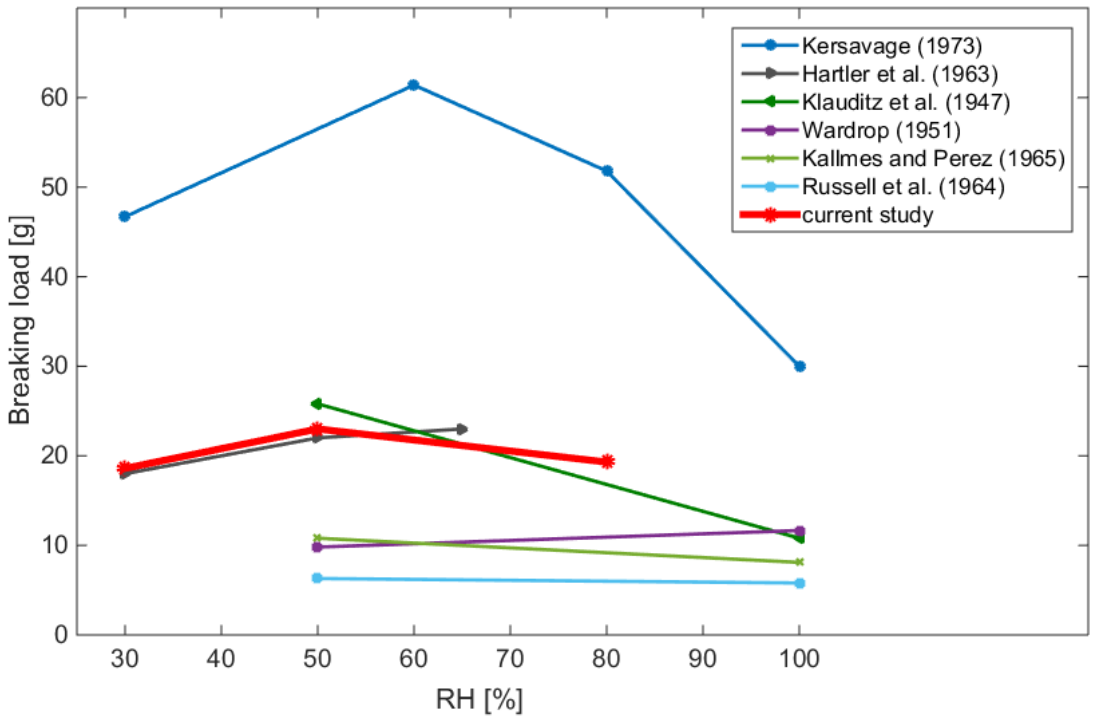


Figure 4.15 Comparison of breaking loads of individual softwood fibres

Same as with the results obtained in this study, besides the wet samples in case of Kersavage (1973), none of the values from the previous studies show a statistically significant difference. Leopold and Thorpe (1968) have attributed the change in breaking load to the breaking of hydrogen bonds within the fibre. In case of fibres with low internal cohesion (i.e. springwood fibres) the strength decreases due to hydrogen bond disruption whereas in case of summerwood fibres, having a higher degree of organisation, the breaking of hydrogen bonds has an opposite effect, distributing stress more evenly across the fibre surface. Wardrop (1951) also attributed increase in breaking load of wet fibres to more uniform stress distribution. Additionally, lower breaking load values in case of dry fibres could be attributed to the possible development of strength reducing flaws during drying (Russell et al., 1964). Higher occurrence of such weak spots, in combination with tension forces during conditioning, could result in a fibre that is already damaged prior to testing. Contrary to that, Klauditz et al. (1947) and Kersavage (1973) attributed higher dry than wet strength to a closer contact and higher cell wall cohesiveness of dry fibres when compared to wet fibres.

The increase in strength is attributed to either the increase in cell wall cohesiveness present at lower moisture content of RH (Kersavage (1973), Klauditz et al. (1947), and Leopold and Thorpe (1968)) or an improvement of internal stress distribution at higher MC moisture contents or RH (Russell et al. (1964), Wardrop (1951), Leopold and Thorpe (1968)). However, it is possible that both mechanisms, increase in stress

distribution and cell wall cohesiveness, coexist and compete at the same time. The nonlinearity of their behaviour, results in a maximum at around 50% RH.

Additionally, there is a third factor that plays a role in the outcome of the testing, the effect of restrained testing. A free standing fibre, when conditioned from 50 to 30% RH will shrink, rotate and twist. By gluing it in one plane, all three natural behaviours are being disabled. Due to these restrictions, the fibre cannot shrink freely, inner tension develop and the fibre becomes more brittle. Due to the tension forces created by the fibre shrinkage, it is possible that cracks in the wall are initiated even without any external load. The embrittlement, in combination with possible crack initiation would account for the loss in the load bearing capacity. An amplified effect of the embrittlement present at lower RH can be seen with softwood fibres which were tested "under restraint" and where the unloading sequence was not performed (values being 35% lower than the values obtained at 50% RH). In case of fibres tested at 80% RH, the opposite effect is taking place and the moisture absorbed from the air act as a softener. Since the fibre is still fixed during moisture absorption and therefore cannot move, it is possible that some internal bonds break, cellulose chains slip, and the load bearing capacity of the softened matrix diminish. Figure 4.16 shows the principle of the changes the fibres undergo upon variation in the relative humidity, the embrittlement which is present with low RH, and softening present at higher RH.

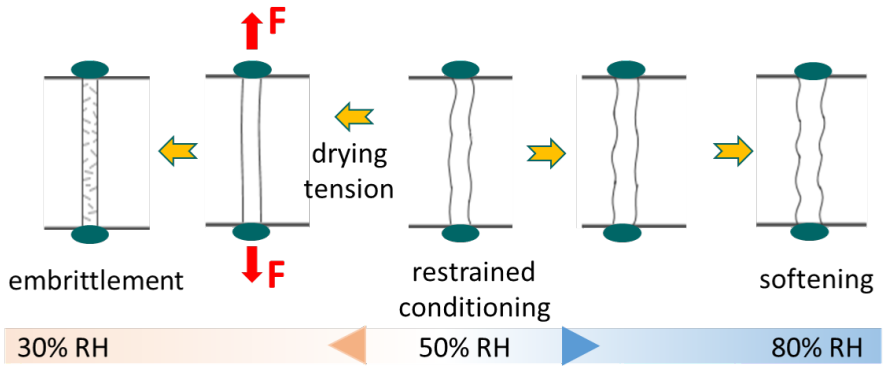


Figure 4.16 Fibre behaviour during conditioning to low or high RH

Same as in the case of individual fibres, it is possible that different results would have been obtained if the fibres were conditioned in an unrestrained state.

4.3 Influence of refining

As described in the Section 3.3. only softwood pulps could be refined and tested using the microtensile tester. Both kraft (UBSK) and sulphite (BSS) pulps were tested in the unrefined state and in three refined states (3000, 6000 and 9000 PFI rev). The analysis of the joint testing success rate is given in Table 4.27.

Table 4.27 Analysis of the joint testing success rate (number in parenthesis represents total number of samples)

	Number of succesfull tests	
rev. PFI	UBSK	BSS
0	14*	12(22)
3000	6 (10)	6 (10)
6000	8 (10)	0 (10)
9000	11(24)	14(20)
*.... Fischer (2013)		

The initial plan was to test a minimum of 10 joints for each group but that was not possible for all the sample groups, especially in case of UBSK joints refined to 3000 rev. PFI and BSS joints refined to 6000 rev. In this case, the joints where the OBA was successfully determined, the joints broke prior to mechanical testing. On the other hand, joints that were mechnically tested did not have the OBA determined (bonded area appeared blurry and disabled positive determination). For that reason, no values for the BSS pulp refined to 6000 rev. PFI were given. The reason for a larger number of unrefined and joints refiend to 9000 PFI to be tested was to ensure that the relatively low and high breaking load values were not an artefact of the measurement system or a highly biased selection favouring only one type of joints.

4.3.1 Breaking load of refined joints

The breaking load values of kraft (UBSK) and sulphite (BSS) pulp are given in Table 4.28. As expected, there was a steady increase in joint breaking load with advancing refining degree.

Table 4.28 Breaking load values of fibre to fibre joints at different levels of refining (number in parenthesis represents standard deviation)

	Breaking load [mN]	
rev. PFI	UBSK	BSS
0	6.58 (4.45)	5.15 (2.61)
3000	7.87 (2.79)	7.77 (6.21)
6000	9.03 (3.30)	-
9000	6.95 (4.12)	7.98 (4.66)
*.... Fischer, 2012		

The 35% increase in breaking loads of sulphite joints (comparison of unrefined joints and joints refined to 9000 rev. PFI) should be regarded with caution since the finding of sulphite fibre to fibre joints at that level was more than double the effort

Table 4.29 t-test analysis of refined joints

UBSK	α	p-value
0 - 3000 PFI	0.05	0.5216
0 - 6000 PFI	0.05	0.1909
0 - 9000 PFI	0.05	0.4389
3000 - 6000 PFI	0.05	0.5026
6000 - 9000 PFI	0.05	0.5794

BSS	α	p-value
0 - 3000 PFI	0.05	0.2179
0 - 6000 PFI	0.05	-
0 - 9000 PFI	0.05	0.0745
3000 - 6000 PFI	0.05	-
6000 - 9000 PFI	0.05	-

needed for the kraft joints or sulphite refined to a lower degree. Such high values should not be regarded as a representative of the whole pulp sample. At such high level of refining, it is surprising that any joints could be found and tested which only confirms the hypothesis that only the strongest fibres were able to undergo extensive mechanical treatment and form bond of sufficient length and strength to withstand mounting, gluing and testing. UBSK pulp had a lower increase in breaking load with a maximum at 6000 PFI rev. Slightly lower pulp development of the UBSK pulp could possibly be attributed to the lignin present in the cell wall. Since the lignin if farily stiff, it might render the fibres more resiliant towards the mechanical treatment. The observed increase in breaking loads are attributed to the higher swelling ability of internally and externally delaminated fibres, and the subsequent higher flexibility and conformability which allows the fibres to come into closer contact with each other. However, none of these differences proved to statistically significant. Similar trends have been observed by Mohlin (1975) and Stratton and Colson (1990). In their work, the lack of statistically significant values was attributed to the relatively same extent of damage the fibres underwent after the initial refining stage. It was believed that the S1 layer was already removed at low refining intensities and that all the bonding, regardless of the refining extent, took place in the S2 layer to a similar extent.

4.3.2 Optically bonded area of refined joints

Optically bonded area results are given in Table 4.30. Similar to the breaking loads there is an increase with advancing refining degree but in this case, the highest values of the OBA are obtained in case of UBSK joints refined to 6000 PFI and BSS joints refiend to 3000 PFI. Even though the OBA of joints refined to 6000 PFI was measured, the results are not included into quantitative disucssion since those joints failed prior to mechanical testing and the subsequent strength calculations were not possible.

There are several possibilities why the highest values are obtained at lower refining degrees but the most plausible ones are that the fibres at 9000 PFI revolutions have already a more significant proportion of externally delaminated cell wall fragments. Such fragments, due to their thickness are invisible to the PLM and their contribution to the bonded area of the fibres is not visible. To ensure that the complete area of joints was visible, the OBA was determined using PLM method and additional investigations were performed using plain light microscopy and different filters. The

Table 4.30 Optically bonded area of joints at different levels of refining (number in parenthesis represents standard deviation)

	OBA [μm^2]	
rev. PFI	UBSK	BSS
0	2198.18 (1016.27)*	1356.38 (534.91)
3000	1843.55 (1250.09)	1991.69 (1274.92)
6000	2300.69 (671.69)	-
9000	1952.54 (840.42)	1958.20 (1007.95)
*.... Fischer (2013)		

development of joints, as well as the difference between the OBA area determined by the PLM and the light microscopy filter is shown in Figure 4.17.

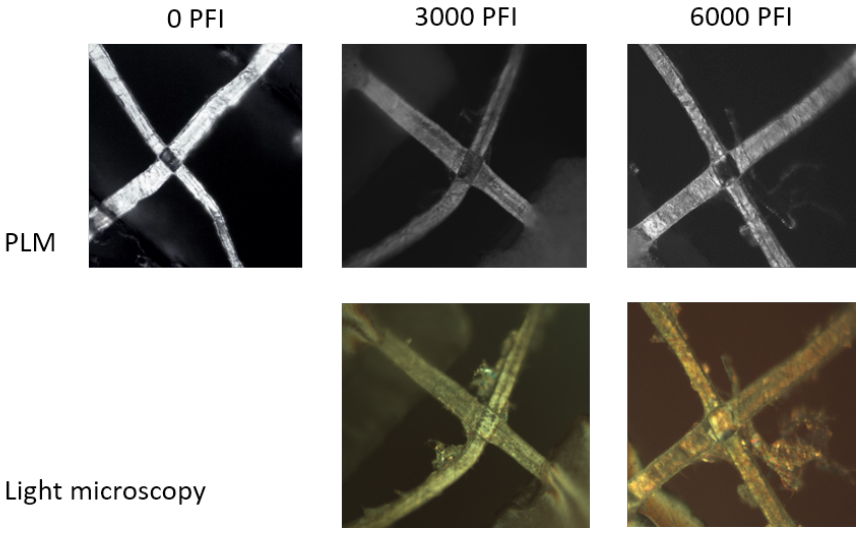
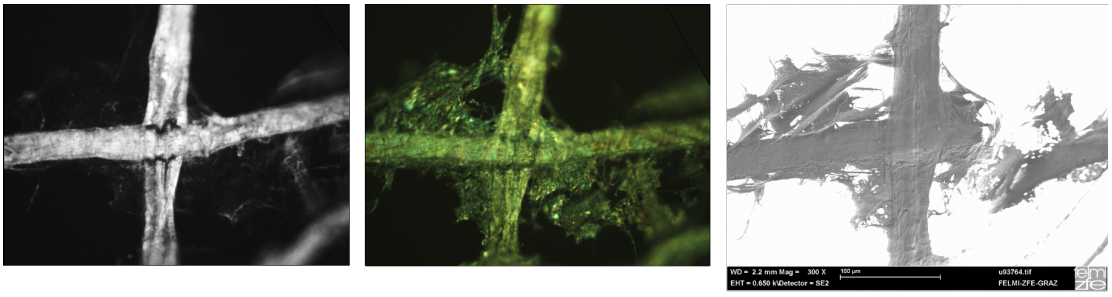


Figure 4.17 Appearance of joints at various refining levels and imaging techniques

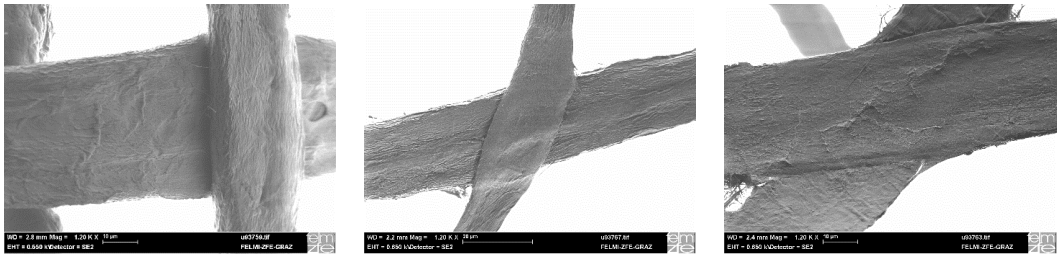
In case of non-refined samples, images using varying filters were not taken since the area was assumed to be free of delaminated cell walls and visible fibrillation. In case of refined joints (3000 PFI and 6000 PFI) however, there is additional bonding or reinforcing of the joints at the corners, which, due to their thickness is invisible to the PLM. To get better images in more detail about these web like structures, ESEM investigations were performed and an example of the images obtained can be seen below (Figure 4.18). When using the PLM, very little or no contact can be seen whereas the light microscopy using colour filters revealed web-like structures at the crossing. Even though the SEM cannot give information of the bonded area, rather just the surface information, the fact that this joint broke at a fibre rather than the bond gives ground to believe that the fibres were indeed bonded.



PLM Light microscopy SEM

Figure 4.18 Sulphite joint refined to 9000 PFI

Even though this is an extreme example of a sulphite joint refined to 9000 PFI revolutions, similar cases, though to a lesser could be observed for all the refined pulps. Figure 4.19 shows three joints of same pulp type (UBSK), non-refined and refined to 3000 and 6000 PFI. From the images, it can be clearly seen how the conformability of the fibres increases upon refining. In case of fibres refined to 6000 PFI or even 9000 PFI (image above) the fibres within a joint appear to fuse within each other, loosing those sharp fibre boundaries usually visible in non-refined joints or joints refined to a lower degree. Additionally, as observed during mechanical testing, such joints were more likely to have a more ductile failure than the unrefined ones.



(a) 0 PFI **(b)** 3000 PFI **(c)** 6000 PFI

Figure 4.19 Sulphite fibre to fibre joints under ESEM

With such joints, not only do we expect a larger area in contact or the bonded area but also a higher degree of bonding. Therefore, it does not come as a surprise that the breaking load of refined joints is higher than that of non-refined joints.

4.3.3 Refined joint strength

Calculated specific bonding strength (SBS) or joint strength (Table 4.31) of tested samples were calculated using the breaking load values and the OBA values.

The slight increase in SBS is attributed to the size and possible underestimations of the bonded area, as well as the higher degree of contact of the more flexible fibres.

Table 4.31 Strength of individual fibre to fibre joints refined to different levels (number in parenthesis represents standard deviation)

	joint strength [N/mm^2]	
rev. PFI	UBSK	BSS
0	3.10 (1.78)*	4.51 (2.92)
3000	5.21 (2.29)	4.18 (2.55)
6000	4.21 (2.01)	-
9000	4.41 (2.29)	4.65 (2.79)
*.... Fischer (2013)		

Unfortunately, none of the values for either tested group (UBHK and BSS) were statistically different from each other. Similar joint strength development was observed by Mayhood et al. (1962) who tested unbeaten, mildly beaten and heavy beaten sulphite and kraft pulps. Even though the increase in strength was only significant on a 10% level of significance, they concluded that severe chemical and mechanical treatment of pulps might cause increase in bond strength. Magnusson et al. (2013) tested unbleached kraft pulps and observed that for a pulp beaten with high-energy input, the joint strength doubles upon refining. The increase in strength was attributed the increase in external fibrillation of the fibres.

4.3.4 Individual fibre tensile testing

The analysis of the success rate of individual fibre tensile testing is given in Table 4.32. In majority of the cases, a higher success rate was observed, presumably due to rigorous selection criteria.

Table 4.32 Success rate of individual fibre tensile tests (number in parenthesis represents the total sample number)

	number of successful tests	
rev. PFI	UBSK	BSS
0	4 (16)	11 (22)
3000	10 (10)	9 (10)
6000	8 (12)	7 (10)
9000	10 (10)	11 (12)

Prior to testing, all the fibres were examined under a light microscope using various polarisation and light filters. In this manner, the fibre containing twist or severe external delamination were excluded. It is clear that such exclusion criteria played in favour of testing only one type of refined fibres but considering that it played a significant role in diminishing the standard deviation of the tested sample, it seemed as an acceptable drawback.

4.3.5 Breaking load of refined fibres

Breaking load of the tested kraft and sulphite fibres is shown in Table 4.33. Before discussing the individual breaking load values, it should be noted that in case of fibres refined to 9000 rev PFI, only the strongest fibres could be tested. If the previous assumptions regarding the random fibre choice resulted in predominantly summerwood fibres being tested, the favouring of one specific fibre type might be even more pronounced in cases where refined fibres were used.

Table 4.33 Breaking load of fibres refined to different levels (number in parenthesis represents standard deviation)

	breaking load [mN]	
rev. PFI	UBSK	BSS
0	221.23 (110.32)	101.43 (62.01)
3000	165.0 (79.27)	138.28 (43.42)
6000	178.46 (69.94)	160.48 (42.61)
9000	179.34 (70.57)	106.71 (60.90)

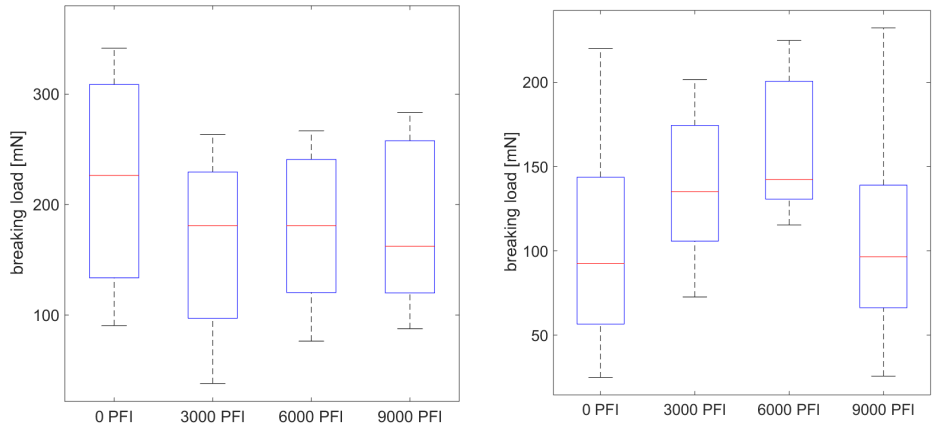
Table 4.34 t-test analysis of refined fibres

UBSK	α	p-value
0 - 3000 PFI	0.05	0.3017
0 - 6000 PFI	0.05	0.4258
0 - 9000 PFI	0.05	0.4066
3000 - 6000 PFI	0.05	0.7114
6000 - 9000 PFI	0.05	0.9794

BSS	α	p-value
0 - 3000 PFI	0.05	0.1500
0 - 6000 PFI	0.05	0.0429
0 - 9000 PFI	0.05	0.8423
3000 - 6000 PFI	0.05	0.3239
6000 - 9000 PFI	0.05	0.0592

Softwood kraft pulps (UBSK) show a decrease in breaking load with advancing refining degree. Even though the differences in the breaking loads seem to be substantial, a t-test with a confidence level of 95% showed no statistically significant differences (see Table 4.34) . In case of the sulphite (BSS) pulp however, the fibres showed an increase in the breaking load with the exception of the highest refining degree of 9000 PFI. At this point, it was extremely hard to even find fibres with sufficient length to be tested. A t-test (confidence level α= 0.05) has revealed statistically significant difference between the non-refined pulp samples and samples refined to 6000 PFI (p-0.0429). Figure 4.20 shows the distribution of the breaking load values for the two pulps (UBSK and BSS). In case of kraft pulp, a decrease in the CV can be observed with the advancing refining degree. This could be attributed to the fact that upon refining, one type of fibres tends to go through refining and still managed to keep the sufficient testing length. Watson and Dadswell (as cited in McIntosh (1968)) state that due to their more rigid nature, summerwood fibres are damaged more during refining than the springwood fibres. This could mean that in case of

the refined fibres, more springwood fibres than summerwood fibres were tested. In case of sulphite fibres, again the opposite trend is visible with the CV increasing with the refining intensity. If the aforementioned assumption is valid, that predominantly one type of refined fibres is being tested, the standard deviation and the CV should decrease. A possible explanation for this behavior could be attributed to the various extent of damage to the fibre walls. Sulphite fibres are weaker and when undergoing severe mechanical treatment, they are more likely to suffer more extensive damage than the kraft fibres. Furthermore, not all fibres will be refined to the same extent, and this, alongside the aforementioned might explain why the value scatter is more pronounced in case of refined fibres.



(a) UBSK **(b)** BSS

Figure 4.20 Breaking load distribution of kraft and sulphite fibres upon refining

4.3.6 Cross sectional area of refined fibres

After tensile testing, the fibres were cut with the microtome and the analysed cross sectional areas of the fibres are given in Table 4.35.

Table 4.35 Cross sectional area of fibres refined to different levels (number in parenthesis represents standard deviation)

	A_{cross} [μm^2]	
rev. PFI	UBSK	BSS
0	271.29 (41.00)	232.50 (77.82)
3000	225.62 (60.72)	266.64 (63.18)
6000	201.23 (63.24)	236.16 (86.58)
9000	271.29 (84.36)	200.50 (106.51)

With kraft pulp, a decrease in the cross sectional area is observed upon refining, with the exception of the fibres refined to 9000 PFI. The explanation for this was already provided in the previous chapter, stating that there is a possibility that only the strongest and biggest fibres were tested. In case of a sulphite pulp, it is probable that the random selection of fibres resulted in only the largest ones to be tested.

4.3.7 Strength of refined fibres

Contrary to expected, the results of the fibre strength calculations do not show any recognisable trends (Table 4.36). In case of kraft fibres (UBSK) the highest strength was obtained in case of fibres refined to 6000 PFI, although this difference was not statistically significant in comparison to the other values (Table 4.37). This increase in case of kraft pulps is attributed to a decrease in the fibre cross sectional area rather than the breaking load.

Table 4.36 Strength of fibres refined to different levels (number in parenthesis represents standard deviation)

	Fibre strength [N/mm^2]	
rev. PFI	UBSK	BSS
0	801.95 (333.68)	454.59 (217.63)
3000	709.74 (278.07)	535.26 (125.39)
6000	890.37 (194.44)	727.91 (204.65)
9000	731.17 (370.52)	542.54 (196.98)

Table 4.37 t-test analysis of refined fibre strength

UBSK	α	p-value
0 - 3000 PFI	0.05	0.5791
0 - 6000 PFI	0.05	0.5682
0 - 9000 PFI	0.05	0.07465
3000 - 6000 PFI	0.05	0.1134
6000 - 9000 PFI	0.05	0.2893

BSS	α	p-value
0 - 3000 PFI	0.05	0.3785
0 - 6000 PFI	0.05	0.0197
0 - 9000 PFI	0.05	0.3374
3000 - 6000 PFI	0.05	0.0548
6000 - 9000 PFI	0.05	0.0692

In case of sulphite pulps, the highest fibre strength was obtained in case of the fibres refined to 6000 rev. PFI. A t-test (confidence level α 0.05) confirmed that this difference is statistically significant (p-value 0.0197). Similar increase in fibre strength (up to a certain point) was observed by Alexander et al. (1968), McIntosh (1968) and Leopold (1966) (as cited by McIntosh (1968)). The increase in fibre strength was attributed to a better stress distribution. It was believed that the fibrils in the fibre, upon refining, loosen up and upon subsequent drying, come into a closer contact with each other. This reorganisation and consolidation of the cell wall reduced the size of the cross sectional area while at the same time, helped to redistribute the stresses more

evenly. In case of this study, the highest strengths were obtained at 6000 rev. PFI, which, for all standard purposes is already a high refining degree. A direct comparison with previous studies was not possible since different refining degrees, refining equipment and different materials have been used. However, the values obtained in this study are in good agreement with the previous ones stating that mechanical treatment (up to a certain extent) has a positive impact on fibre strength. Swelling, opening of the pores and the cell wall delamination, normally associated with refining, appear to results in a higher cohesiveness of the cell walls and reorganisation of the fibrils in one direction. However, these statements could not have been confirmed. Whne it comes to the extent of delamination or the loss of S1 layer, microscope investigations used in this study only allowed for identification of heavily delaminated fibres (i.e. a portion of a cell wall was missing) but subtle changes on the surface or the absence of the aforementioned layer could not be positively identified.

Chapter 5

Conclusion and Outlook

The guiding principle of every study dealing with investigations of individual fibres and fibre to fibre joints is the desire to understand the properties and the behaviour of paper. In this study, the breaking loads and strength of individual fibres and fibre to fibre joints depending on the type of pulp, environmental conditions and the degree of refining have been presented.

When comparing the breaking loads of different pulps, the breaking load of joints appears to be influenced by the size of the bonded area rather than the cooking process. BHK (hardwood kraft pulp) exhibit the lowest breaking loads (1.82 mN), followed by BSS (softwood sulphite pulp, 4.72 mN) and UBSK (softwood kraft pulp, 6.58 mN). When normalising the breaking load with the OBA, BHK (hardwood joints) exhibit the highest joints strength (5.32 MPa), followed by the BSS (softwood sulphite pulps, 4.51 MPa) and lastly, UBSK (softwood kraft pulp, 3.10 MPa). Since it was not possible to obtain pulps prior and after the bleaching process, the effect of bleaching on joints strength could not be investigated. The breaking load of individual fibres exhibited the same trends as the breaking loads of joints and in this case, the size of the fibres and the cooking process play a pivotal role. This effect can be especially seen when comparing strength values of different pulps. In this case, the kraft fibres, regardless of being hardwood or softwood, exhibited strengths in a similar order of magnitude (800-1100 MPa) while the sulphite fibres were roughly 50% weaker. These findings are in good agreement with previous studies focused on differences between sulphite and kraft fibres (Leopold and Thorpe, 1968) stating that the lower breaking loads in case of sulphite pulps are attributed to the cooking process which degrades the fibres to a greater extent than the kraft process.

When exposed to different relative humidity, both fibres and joints exhibit the maximum of breaking load at 50% RH, with decrease when approaching either end of the RH scale. The values obtained in case of fibres tested at varying RH are in good agreement when compared to the study of Kersavage (1973). The decrease in breaking load at lower RH is attributed to the embrittlement of the fibres and an amplified effect of naturally existing cell wall defects, whereas the same reduction observed at 80% RH is attributed to the softening of the cell wall and possible slippage of cellulosic chains. Since it was not possible to determine the cross sectional area of the fibres tested at 30 and 80% RH, fibre strength could not be calculated. However, if we assume that the amount of the load bearing components stays the same and only the stress distribution changes, any reduction would not be visible in the final value, i.e. stress but rather the shape of the stress/strain curves. In case of joints, no comparison of validation with previous studies was possible but some insight into behaviour of joints could be obtained by considering the effects that govern the RH response in fibres. The changes in the fibre dimensions and mechanical properties during exposure to high or low RH influence the shape and size of the bond. The dried in stresses present at 50% RH would increase during exposure to low RH, and reduce during exposure to high humidity. A combination of the changes in the dried in stresses, changes in the shape and size of bond, and partial failure prior to testing, would ultimately cause a reduction in breaking load. Similar as in the case of individual fibres, the size of the bonded area could not be measured in the set humidity and strength calculations were therefore not possible. When considering the behaviour of fibres and joints in different RH, one must bear in mind that the results presented here only refer to the used testing procedure and that different results could have been obtained if the fibres had been conditioned in an unrestrained state.

In case of refining, the maximum strength was obtained with fibres refined to 6000 PFI rev. Considering that an increase in the cross sectional area could be observed, this conclusion raises some questions as to how reliable these results actually are. Same as in case of any other tensile test that has been conducted; the selection of fibres was random and, as long as the fibre did not suffer extensive delamination, it was considered acceptable for testing. Since refining to such high degree as 9000 PFI revolustions is bound to cause damage to the fibre, it might be possible that only the strongest, and/or fibres that underwent refining process without being refined, were tested. Since there is no known method to determine the extent of refining on an individual fibre, the results obtained during this study should be regarded with a certain amount of scepticism. In case of individual fibre to fibre joints, constant increase in joints strength with refining degree can be observed. Undoubtedly, such increase is attributed to the higher flexibility of the fibres and the consequent increase in the bonded area. Even more interesting, refined fibres which exhibited external fibrillation or partial cell wall delamination appeared to adhere to the fibre in greater

vicinity, rather than the original fibre. The adhering fibrils tended to form somewhat of a web like structure, which was visible in ESEM micrographs. Such joints not only formed stronger joints, but also exhibited more ductile failure that the unrefined joints. The strength development is in accordance with the studies of Mayhood et al. (1962), who also observed an increase in joint strength but no statistically significant difference. Due to relatively large refining degree increment used in this study, it is possible that higher strength development might be present in one of the intermediate refining levels.

Outlook

When dealing with natural materials such as pulp fibres, one can never obtain a definite asnwer to the question - What governs the strength of fibres in given conditions. The complexity of the testing and the amount of time needed to obtain values by direct testing result in a small number of samples being tested. The evaluation and interpretation is further hindered by large standard deviations. To get more conclusive answers, the deviation should be excluded by employing as many determination factors as possible. Some of the factors that could reduce the large variations would be the usage of the exactly the same testing conditions, procedures and parametres for all tests. In case of joint testing, the interplay of different modes of loading should be excluded by gluing the free ends of the fibres as close to the joint as possbile. Careful preselection of fibres based on the type of fibres (earlywood/latewood) and possible usage of fibres with known microfribril angle is another factor that could decrease the variation in the obtained values. In case of refined fibres, a method of determining the extent of reifning on a single fibre level would be beneficial. With such method at hand, it might be possible to classify the fibres based on the introduced and natural defects and gain a better understanding of how the strength and E-modulus change due to refining.

Nevertheless, the most important factor would be the number of samples. A setup capable of faster testing with a high success rate and reliability would offer a larger database and better statistics. Furthermore, values obtained by such tests would provide a solid platform for future numerical modelling.

Appendix A

Table A.1 UBSK fibres (0 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	VTT-1	267.894	-	-
2	VTT-2	188.833	-	-
3	VTT-3	420.706	-	-
4	VTT-4	151.229	-	-
5	VTT-5	102.833	-	-
6	VTT-6	150.283	-	-
7	VTT-7	-	405.858	-
8	VTT-8	275.837	263.720	1045.948
9	VTT-9	125.615	-	-
10	VTT-10	561.703	-	-
11	VTT-11	341.567	326.680	1045.570
12	VTT-12	319.771	-	-
13	VTT-13	310.278	-	-
14	VTT-14	-	-	-
15	VTT-15	90.475	267.077	338.759
16	VTT-16	177.036	227.695	777.518
mean		248.861	298.206	801.949
stand. dev		134.593	69.875	524.538
no outliers				

Table A.2 UBSK fibres (3000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	M-3-1	263.589	281.381	936.772
2	M-3-2	97.103	144.350	672.697
3	M-3-3	169.699	207.007	819.774
4	M-3-4	38.008	118.226	322.118
5	M-3-5	52.753	258.778	203.858
6	M-3-6	226.301	245.145	923.211
7	M-3-7	232.474	275.599	843.523
8	M-3-8	229.488	284.502	806.634
9	M-3-9	148.255	175.379	845.344
10	M-3-10	192.295	265.805	723.447
mean		165.004	225.615	7090.738
stand. dev		79.270	60.716	278.070
no outliers				

Table A.3 UBSK fibres (6000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	M-6-1	143.717	-	-
2	M-6-2	204.315	251.352	812.149
3	M-6-3	247.750	234.207	1057.826
4	M-6-4	132.915	248.845	534.128
5	M-6-5	76.387	79.063	966.153
6	M-6-6	266.728	229.210	1163.683
7	M-6-7	157.853	183.882	858.449
8	M-6-8	107.895	141.382	763.145
9	M-6-9	234.049	241.926	967.439
10	M-6-10	121.835	-	-
mean		169.326	201.233	890.371
stand. dev		64.823	62.236	194.443
no outliers				

Table A.4 UBSK fibres (9000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	MR-2	93.387	156.605	596.321
2	MR-3	87.693	378.311	231.800
3	MR-4	257.272	180.099	1431.085
4	MR-6	205.272	320.882	639.714
5	MR-8	262.184	230.732	1136.312
6	MR-9	283.381	292.651	968.322
7	MR-10	119.987	412.600	290.808
8	MR-11	159.445	296.265	538.183
9	MR-12	158.999	246.723	644.444
10	MR-13	165.304	198.043	834.690
mean		179.339	271.291	731.168
stand. dev		70.571	84.356	370.522
no outliers				

Table A.5 UBSK fibres tested at 30% RH with pretension

Nr.	sample	breaking load [mN]
1	T-6	180.034
2	T-7	61.792
3	T-9	146.906
4	T-11	197.201
5	T-12	146.001
6	T-13	102.734
7	T-20	171.405
8	T-21	141.003
9	T-22	75.072$*$
mean		143.385
stand. dev		46.781
$*$ .... excluded due to twist		
no outliers		

Table A.6 UBSK fibres tested at 30% RH without pretension

Nr.	sample	breaking load [mN]
1	101	256.497
2	102	141.130
3	103	128.242
4	104	320.826
5	105	86.018
6	106	301.219
7	107	306.305
8	108	131.376
9	109	73.620
10	110	121.986
mean		186.722
stand. dev		97.723
no outliers		

Table A.7 UBSK fibres tested at 80% RH

Nr.	sample	breaking load [mN]
1	T-1	206.308∗
2	T-2	226.830
3	T-4	266.999∗
4	T-5	274.260
5	T-8	166.506
6	T-10	89.998
7	T-15	302.305
8	T-16	97.478
9	T-17	182.357
10	T-18	118.422
11	T-19	287.566
mean		193.969
stand. dev		82.720
∗ .... excluded due to twist		
∗ ∗ .... pulled out of the glue		
no outliers		

Table A.8 UBSK joints (3000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	M-1-3000	10.811	4293.400	2.518
2	M-2-3000	3.704	1523.700	2.431
3	M-3-3000	8.452	1015.800	8.320
4	M-4-3000	-	1187.100	-
5	M-5-3000	-	1598.200	-
6	M-6-3000	5.716	964.824	5.925
7	M-7-3000	7.859	1916.900	4.100
8	M-8-3000	10.696	1346.700	7.942
mean		7.873	1730.828	3.905
stand. dev		2.792	1082.531	2.785
no outliers				

Table A.9 UBSK joints (6000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	M-601	-	2117.600	-
2	M-602	5.783	3711.400	1.558
3	M-603	8.260	2649.200	3.118
4	M-604	5.976	1688.400	3.539
5	M-605	8.733	2188.600	3.990
6	M-606	6.339	2021.500	3.136
7	M-607	13.080	1739.500	7.519
8	M-608	9.398	1851.800	5.075
7	M-609	14.661	2555.100	5.738
8	M-610	4.359	-	-
mean		8.510	2280.344	4.209
stand. dev		3.454	631.262	2.011
no outliers				

Table A.10 UBSK joints (9000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	RDUKP-1	17.519	2384.900	7.346
2	RDUKP-2	9.041	3842.700	2.353
3	RDUKP-3	6.976	-	-
4	RDUKP-4	7.261	-	-
5	RDUKP-5	14.181	-	-
6	RDUKP-6	8.849	1083.900	8.164
7	RDUKP-7	2.831	-	-
8	RDUKP-8	3.688	-	-
9	RDUKP-9	4.783	-	-
10	RDUKP-10	1.721	-	-
11	RDUKP-11	-	1608.100	-
12	RDUKP-12	-	1308.600	-
13	RDUKP-13	2.770	-	-
14	RDUKP-14	3.992	1665.400	2.397
15	RDUKP-15	5.470	-	
16	RDUKP-16	8.836	1658.300	5.328
17	RDUKP-17	-	-	-
18	RDUKP-18	4.166	985.892	4.226
19	RDUKP-19	4.869	1409.800	3.454
20	RDUKP-20	8.096	2651.000	3.054
21	RDUKP-21	4.121	1400.300	2.943
22	RDUKP-22	4.596	2542.600	1.807
23	RDUKP-23	8.637	-	-
24	RDUKP-24	13.735	1853.100	7.412
mean		6.959	1876.507	4.408
stand. dev		4.120	791.686	2.293
no outliers				

Table A.11 UBSK joints tested at 30% RH

Nr.	sample	breaking load [mN]
1	1	6.288
2	2	1.772
3	3	3.321
4	5	2.262
5	6	3.484
6	7	4.174
7	8	4.180
8	9	10.464
9	10	2.527
mean		193.969
stand. dev		82.720
no outliers		

Table A.12 UBSK joints tested at 80% RH

Nr.	sample	breaking load [mN]		
exposure time		2 hrs	4 hrs	8 hrs
1	-	1.074	2.351	3.541
2	-	4.605	6.536	1.031
3	-	1.669	4.862	3.205
4	-	2.274	2.339	2.759
5	-	3.889	9.077	4.671
6	-	2.251	4.703	4.431
7	-	3.577	2.321	1.539
8	-	3.378	4.495	2.895
9	-	5.339	1.820	2.173
10	-	3.105	3.738	5.904
mean		3.119	4.275	3.215
stand. dev		1.320	2.273	1.487
no outliers				

Table A.13 BSS fibres (0 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	S-1	53.420	-	-
2	S-2	60.328	-	-
3	S-3	56.578	-	-
4	S-4	64.270	-	-
5	S-5	240.994	-	-
6	S-6	70.510	-	-
7	S-7	38.716	-	-
8	S-8	102.574	-	-
9	S-9	63.104	-	-
10	S-10	24.898	101.097	246.282
11	S-11	189.677	346.314	547.704
12	S-12	68.516	355.247	192.868
13	S-13	92.546	198.366	466.544
14	S-15	157.911	195.828	806.376
15	S-16	51.079	-	-
16	S-17	220.056	287.470	765.494
17	S-19	101.026	190.662	529.869
18	S-20	55.213	209.498	263.548
19	S-21	94.148	196.690	478.661
20	S-22	60.628	243.848	248.629
mean		93.310	232.502	454.597
stand. dev		60.855	217.634	217.634
no outliers				

Table A.14 BSS fibres (3000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	S-1-3000	194.455	244.950	793.857
2	S-2-3000	135.044	219.600	614.956
3	S-3-3000	142.903	287.716	496.680
4	S-4-3000	167.770	292.336	573.895
5	S-5-3000	108.178	158.158	683.991
6	S-6-3000	123.303	308.289	399.958
7	S-7-3000	201.671	362.658	556.090
8	S-8-3000	98.634	211.051	467.348
9	S-9-3000	72.642	315.024	230.591
mean		138.289	266.642	535.263
stand. dev		43.425	63.188	125.399
no outliers				

Table A.15 BSS fibres (6000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	S-6-1	142.264	170.581	833.944
2	S-6-2	115.386	197.582	583.994
3	S-6-3	163.420	219.185	745.581
4	S-6-4	213.035	257.603	826.990
5	S-6-5	140.975	-	-
6	S-6-6	224.836	251.982	892.271
7	S-6-7	130.431	-	-
8	S-6-8	129.216	146.426	882.465
9	S-6-9	135.236	409.755	330.041
10	S-6-10	192.490	-	-
mean		158.729	236.159	727.905
stand. dev		38.253	86.578	204.653
no outliers				

Table A.16 BSS fibres (9000 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [μm^2]	strength [N/mm^2]
1	S-9-1	63.825	108.539	588.039
2	S-9-2	104.409	134.771	774.713
3	S-9-3	181.252	261.146	694.065
4	S-9-4	153.054	-	-
5	S-9-5	41.313	92.656	445.874
6	S-9-6	25.677	108.770	236.063
7	S-9-7	147.596	264.344	558.346
8	S-9-8	232.288	276.491	840.127
9	S-9-9	96.521	213.803	451.446
10	S-9-10	73.526	141.675	518.980
11	S-9-11	113.137	448.287	252.376
12	S-9-12	94.246	155.036	607.897
mean		110.570	200.502	542.539
stand. dev		59.587	106.515	196.978
no outliers				

Table A.17 BSS fibres at 30% RH

Nr.	sample	breaking load [mN]
1	TT-1	-
2	TT-2	63.281
3	TT-3	81.090
4	TT-4	54.970
5	TT-5	91.982
6	TT-6	138.755
7	TT-8	143.955
8	TT-9	247.593$*$
9	TT-10	47.340
10	TT-11	66.758
mean		86.016
stand. dev		36.928
$*$ not included		
TT-9 value is an outlier		

Table A.18 BSS fibres at 80% RH

Nr.	sample	breaking load [mN]
1	TT-1	204.464∗
2	TT-2	23.522
3	TT-3	53.055
4	TT-4	41.718
5	TT-5	50.397
6	TT-6	280.561
7	TT-7	121.689
8	TT-8	112.320
9	TT-9	38.988
mean		63.098
stand. dev		38.128

∗ twisted fibre, excluded
TT-6 value is an outlier

Table A.19 BSS joints (0 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	DBNSP-1	2.522	2155.900	1.170
2	DBNSP-2	3.290	1212.600	2.713
3	DBNSP-3	0.797	1260.200	0.632
4	DBNSP-4	5.936	1020.000	5.819
5	DBNSP-5	10.629	1092.300	9.731
6	DBNSP-6	4.356	902.470	4.827
7	DBNSP-7	-	933.579	-
8	DBNSP-8	5.685	543.643	10.457
9	DBNSP-9	5.770	1797.200	3.210
10	DBNSP-10	6.034	2318.400	2.603
11	DBNSP-11	-	2325.400	-
12	DBNSP-12	4.061	888.093	4.573
13	DBNSP-13	-	2831.100	-
14	DBNSP-14	3.981	1482.800	2.685
15	DBNSP-15$*$	-	1485.800	-
16	DBNSP-16	4.213	1073.800	3.924
17	DBNSP-17	-	2099.100	-
18	DBNSP-18	8.480	1885.500	4.497
19	DBNSP-19	2.719	-	-
20	DBNSP-21	1.688	-	-
mean		4.727	1517.105	4.513
stand. dev		2.640	633.825	2.924
mode III loading - excluded no outliers				

Table A.20 BSS joints (3000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	S-3000-1	4.660	1400.200	3.328
2	S-3000-2	4.055	1018.000	3.984
3	S-3000-3	4.723	3581.900	1.319
4	S-3000-4	-	1730.600	-
5	S-3000-5	1.943	782.031	2.473
6	S-3000-6	16.775	3617.300	4.683
7	S-3000-7	14.494	1550.700	9.347
8	S-3000-8	2.291	-	-
mean		6.991	1954.390	4.181
stand. dev		6.040	1168.010	2.548
no outliers				

Table A.21 BSS joints (6000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	S-6000-1	6.197	-	-
2	S-6000-2	5.180	-	-
3	S-6000-3	4.705	-	-
4	S-6000-6	9.609	-	-
5	S-6000-7	5.434	-	-
6	S-6000-8	-	1853.100	-
7	S-6000-9	-	-	-
8	S-6000-10	-	1083.900	-
mean		6.225	1468.500	-
stand. dev		1.967	543.907	-
no outliers				

Table A.22 BSS joints (9000 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	SDR-1	5.004	772.857	6.475
2	SDR-2	-	-	-
3	SDR-3	13.703	4106.400	3.337
4	SDR-4	3.817	3560.100	1.072
5	SDR-5	-	1940.100	-
6	SDR-6	16.523	1412.500	11.697
7	SDR-7	2.464	1561.700	1.578
8	SDR-8	-	564.317	-
9	SDR-9	6.418	1352.100	4.747
10	SDR-10	-	1342.700	-
11	SDR-11	8.293	1812.500	4.575
12	SDR-12	6.700	1610.000	4.161
13	SDR-13	8.441	1093.600	7.718
14	SDR-14	7.945	3273.900	2.429
15	SDR-15	17.278	2508.800	6.887
16	SDR-16	3.728	1192.500	3.126
17	SDR-17	6.484	1555.800	4.168
18	SDR-18	4.927	1602.000	3.076
19	SDR-19	4.669	-	-
20	SDR-20	4.707	-	-
mean		7.569	1838.934	4.646
stand. dev		4.486	977.492	2.796
no outliers				

Table A.23 BSS joints at 30% RH

Nr.	sample	breaking load [mN]
1	JS-1	5.439
2	JS-2	1.826
3	JS-3	3.715
4	JS-4	1.901
5	JS-5	7.866
mean		4.150
stand. dev		2.555
no outliers		

Table A.24 BSS joints at 80% RH

Nr.	sample	breaking load [mN]
1	J-1	10.681∗
2	J-2	4.265
3	J-3	3.842
4	J-4	2.306
5	J-5	1.480
6	J-6	3.154
7	J-7	2.888
mean		2.890
stand. dev		1.054
∗ J-1 value is an outlier		

Table A.25 BHK fibres (0 PFI)

Nr.	sample	breaking load [mN]	cross sectional area [N/m m^2]	strength [N/mm^2]
1	TT4	48.322	35.12	1375.904
2	TT5	32.937	35.12	937.830
3	TT8	23.593	35.12	671.777
4	TT9	36.112	35.12	1028.258
5	TT20	28.836	35.12	821.075
6	TT14	42.503	35.12	1210.229
7	TT15	24.872	35.12	708.188
8	TT17	73.306	35.12	2087.313
mean		38.810	35.12	1105.072
stand. dev		16.306	-	464.295
no outliers				

Table A.26 BHK fibres at 30% RH

Nr.	sample	breaking load [mN]
1	T-2	45.040
2	T-4	33.559
3	T-5	8.999
4	T-7	23.991
5	T-8	17.314
6	T-9	11.422
7	T-10	27.727
8	T-15	24.357
mean		24.051
stand. dev		11.808
no outliers		

Table A.27 BHK fibres at 80% RH

Nr.	sample	breaking load [mN]
1	T-17	21.304
2	T-19	33.559
3	T-20	5.464
4	T-21	47.721
5	T-22	20.024
6	T-23	36.271
mean		27.397
stand. dev		14.851
no outliers		

Table A.28 BHK joints 0 PFI)

Nr.	sample	breaking load [mN]	OBA [μm^2]	strength [N/mm^2]
1	H1	2.002	-	-
2	H2	3.002	-	-
3	H3	1.999	-	-
4	H4	1.041	91.750	11.343$*$
5	H11	2.211	809.907$*$	2.730
6	H15	1.847	-	-
7	H17	1.609	-	-
8	H18	1.594	240.501	6.627
9	H20	1.371	-	-
10	H21	1.841	-	-
11	H24	1.352	-	-
12	H28	1.669	-	-
13	H34	2.446	-	-
14	H37	1.568	396.406	3.956
15	H38	2.309	368.900	6.258
16	H39	1.621	260.495	6.222
17	H48	1.377	392.092	3.512
mean		1.815	291.691	5.315
stand. dev		0.480	118.808	1.461
$*$ outlier, excluded				

Table A.29 BHK joints at 30% RH

Nr.	sample	breaking load [mN]
1	H-1	1.061
2	H-2	0.985
3	H-3	0.872
4	H-4	3.126
5	H-5	2.914
6	H-6	3.129
7	H-7	1.905
mean		1.999
stand. dev		1.046
no outliers		

Table A.30 BHK joints at 80% RH

Nr.	sample	breaking load [mN]
1	H2	1.543
2	H3	0.365
3	H4	0.962
4	H7	2.780
5	H8	1.160
6	H9	3.162
7	H10	1.432
8	H13	2.117
mean		1.690
stand. dev		0.941
no outliers		

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