Pulp and Paper Chemistry and Technology Volume 3 Paper Chemistry and Technology

Edited by Monica Ek, Göran Gellerstedt, Gunnar Henriksson

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Paper Chemistry and Technology

Edited by Monica Ek, Göran Gellerstedt, Gunnar Henriksson

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Foreword

The production of pulp and paper is of major importance in Sweden and the forestry industry has a profound influence on the economy of the country. The technical development of the industry and its ability to compete globally is closely connected with the combination of high-class education, research and development that has taken place at universities, institutes and industry over many years. In many cases, Swedish companies have been regarded as the initiator of new technology which has started here and successively found a general world-wide acceptance. This leadership in knowledge and technology must continue and be developed around the globe in order for the pulp and paper industry to compete with high value-added forestry products adopted to a modern sustainable society.

The production of forestry products is based on a complex chain of knowledge in which the biological material wood with all its natural variability is converted into a variety of fibre-based products, each one with its detailed and specific quality requirements. In order to make such products, knowledge about the starting material, as well as the processes and products including the market demands must constitute an integrated base. The possibilities of satisfying the demand of knowledge requirements from the industry are intimately associated with the ability of the universities to attract students and to provide them with a modern and progressive education of high quality.

In 2000, a generous grant was awarded the Department of Fibre and Polymer Technology at KTH Royal Institute of Technology from the Ljungberg Foundation (Stiftelsen Erik Johan Ljungbergs Utbildningsfond), located at StoraEnso in Falun. A major share of the grant was devoted to the development of a series of modern books covering the whole knowledge-chain from tree to paper and converted products. This challenge has been accomplished as a national four-year project involving a total of 30 authors from universities, Innventia and industry and resulting in a four volume set covering wood chemistry and biotechnology, pulping and paper chemistry and paper physics. The target reader is a graduate level university student or researcher in chemistry / renewable resources / biotechnology with no prior knowledge in the fields of pulp and paper. For the benefit of pulp and paper engineers and other people with an interest in this fascinating industry, we hope that the availability of this material as printed books will provide an understanding of all the fundamentals involved in pulp and paper-making.

For continuous and encouraging support during the course of this project, we are much indebted to Yngve Stade, Sr Ex Vice President StoraEnso, and to Börje Steen and Jan Moritz, Stiftelsen Erik Johan Ljungbergs Utbildningsfond.

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1 Structure of the Fibre Wall

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1.1 Background

When the structure and the swelling of the cell wall of the fibres are discussed, there is often a focus on how the water is accommodated in the fibre wall. The water in the cell wall is usually divided into water in a gel phase and water in voids in the fibre wall. However, some authors also claim that the concept of the fibre wall as a gel is an unnecessary exercise, since most of the effects achieved by changing the chemical environment around the fibres can be explained by a swollen surface layer of the fibres, see e.g. Pelton (1993). Without entering this debate, it is a fact that the discussion about how the water is accommodated in the fibre wall is very dependent on the structure of the wall and how this fibre wall is changed by different process conditions. Therefore it is necessary to start by discussing the current understanding of the structure of the fibre wall and how it is changed upon for example lignin and hemicellulose removal.

1.1.1 Current Understanding of the Structure of the Fibre Wall

Our current understanding of the structure of the cell wall of papermaking fibres is dominated by the work of Stone and Scallan, see e.g. Lindström (1986), and their work will therefore be reviewed in some detail. In an early paper, Stone and Scallan (1965a) introduced the concept of the multilamellar structure of the fibre wall with the lamellae arranged concentrically with the cell wall axis. The number of lamellae was dependent on the degree of swelling and upon drying the lamellae join together. According to their measurements, the water-swollen cell wall consisted of several hundred lamellae each less than 100 Å thick and separated by an average distance of about 35 Å. These results were obtained through nitrogen gas adsorption and the lamellar structure was "visualised" through a methacrylate embedding followed by scanning electron microscope analysis. This latter technique results in an unnatural swelling of the fibre wall and the results can at best be used for qualitative discussions. The nitrogen gas adsorption, however, is very accurate and these results also showed that the saturation point of the cell wall was 0.3 cm³/g.

The basis behind the nitrogen adsorption method is an adsorption isotherm of nitrogen onto the fibres (Haselton 1954). The fibres are exposed to an increasing concentration, i.e increasing pressure, of N_2 gas and the amount of nitrogen adsorbed onto the fibres is determined at the different N_2 pressures. Up to a monolayer coverage of nitrogen on the fibres the adsorption can be described by the BET equation, i.e. equation (1.1).

$$p / v(p_0 - p) = 1 / v_m c + [(c - 1) / v_m c] \cdot p / p_0$$
(1.1)

where

p = Pressure in mm Hg of the gas at a certain temperature $p_0 =$ Vapour pressure of the pure gas at the same temperature v = Volume of adsorbed gas in ml (STP) $v_m =$ Volume of the gas in ml (STP) to form a monolayer c = Constant

By applying this equation to the adsorption of nitrogen onto the fibres the volume of gas needed to form a monolayer, v_m , on the fibres can be determined and by using this entity and the size of the molecules the specific surface area of the fibres can be determined according to equation (1.2).

Area =
$$\frac{N v_m L}{22,400 \cdot 10^{20}} \text{ m}^2/\text{g}$$
 (1.2)

where

N = Avogadros number

 v_m = Volume of the gas in ml (STP) to form a monolayer (ml/g adsorbent)

L = Molecular crossectional area in Ångström²

A combination of the specific surface area of the fibres and the specific volume of the material in the fibre wall the thickness of lamellae in the fibre wall can then be calculated from equation (1.3) by assuming a cylindrical lamellae arrangement in the fibre wall

$$t = \frac{2V}{A} \tag{1.3}$$

where

V = Specific volume of the material in the fibre wall

- A = Specific surface area of the fibre wall
- T = Thickness of the concentric lamellae in the fibre wall

For air dried chemically delignified fibres a specific surface area of $1 \text{ m}^2/\text{g}$ can usually be measured and assuming a specific volume of the material to be 0.63 cm³/g, equation (1.3) leads to a thickness of the lamellae of 1.28 µm whereas a similar calculation for a solvent exchanged fibre with a specific surface area of around $100 \text{ m}^2/\text{g}$ leads to a lamellae thickness of 128 µm.

From the adsorption of nitrogen on the fibres it is also possible to determine the total void volume inside side the fibre wall by performing the adsorption measurements at higher nitrogen pressures.

Stone and Scallan (1965b) also introduced a pulp preparation technique, where the wood chips could be delignified under extremely well controlled conditions and the first results with this technique were virtually the same as the earlier published results regarding the multilamellar structure of the fibre wall. They were also able to show that the specific surface area and the volume of voids in the fibre wall, from nitrogen gas adsorption, increased as the degree of delignification increased. The surface area increased from $13.3 \text{ m}^2/\text{g}$ at a yield of 95.4% for kraft pulps to $274 \text{ m}^2/\text{g}$ at a yield of 47.6%. Corresponding figures for the void volume in the fibre wall were 0.019 and 0.578 cm³/g.

By applying the same technique for delignification, Stone and Scallan (1967) prepared a number of kraft pulps with different yields and they then characterised these pulps with N_2 adsorption, pressure plate analysis and a method where they determined the non-solvent water in the fibre wall. In this latter technique, macromolecules with a molecular mass too high to allow for penetration into the fibre wall were used and by knowing the total amount of water in the system and the concentration of the macromolecules in the water phase, it was possible to determine the volume of the fibre wall inaccessible to the polymer. In the pressure plate technique, a water-saturated sample is subjected to an increasing air pressure and the volume of liquid remaining in the sample is measured at different pressures. From this it is then possible to estimate a total void volume of the fibre wall. The results of this comparison are summarised in *Table 1.1*.

Pulp yield (%)	Lignin (%)	Volume (cm³/g) from N ₂ ads.	Volume (cm³/g) from pressure plate	Volume (cm ³ /g) from non-solvent water
100	27.0	0.01	0.4	0.42
92.4	27.3	0.04	0.67	0.70
89.0	27.6	0.08	0.74	(0.66)
80.0	28.5	0.27	0.86	0.92
77.8	28.2	0.33	0.94	0.94
70.4	25.2	0.54	1.06	1.08
61.6	19.3	0.63	1.16	1.22
53.4	12.3	0.55	1.21	1.28
48.7	6.5	0.57	1.14	1.21

Table 1.1. Summary of the results from the void volume estimation of the fibre from laboratory prepared kraft pulps as detected by different methods. From Stone and Scallan (1967).

It can be seen in the table that there is a large difference in the void volumes as determined by the nitrogen gas adsorption and by the other techniques. From measurements on water-saturated samples, which had been subjected to different degrees of water removal before solvent exchange drying and analysis with N_2 adsorption, the authors concluded that the value obtained with the pressure plate method and the non-solvent water method was "correct". This term was then called the fibre saturation point (FSP) since it included water in the gel phase of the fibre wall and in the void volume of the fibre wall. When the yield of the pulp was decreased, the number of fibres/g increased and, in order to compensates for this, Stone and Scallan (1967) multiplied the FSP with the yield and were hence able to compare the water associated with the same number of fibres for the different yields. Assuming a density of the components in the fibre wall they were also able to calculate how the solid material decreased with decreasing yield. They also made a further division of the pores in the fibre wall into macro-pores, i.e. the pores that could be determined with nitrogen adsorption, and micro-pores, which were defined as the difference between the FSP-value and the nitrogen adsorption value. A representation of this is given in *Figure 1.1*.



Figure 1.1. The different volumetric changes in the fibre wall occurring when the degree of delignification is increased. The graph shows the volumetric changes from one gram of wood, i.e. the yield times the FSP-value, and the volume of solid is calculated from an assumed fibre wall material specific volume of 0.667 cm³/g. The macro-pore water is defined as the volume of N_2 adsorption and the micro-pore water is defined as the difference between the FSP-value and the macro-pore volume. From Stone and Scallan (1967) and the data are collected from experiments with a kraft pulp.

There is a small increase in the volume of the fibre wall at the beginning of the cook when the yield decreases but the fibre wall thickness is constant between 95% and 70% yield and the obvious interpretation of this is that the volume of material removed is filled with water. Below a 70% yield, the situation is different and the fibre wall volume decreases as the yield decreases.

In a continuation of this series of papers (Stone and Scallan 1968) the authors used the solute exclusion technique to determine how the size of the pores of the fibre wall changes as the yield of the pulp decreases. By using macromolecules with known dimensions and measuring how the volume of non-solvent water changed with the molecular mass, it was possible to estimate the size distribution of the pores of the fibre wall. However, the interpretation of the data is not straightforward since the shape of the pore is very important for the partitioning of the molecules between the fibre-wall and the solution when the size of the molecule and the size of the

pore are similar, Lindström (1986) and Alince (1991). It can nevertheless be concluded that Stone and Scallan (1968) showed that the size of the pores, i.e. the pore width, in the fibre wall increases as the yield decreases, that an approximate size of the pores in the wood is between 5 and 40 Å and that the size of the pores in the fibre wall of a pulp with a yield of 44.6% is between 10 and 100 Å.

This was definitely a large step in our understanding of the structure of the fibre wall and this picture is still very dominating. It should however be stressed that these figures must be taken as relative. Recent experimental evidence (van de Ven 1997, Li et. al 1993, Häggqvist et al 1998, Andreasson et al 2003 and Maloney et al 1999) has shown that the absolute value of the pore size may be different from the values given by Stone and Scallan (1968) and this will discussed later on in this chapter.

Stone and Scallan (1968) also used the solute exclusion technique to suggest a new structural model of the fibre wall where the earlier defined macro-pores were found to be of the order of 25-300 Å. This was defined as the interlamellar pore width and the micropore was defined as intralamellar pores in the size range of 5-25 Å, although the authors stated that the upper limit was somewhat arbitrarily determined. Based on these results and on electron micrographs, Scalan (1974) introduced the now very well known picture of how the internal fibrillation takes place with increasing swelling of the fibre wall. This figure is shown in *Figure 1.2*.



Figure 1.2. Schematic view of how the fibrillation of the fibre wall takes place when the swelling is increased. From Scallan (1974).

It should be pointed out that the forces causing this fibrillation can not be solely the swelling forces within the fibre wall. There is also a need for a considerable mechanical action on the fibre wall in order to make this fibrillation occur.

In the models presented by Stone and Scallan the arrangement of different chemical components in the fibre wall is not discussed, even though some comments were made regarding the arrangement of pores around the cellulosic microfibrils (Stone and Scallan 1968). In order to fill this gap in knowledge, Kerr and Goring (1975) conducted work in which they studied ultra-thin microtome sections of permanganate-stained fibres from black spruce with transmission electron microscope. They showed that cellulose was not stained by the permanganate and that only a minor part of the hemicellulose was stained, which means that it was possible to see the distribution of the lignin in the fibre wall. From cross-sections both along the fibres and across the fibres, they concluded that the ultrastructural arrangement of the different components of the fibre wall could be represented by the picture shown in *Figure 1.3*.



Figure 1.3. Schematic representation of the ultrastructural arrangement of cellulose, lignin and hemicellulose in the fibre wall of black spruce tracheids. From Kerr and Goring (1975).

In this picture, 1-2 fibrils are associated in the radial direction, with a size of 35-70 Å, whereas 3-4 fibrils are associated in the tangential direction, with a dimension of 104-140 Å. When the authors started to compare the amounts of the different components in the fibre wall, they found literature values corresponding to 0.26:0.45:0.29 for the lignin: cellulose: hemicellulose and in the microtome sections they found that the proportion stained by the permanganate was equivalent to 0.45. This means that a fraction of the hemicellulose had been stained by the permanganate and might therefore be assumed to be associated with the lignin. The rest of the hemicellulose was assumed to be associated with the cellulose microfibrils.

1.1.2 Recent Developments in the Evaluation of the Pore Structure of Fibres

Since the properties of the fibre wall will be determined both by the type of material in the fibre wall and how it is organised inside the fibre wall large research efforts have recently been conducted to find a more elaborate structure determination of the fibre wall (van de Ven 1997, Li et. al 1993, Häggqvist et al 1998, Andreasson et al 2003, Duchesne et al 1999 and Maloney et al 1999).

First of all the use of new techniques for determination of fibre structure via cryofixation and deep etching of the fibres followed by Field Emission Scanning Electron Microscopy (FE-SEM) should be mentioned (Duchesne 1999). This technique has revealed a new very open structure of the fibre wall, for most commercial chemical pulps in their never dried form, where the fibrils are clearly separated. The openings between the fibrils are of the order of 10–50 nm, naturally depending on the degree of delignification, and the lateral dimension of fibril aggregates are shown to be of the order 10–20 nm. This is demonstrated in *Figure 1.4* where a Cryo-FE-SEM image of the swollen fibrillar structure of the fibre wall is demonstrated for delignified fibres from spruce. In *Figure 1.5*, a similar section from an air dried spruce fibre is shown. It should be stressed that the scale in the figures is the same and the size of the bar is 100 nm in both diagrams.



Figure 1.4. High resolution Cryo-FE-SEM micrograph showing the surface structure of a frozen hydrated kraft pulp fibre from spruce. The bar in the figure corresponds to 100 nm. (Duchesne 1999).

From these two figures it is clear that the openings in the fibre wall are larger then the pore size as estimated with the solute exclusion technique but this might not be so unexpected since this method is known not to be able to determine the correct pore size distribution of the fibres eventhough it is excellent for a determination of the Fibre Saturation Point (FSP) as defined earlier. It is also clear from these figures that drying in air lads to a collapse of the pores in the fibre wall most likely caused by the capillary forces between the fibrils during drying.

Despite the elegance of these types of micrographs it is very difficult to quantify the pore size and pore size distribution from these figure based on single fibre evaluations. Methods based on some type of average property is the fibres is therefore of very large interest and Li et al 1999 used ²H and ¹H NMR relaxation measurements to determine the pore size distribution within pulp fibres. With this technique the relaxation of water molecules within the fibres are

determined from NMR spin lattice relaxation profiles using D_2O and H_2O as probe liquids. The principal behind the method is schematically shown in *Figure 1.6*.



Figure 1.5. FE-SEM micrograph of an air dried kraft pulp fibre from spruce. The bar in the figure corresponds to 100 nm (Duchesne 1999).



Figure 1.6. Schematic representation of the principal behind the NMR relaxation method. It is assumed that two types of water exist in the fibre wall, bound water and free water.

As indicated in the figure the method is based on a number of assumptions. First of all it is assumed that two types of water molecules exists within the fibre wall, bound water that will be affected by the surface of the fibres and free water with the same properties as bulk water. This means that the method will determine a surface to volume ratio of the water inside the fibre wall. In order to calculate and average pore radius of the fibre wall it is also assumed that the pores within the fibre wall has a cylindrical arrangement, similar to that shown in *Figure 1.2*. In mathematical terms this can be summarised by equation (1.4) and (1.5)

$$M(\tau) = M_0 \left[1 - 2\exp\left(-\frac{\tau}{T_1}\right) \right]$$
(1.4)

where

 $M(\tau)$ = Magnetization at time τ M_0 = Magnetization at time 0 T_1 = The population-averaged relaxation time

 T_1 will be determined by the relaxation time of the free water, T_{1F} and the relaxation time of bound water, T_{1B} , and the amount of water in the different states. Assuming a cylindrical geometry the relation between T_1 and T_{1F} and T_{1B} can be written

$$\frac{1}{T_{1}}(r) = P_{B}\frac{1}{T_{1B}} + (1 - P_{B})\frac{1}{T_{1F}} = \frac{1}{T_{1F}} + \frac{Sn}{V\rho}(\frac{1}{T_{1B}} - \frac{1}{T_{1F}}) = \frac{1}{T_{1F}} + \frac{2n}{r\rho}(\frac{1}{T_{1B}} - \frac{1}{T_{1F}}) = \alpha + \frac{\beta}{r}$$
(1.5)

where

 T_1 = Population averaged relaxation time in a pore with a uniform pore size

 T_{1B} = Relaxation time of bound water

 T_{1F} = Relaxation time of free water

 P_B^{T} = Fraction of water dynamically perturbed by the surface

S = Specific surface area of the a pore in the solid

V = Volume of a pore in the solid

n = Amount of "bound" water

 ρ = Density of the liquid

r = radius of the pore

$$\alpha = \frac{1}{T_{1F}}$$

$$\beta = \frac{2n}{\rho} (\frac{1}{T_{1B}} - \frac{1}{T_{1F}})$$

A crucial parameter in order to convert the magnetization data to a pore size distribution data is the b parameter in equation 5 and details about the determination of this parameter is given in (Li et al 1993). However, as can be seen in this set of equations it is possible to calculate a pore size distribution from NMR relaxation measurements after some assumptions about the geometry of the fibre wall.

Andreasson et al (2003) conducted an investigation similar to the investigation by Stone and Scallan (1965b) where a set a kraft pulps from carefully selected chips were carefully delignified and then subjected to NMR relaxion measurements and a typical result from these measurements are shown in *Figure 1.7*.



Figure 1.7. Pore size distribution of pores within the fibre for a set of kraft pulps from spruce, delignified to different yield, as determined with NMR relaxation measurements (Data from Andreasson 2003).

As can be seen from this figure the average pore radius increases from 10 nm to around 23 nm as the kappa number is changed from 110 to 35 and then again decreases to around 17 nm as further lignin and hemicellulose is removed to a kappa number of 15. Simultaneous measurements of the total volume of liquid held by the fibre wall, for the different fibres shown in Figure 1.6, also showed that as the hemicellulose an the lignin is removed from the fibre wall the volume of the fibre wall is not dramatically changed which is agreement with the data shown in *Figure 1.1.* This also supports the hypothesis that as material is removed from the fibre during kraft pulping empty spaces are created within the fibre wall but that the total volume of the fibre wall is fairly constant. The pore sizes as determined with the NMR relaxation technique is also in very good agreement with the size of the pores as determined with the cryo-FE-SEM technique as shown in Figure 1.4. The discrepancy between the NMR/cryo-FE-SEM and the pore sizes as determined with the Solute Exclusion Methods (Stone and Scallan 1968) might naturally have several causes. However, when examining the structure of the fibre wall as revealed in Figure 1.4 it seems plausible to suggest that the different methods are sensitive to/measures different parts of the fibre wall. In order to be able to characterise the pores inside the fibre wall the polymers used in the solute exclusion technique have to enter through the pores in the external part of the fibre wall. As can be seen in figure the S1 layer has a considerable amount of small pores that will restrict the polymers, used in the SEC method, from entering the fibre wall and therefore the SEC method will most probably be sensitive to the pores in the outermost layers of the fibre wall. As was mentioned earlier the NMR relaxation method will measure the surface to volume ratio of water inside the fibre wall and therefore this method will give an average of all pores within the fibre wall. With this in mind it might be suggested that the different methods are sensitive to different parts of the fibre wall and therefore they are complementary to each other. It should also, once again be stated, that the SEC method can not be used to determine the pores size distribution of the fibres unless the shape of the pores inside the fibre wall are used to

correct the SEC data. Since this shape of the pores is not known the method is hard to use more than for a qualitative discussion of the pore size distribution.

Another method based on polymer adsorption has also been used to estimate the pore size of the pores within the fibre wall (van de Ven 1997). In this method, different cationic polyelectrolytes, i.e. cationic polyethyleneimines, are adsorbed to fibres and compared with the adsorption to a microcrystalline cellulose (MCC) with virtually no internal pores. The results are then presented as adsorbed amount as a function of the size of the adsorbing molecules and at a certain size there will be a decrease in the adsorbed amount for the porous fibres, compared with the MCC, since these molecule will have no access to the internal parts of the fibre wall. Typical results from these measurements are shown in *Figure 1.8* and as can be seen there is a break in the curves for the fibres at a molecular size of 13 nm and assuming that the pores have to be 3-5 times larger for the molecules to enter the average pore size would be 40-65 nm which is of the same order of magnitude as determined with the NMR technique and the cryo-FE-SEM.



Figure 1.8. Adsorption of PEI, cationic polyetyleneimine, of different molecular mass, size, to two different types of pulp fibres and to MCC at pH=10. Adsorption capacity in mg/g is compared with specific adsorption in mg/m² (van de Ven 1997).

It is naturally difficult to exactly explain the difference between the SEC method and the polyeletrolyte adsorption method and van de Ven (1997) tried to explain the difference partly by the difference in the driving force for interaction with the fibres between the dextrans used in the SEC and the PEI used in the adsorption method. The dextrans have no interaction at all with the fibre surface and might be very sensitive to depletion effects in small pores whereas this is not applicable for the PEI. It can nevertheless be summarised that the PEI adsorption results in pores somewhat larger than the NMR relaxation method but they are of the same order of magnitude and it should be kept in mind that the PEI molecules are by no means monodisperse and therefore the agreement between the two methods is very good.

The final method that recently has been developed for pore size measurements is the thermoporosimetry method (Maloney 1999). The basis behind this method is that water in small cavities will have a lower freezing point compared with free water. This can mathematically be described with Gibbs-Thompson equation, equation (1.6).

$$D = \frac{4VT_0\sigma_{ls}}{\Delta H_m \ln \frac{T}{T_0}}$$
(1.6)

where

D = diameter of the pore V = molar volume of solvent σ_{ls} = surface tension between solid and liquid ΔH_m = latent heat of melting T = Melting temperature T_0 = Melting temparetaure of pure water

With this method a sample of wet fibres is first frozen and then the temperature is increased and the latent heat of melting is recorded and transformed to a melted amount of water per gram of fibres. From these data a pore size distribution curve can then be calculated up to rather large pores which is unique for this method and a typical pore size distribution from measurements with water is shown in *Figure 1.9*. The maximum pore size that could be determined, with water as a solvent, was around 500 nm and as indicated in the figure there is still a big difference in pore volume at this pore size as compared with FSP measurements. It was postulated (Maloney 1999) that the difference between the FSP and Thermoporosimetry data was due to macropores in the fibre wall and the pores as determined with the thermoporosimetry method was termed micropores. These micropores consist of pores larger than 1 nm and pores with non-freezing water, i.e. pores smaller than 1 nm which is the lower detection limit for water.



Figure 1.9. Pore size distribution of bleached softwood kraft fibres in their Na^+ form as determined with thermoporosimetry in water. The classification of the pores in micropores and macropores is indicated in the figure and the location of the FSP bar is arbitrary and should not be confused with a certain pore size (Maloney et al 1999).

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There are however several limitations with this method. Due to limitations in the equipment smaller pores than 1 nm in water can not be determined with this method and for another solvent, cyclohexane it was found that the minimum pore size was around 7 nm. Cyclohexane is recommended for use instead of water since it is known not to cause any disturbances of the fibre structure upon freezing, which was found for water, and water has to be exchanged to cyclohexane via a solvent exchange procedure before testing. Another advantage with using cyclohexane is that larger pores can be determined with this solvent. It should though be kept in mind that the solvent exchange might cause a structure change of the fibre wall that is very hard to quantify.

The liquid contained in pores that can not be measured with the thermoporosimetry method was assumed (Maloney et al 2001) to have a log-normal size distribution and together with the measurable pores a bimodal pore size distribution curve can be presented from these types of measurements. A typical pore size distribution from measurements with never dried bleached softwood fibres, both beaten and unbeaten, are shown in *Figure 1.10*.



Figure 1.10. Pore size distribution for a never dried bleached softwood pulp where the pores smaller than 10 nm have been assumed to have a log-normal size distribution. Data for both beaten and unbeaten fibres are shown. The bimodal size distribution is a result of the assumed log-normal size distribution of the pores smaller than 10 nm but might be supported by literature data (Maloney et al 2001).

As seen in this figure pore sizes up to $3 \mu m$ can be measured with this method and it is also clear that a mechanical beating changes the larger pores in the fibre wall.

1.2 Concluding Remarks

As has been made obvious from this chapter a lot of hard work and a lot of advanced equipment have been applied to determine the pore size of the pores within the fibre wall and the pore size distribution. It is also clear that different techniques will measure different parts of the fibre wall and a lot of effort have over the years been spent on debating which method that is correct and which method that is not. In the opinion of the author all methods have drawbacks and advantages and it is absolutely essential that the user of the different methods should have a deep insight into the principals of the methods before starting to interpret the results from the measurements. It is the aim of this chapter to give an insight into the knowledge about the structure of the fibre wall and into the basics behind the different measuring principles.

It seems as if there is an agreement about that the radius of the pores in the fibre wall is around 10 to 80 nm, naturally depending on which type of fibres that are studied and how they are treated, and that there is a difference in the size in the exterior part of the fibre wall and in the interior part of the fibre wall. This will naturally be very important when depositing some functional additive within the fibre wall but it will naturally also be very important for the flex-ibility of the fibres and the way the fibres will conform towards each other during drying and consolidation of paper. These latter correlations are not clear but there are many new and advanced methods available for characterisation of the pores within the fibre wall.

1.3 References

- Alince, B. (1991) Tappi J. 11: 200.
- Andreasson, B., Forsström, J. and Wågberg, L. (2003) Cellulose 10: 111.
- Duchesne, I. and Daniel, G. (1999) Nordic Pulp Paper Res. J. 14, 2: 129.
- Häggqvist, M., Li, T.-Q. and Ödberg, L. (1998) Cellulose 5, 1: 33.
- Haselton, W.R. (1954) Tappi 37, 9: 404.
- Li, T.-Q., Henriksson, U. and Ödberg, L. (1993) Nordic Pulp Paper Res. J. 8, 3: 326.
- Lindström, T. (1986) In: A. Bristow and P. Kolseth (Eds.) Paper Structure and Performance. New York, Basel: Marcel Dekker, Inc., p.75 and p.99.
- Maloney, T.C. and Paulapuro, H. (1999) J. Pulp Paper Sci. 25, 12: 430.
- Maloney, T.C. and Paulapuro, H. (2001) In: C.F. Baker (Ed.) The Science of Papermaking. Trans. 12th Fundamental Res. Symposium held at Oxford. The Pulp & Paper Fundamental Res. Soc., p. 897.
- Pelton, R. (1993) Nordic Pulp Paper Res. J. 8, 1: 113.
- Scallan, A.M. (1974) Wood Sci. 6, 3: 266.
- Stone, J.E. and Scallan, A.M. (1965a) J. Polym. Sci.. Part C 11: 13.
- Stone, J.E. and Scallan, A.M. (1965b) Pulp Paper Mag. Canada 66, 8: T407.
- Stone, J.E. and Scallan, A.M. (1965c) In: F. Bolam (Ed.) Consolidation of the Paper Web, Transact. Symp. Cambridge, Vol. 1. London, UK: Tech. Sect. Brit. Paper Board Makers Assoc., p.1453.
- Stone, J.E. and Scallan, A.M. (1967) Tappi 50: 10496.
- Stone, J.E. and Scallan, A.M. (1968a) Cellulose Chem. Techn. 2, 3: 343.
- Stone, J.E. and Scallan, A.M. (1968b) Pulp Paper Mag. Canada 69, 6: T288.
- van de Ven, T.G.M.and Alince, B. (1997) In: C.F. Baker (Ed.) *The Fundamentals of Papermaking, Trans. 11th Fundamental Res. Symp. Cambridge.* Pira International, p. 771.

2 Structure and Properties of Fibres

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2.1 Introduction

The physical properties of plant fibres like stiffness, strength and swelling due to moisture uptake, are highly dependent on the structure or morphology of the cell wall. In plants nature has evolved an optimal utilization of the wood polymers in the structural arrangement of these within the cell wall. Thus trees are provided by their tracheids, the fibres, with a strength to rise over a 100m, to withstand hurricane winds swinging the crown in all directions, to be downloaded with tons of snow and ice and still being able to transport water up to the crown. Thus the fibre construction as a hollow, laminated fibre reinforced tube is optimised both with regard to its design and to strength criteria in both its transverse and longitudinal direction and as well with regard to compressive and tensile forces.

2.2 Cell Wall Structure

The structural organisation of the cell wall regulating its mechanical and physical properties may be grouped into the following hierarchical levels:

- the layered structure of the fibre wall
- the fibre reinforced structure of each cell wall layer
- · the orthortropic organisation of the matrix components
- the polymer chemistry of the constituents

2.2.1 Cell Wall Layers

With its organisation into a layered structure of plies, cell wall layers, with the reinforcements of cellulose fibrils in different directions the fibre resembles in a way that of a man made pipe for pressure applications. When there are demands for high strength properties in different directions a laminated oriented ply construction generally offers a good solution. This is what is often used in the fibre reinforced composite field for complicated constructions as for instance rotor blades for wind turbines and has long been used for example as plywood for the demand of strong, lightweight boxes. In the case of the fibre construction essentially three layers may be distinguished, see *Figure 2.1*. The thinner outer and inner layers, which are the S_1 and S_3 layers, have the reinforcing cellulose fibrils arranged at a high angle to the fibre direction. These layers provide the fibre with its transverse stiffness allowing it to be used as pipes for the water transport within the stem. In the middle, between these layers lies the S₂ layer which is distinguished by its low fibril angle. This layer makes up about 70 to 80 % of the material of the wood fibre and it is thus dominating the mechanical properties of the fibre. Due to its low fibril angle the S_2 layer provides the fibre with a very high stiffness and strength in the longitudinal fibre direction thus providing the tree with its strength properties for supporting the load of itself as well as for withstanding the bending forces acting on the stem caused by the blowing winds.



Figure 2.1. Schematic picture of a wood fibre in this case liberated intact from the wood so that the middle lamella, M, remains on the fibre surface as from a low refined high temperature thermomechanical pulp. P is the primary wall with irregular structure of the cellulose fibrils while in the secondary wall layers, the S_1 , S_2 , S_3 , the cellulose fibrils are ordered at a specific angle.

Morphologically the softwood trees creates thin walled earlywood fibres in the spring mainly providing for water transport and thick-walled latewood fibres in late summer mainly providing the tree with the strength properties. Thus latewood fibres have a more or less rectangular cross section with a large thickness of the wall whereas the earlywood fibres are square to hexagonal in cross section. For the cell wall layers the largest difference is in the thickness of the second-ary S₂-wall so that the relative proportion between the layers differs somewhat between the two fibre types, see *Table 2.1* (Fengel and Stoll 1973).

Cell wall layer	Average thickness (µm)		Relative contribution (%)	
	Earlywood	Latewood	Earlywood	Latewood
ML/2	0.09	0.09	4.2	2.1
S ₁	0.26	0.38	12.5	9.0
S ₂	1.66	3.69	78.7	85.4
S ₃	0.09	0.14	4.5	3.3
S	2.10	4.30	99.9	99.8

Table 2.1. The difference in thickness of the cell wall layers between earlywood and latewood fibres of Norway spruce (*Picea abies*) (Fengel and Stoll 1973).

2.2.2 Fibre Reinforced Structure

Each of the cell wall layers of the fibre is composed of a mixture of the main wood polymers cellulose, lignin and hemicelluloses. The distribution between these polymers differs somewhat between the cell wall layers, see *Figure 2.2*, which to some extent affects properties but mainly the dissolution of lignin during pulping and bleaching processes. For the polysaccharides there is also a difference in the composition among the different cell wall layers, see *Table 2.2* (Meier 1961). As seen the outermost layers, the primary wall and middle lamella differs in particular in their high content of pectic substances such as arabinan and galactan. Within the secondary wall there is a higher relative content of xylan in the S_1 - and S_3 -walls than in the S_2 -wall in comparison with glucomannan.



Figure 2.2. Distribution of the principal chemical constituents within the cell wall layers of softwoods. The diagram is based upon the one given by Panshin (Panshin and Zeeuw 1980) but modified for the lignin content in the compound middle lamella (ML+P) according to Westermark et al. (Westermark et al 1988).

The arrangement of the wood polymers within the cell wall is that of a fibre reinforced structure with partly crystalline cellulose fibrils as the reinforcing materials in a matrix of the other, amorphous wood polymers; lignin and hemicelluloses. The present conception of the structure favours that the cellulose microfibrils, 3 to 4 nm in cross section (Larsson et al 1999) are aggregated into larger entities, the cellulose fibrils or cellulose aggregates, of an average cross section of 20 nm (Duchesne and Daniel 2000, Fengel 1970) in which most probably some of the glucomannan is incorporated (Fengel 1970, Atalla et al 1993, Salmén 2000). Adjacent to these aggregates mostly glucomannan is arranged in parallel with the fibrils (Åkerholm and Salmén 2001). In the space in-between these aggregates, occupying about 3 to 4 nm (Terashima et al 1993), it is likely that the lignin matrix is interspaced with xylan entities (Salmén and Olsson 1998), see *Figure 2.3*.

Polysaccharide	ML+P ^a	S ₁	S ₂ outer part	S_2 inner part + S_3
Spruce				
Galactan	16.4	8.0	0.0	0.0
Arabinan	29.3	1.1	0.8	0.0
Cellulose	33.4	55.2	64.3	63.6
Glucomannan	7.9	18.1	24.4	23.7
Glucuronoarabinoxylan	13.0	17.6	10.7	12.7
Pine				
Galactan	20.1	5.2	1.6	3.2
Arabinan	29.4	0.6	0.0	2.4
Cellulose	35.5	61.5	66.5	47.5
Glucomannan	7.7	16.9	24.6	27.2
Glucuronoarabinoxylan	7.3	15.7	7.4	19.4

 Table 2.2. Percentages of polysaccharides in the different cell wall layers of the fibre wall to Meier (Meier 1961).

^{a)} Contains a high percentage of pectic acid as well





2.2.3 Matrix Organisation

There are strong indications that the arrangement of the cellulose aggregates and the lignin rich matrix shows a pattern of a tangential lamellation when viewing the fibre in a transverse crosssection (Ker and Goring 1975). This is also evident when observing the structure of the cross section of the secondary wall by AFM, *Figure 2.4*, where a structural arrangement of the fibril aggregates in the tangential direction is appearing (Fahlén and Salmén 2003). The spacing inbetween the fibril aggregates are also of such small dimensions that it is clearly necessary on a volumetric basis that some of the hemicelluloses will be arranged in-between the cellulose microfibrils within the cellulose aggregates (Salmén 2000).



Figure 2.4. Atomic Force Microscopic, AFM- image of a transverse cross section of the secondary wall of a spruce fibre. Cellulose aggregates averaging 18 nm arranged in a pattern of tangential lamellation is evident (Fahlén and Salmén 2003).

Such a structure is also what may be concluded from the change in shape of the fibre due to dissolution of mainly lignin but also some hemicelluloses during pulping. With a radial arrangement of lignin lamellas, the fibre would after removal of lignin had shrunk but with maintained thickness. On the other hand with a tangential lamelation the thickness would have decreased keeping the fibre diameter essentially constant, see *Figure 2.5*. That the latter case is what happens was shown in the nineteen seventies by Stone et al. (Stone et al 1971).

The dissolution of lignin and hemicelluloses during pulping give rise to wholes in the fibre wall, generally termed pores. This lignin diffused out of the cell wall has been found to have a molecular weight corresponding to a spherical diameter of between 3.5 to 10 nm (Willis et al 1987, Favis et al 1984). This corresponds well with the size of the pores created in the fibre wall, which with indirect methods have been indicated to be between 5 to 15–20 nm in diameter (Berthold and Salmén 1997, Stone and Scallan 1967) as seen from *Figure 2.6*. In TMP which correspond to wood, i.e. chemically intact fibres, the water uptake in the material occurs as designed to apparent pore sizes below 2 nm and is due to a swelling of the matrix wood polymers. In the chemical pulps water uptake occurs to a larger extent in pores above 2 nm i.e. where no



Figure 2.5. Schematic illustration of the possible ways of fibre wall shrinkage due to delignification followed by drying. In reality pulping of fibres results in a change in the fibre form in such a way that the fibre form is maintained while the fibre wall thickness decreased thus essentially the behaviour for a tangential lamella organization (Stone et al 1971).

pores exists for the TMP, thus in holes created by the dissolution of lignin and hemicelluloses. The creation of these pores is essential for the development of a fibre that is flexible and compressible and therefore this is essential for the improvement of the fibre bonding potential of the fibres.



Figure 2.6. The apparent pore size distribution for a TMP, a Kraft softwood pulp and a bleached softwood pulp determined by Inverse Size Exclusion Chromatography, ISEC. Error bars represents standard deviation (Berthold and Salmén 1997).

The size of the lignin molecules diffused from the cell wall are much larger than the corresponding tangential and radial space s in the fibre wall between cellulose aggregates pointing to that the lignin has a lager spread in the length direction of the fibre as also indicated by the schematic illustration of lignin dissolution by Favis and Goring (Favis and Goring 1984) as developed from the well-known structure of the Kerr-Goring model (Kerr and Goring 1975) of the fibre wall shown in *Figure 2.7*. This size of the lignin molecules that are dissolved also points to the fact that the lignin in the fibre wall behaves as a mechanically heterogeneous material. For this to occur a size of the polymer in the order of 5 to 15 nm in diameter is required (Kaplan 1976, Schick and Donth 1981). This means that the lignin in the fibre wall may show a single softening behaviour, i.e. a single glass transition temperature, which also has been determined to occur at 90 °C (1 Hz) for water saturated conditions of the fibre material (Salmén 1984).



Figure 2.7. Schematic illustration of the dissolution of lignin out of the fibre wall (Favis and Goring 1984) developed from the well-known model picture of the secondary cell wall the Kerr-Goring model (Kerr and Goring 1975). The lignin entities have been shown to appear as flakes, which may with an orientation in the tangential/ length direction be fitted into the spacing between the cellulose aggregates.

2.2.4 Wood Polymer Properties

From the structure of the fibre wall it is clear that the cellulose aggregates, which are highly oriented in the direction of the length of the fibre gives the fibre its highly anisotropic properties. This however means that it will be the properties of the other wood polymers, the hemicelluloses and the lignin, which will have a large influence on properties in the transverse direction (Bergander and Salmén 2001). Of the wood polymers, cellulose, hemicelluloses and lignin most attention has been given to the cellulose when it comes to determining mechanical properties of the wood constituents. The rationale is of course the cellulose being the stiff reinforcing material in the composite and therefore the component that to a high degree determines the properties of the fibre in the most important direction, its length. More and more evidence have though been established suggesting an orientation of both hemicelluloses and lignin in the direction of the cellulose fibrils, mainly based on spectroscopic data (Åkerholm and Salmén 2001, Åkerholm and Salmén 2003). It is suggested that the cellulose and hemicelluloses acts as templates for the lignin deposition thus giving also the lignin an orientation in relation to the cellulose fibrillar direction (Atalla 1998). An orientation in the plane of the cell wall has also been indicated from Raman spectroscopy (Agarwal and Atalla 1986) as also depicted in *Figure 2.8*.

Cellulose

For cellulose there are both theoretical estimates as well as experimental determinations of its elastic properties. Most recent analysis tends to favour values in the longitudinal direction for the cellulose crystalline region between 120 to 170 GPa (Tashiro and Kobayashi 1991, Kroon-Batenburg et al 1986) although there are some older theoretical estimates of such high values as 246 and 319 GPa (Gillis 1969). When comparing theoretical estimates with experiments both



Figure 2.8. Schematic picture of the arrangement of the wood polymers, cellulose, lignin and hemicelluloses in the secondary wall structure of wood fibres. All of the wood polymers have an orientation with the main axis in the direction of the fibre, i.e. following the direction of the cellulose fibrils. The lignin is also oriented with the plane of the molecule in a transverse direction to the fibre wall (Åkerholm and Salmén 2003).

for cellulose I, as well as the experimentally easier material cellulose II, a reasonable value of a modulus seems to be ca 134–136 GPa for the stiffness of cellulose I (Kroon-Batenburg et al 1986, Sakurada et al 1962).

Hemicellulose

For hemicelluloses material data are extremely scarce. Cousins' data on extracted xylan fractions (Cousins 1978), which might be considered as representative indicate a random value of the elastic modulus for the dry material of 8 GPa. However it is known that hemicelluloses will crystallize when isolated which would affect the modulus determinations. It is also known that the hemicelluloses at least the glucomannan is oriented along the cellulose fibrils within the fibre wall (Liang et al 1960, Keegstra et al 1973, Åkerholm and Salmén 2001). This means that the in-situ hemicelluloses might have a bulk modulus that is lower than that determined by Cousins but that the orientation will mean that it is stiffer in the fibre direction and much weaker in its transverse direction.

Lignin

Also when it comes to lignin data only exists for extracted materials, which then have been severely modified compared to the original material inside the cell wall. Under dry conditions values for an isotropic lignin between 4 to 7 GPa have been reported (Cousins 1976, Cousins et al 1975). In the native cell wall it is though highly probable that also the lignin is orthotropic with a preferred orientation in the direction of the cellulose fibrils (Åkerholm and Salmén 2003). Data given in *Table 2.3* of the elastic properties of the wood polymers may be seen as reasonable estimates. Where the values for cellulose are highly probable while the values for lignin and hemicellulose should only be considered as in the right range indicating their orthotropic nature as well as their moisture sensitivity.

Polymer		Dry conditions	Moist conditions
Cellulose			
	E _x	134 GPa	134 GPa
	Ey	27.2 GPa	27.2 GPa
	G	4.4 GPa	4.4 GPa
	u	0.1	0.1
Hemicellulose			
	E _x	4.0 GPa	40 MPa
	Ey	0.8 GPa	8 MPa
	G	1.0 GPa	10 MPa
	u	0.2	0.2
Lignin _x			
	E _x	2.0 GPa	2.0 GPa
	Ey	1.0 GPa	1.0 GPa
	G	0.6 GPa	0.6 GPa
	u	0.3	0.3

Table 2.3. Estimates of mechanical data for wood polymers.

Moisture sorption characteristics

All of the wood polymers are hygroscopic and thus readily absorbs moisture from the surrounding air in relation to its relative humidity, RH. The extent of moisture sorbed is directly associated with the number of hydrophilic sites, i.e. the hydroxyl, OH-groups and the carboxylic COOH-acid groups. For sulphonated fibres also sulphonic SO₃ H-acid groups do adsorb water. The acidic groups adsorb considerably more water around them as compared to the hydroxyl groups. Also, for these acidic groups the number of water molecules adsorbed depend on the conterion so that for the carboxylic acid groups sodium (a monovalent ion) sorbs more than calcium (a divalent ion) which sorbs more than the acidic proton form while for the sulphonic acid groups the acidic proton form sorbs more than the sodium which sorbs more than the calcium (Berthold et al 1996). For the normal wood fibre the content of acidic groups are though rather low so that only at the highest relative humidities effects are visible. Of more importance is the relative composition of the fibre as can be seen from Figure 2.9 showing the absorption for the different wood polymers as well as for TMP-fibres (Takamura 1968). The lignin has a lower content of hydroxyl groups as compared to the hemicelluloses while the lower adsorption for the cellulose is due to its crystalline/paracrystalline regions, which are not adsorbing any water. The adsorbed amount of moisture for the pulp fibre may as seen be accurately calculated from the sum of adsorption for its components, cellulose, hemicellulose and lignin, knowing the relative amount of these in the fibre (Takamura 1968). It is also obvious, the parallel sorption curves, that it is the same mechanisms, i.e. that of the sorption by the hydroxyl which are dominating the behaviour for the wood polymers.



Figure 2.9. Moisture content (gram water per 100 gram of moist sample) as a function of RH for the wood polymers; lignin, cellulose, hemicelluloses as well as for a TMP of pine. The calculated relationship is based on the relative amount of the wood polymers in the TMP and the absorption curves for these. Redrawn from data of Takamura (Takamura 1968).

2.2.6 Softening

As the constituents of the wood fibre are polymeric components their properties are highly dependable on their softening temperature, the glass transition temperature. In completely dry conditions all of the wood polymers softens at very high temperatures (Back and Salmén 1982), 230 °C for cellulose, 205 °C for lignin and around 170 to 180 °C for hemicelluloses as illustrated in *Figure 2.10* by the drop in elastic modulus for papers of different composition (Salmén 1979). This is for the carbohydrates partly a reflection of the high hydrogen bonding capacity.



Figure 2.10. The identification of separate glass transition temperatures for hemicellulose at 175 °C, for lignin at 205 °C and for disordered cellulose at 230 °C in the elastic modulus –temperature curves from papers selectively extracted of either lignin or hemicelluloses respectively (Salmén 1979).

This fact makes the wood polymers also highly sensitive to their moisture content as moisture functions as a softener, a low molecular weight component lowering the softening temperature, for them, *Figure 2.11* (Salmén 1990, Salmén 1982). Thus for the hemicelluloses the softening temperature is lowered even below zero at high moisture contents, approaching 100 % RH,



Figure 2.11. Glass transition temperature of wood polymers as a function of moisture content (Salmén 1990). Lignin has a limiting reduction of the glass transition due its three-dimensional structure. For cellulose the crystal-line restrictions shifts the transition in the way that higher moisture contents are needed for the required mobility to result in a softening.

while for lignin the branched structure limits the transition temperature to about 70 °C under fully wet conditions (Salmén 1984). The cellulose disordered regions makes the softening of these not particularly pronounced and for conditions where it may influence properties its transition is most likely shifted to higher moisture contents due to the restrictions from crystalline regions as schematically shown in *Figure 2.11*.

2.3 Fibre Properties

The mechanical properties of wood fibres are as discussed in section 2.2 highly dependent on the stiffness of the cellulose fibrils and the arrangement of these in the thickest cell wall layer the S_2 -layer. When isolating the fibres, especially the earlywood fibres of chemical pulps made from softwood they will tend to collapse, as illustrated in *Figure 2.12* while latewood fibres and thick-walled hardwood fibres more or less tend to maintain their shape. In softwoods the earlywood fibres dominate in terms of number of fibres and the collapse favours a structure giving much higher flexibility of the fibres a phenomena that is improved with the extent of the pulping and beating processes. In the wet, swollen state, the differences in fibre flexibility is not that pronounced, *Figure 2.13*, although earlywood fibres are more flexible than latewood fibres (Hattula and Niemi 1988). The most significant factor influencing the wet fibre flexibility is the yield of the pulp. With the dissolution of lignin and the creation of pores in the cell wall these will make the fibre to appear as a delaminated structure under wet conditions, which renders its high flexibility. With beating this delamination of the fibre wall is further enhanced but the effect is much smaller than the yield effect (Hattula and Niemi 1988).



Figure 2.12. Schematic drawings of latewood and earlywood fibres and their collapse modes as a result of drying: after Jayme and Hungher (Jayme and Hunger 1961).



Figure 2.13. Wet fibre flexibility of softwood spruce Kraft fibres as a function of beating degree for two pulps of different yield as determined by the method of Tam Doo and Kerekes (Tam Doo and Kerekes 1981). Earlywood fibres shows a higher wet fibre flexibility than latewood fibres (Hattula and Niemi 1988).

2.3.1 Stress Strain Properties

The tensile stress-strain properties of wood fibres are highly dependent on the angle of the cellulose fibrils within the S_2 -layer, the fibril angle a shown in *Figure 2.14* for data on chemical pulp fibres of black spruce. For small angles less than 10 degrees the fibres are highly elastic,



Figure 2.14. Stress-strain curves of single chemical pulp fibres of black spruce. Redrawn from Page and El-Hosseiny (Page and El-Hosseiny 1983). At low fibril angles the cellulose fibrils gives the high stiffness and strength of the fibre while at the high fibril angles the shearing of the matrix and an unwinding of the structure gives the extremely high extensibility of the fibre.



Figure 2.15. The fibril angle for individual fibres in an annual ring in the mature wood of a spruce wood tree measured with confocal laser scanning microscopy (Bergander 2001). In the earlywood the fibril angle various considerably while it in the latewood fibres is rather constant.

have high strength values and show a more or less brittle behaviour. For high fibril angles the behaviour is more like that of a ductile material exhibiting very high straining levels. Due to the high fibril angle for these fibres most of the deformation probably occurs due to a flow of the hemicellulose/hemicellulose-lignin matrix resulting in an orientation of the cellulose fibrils in the longitudinal fibre direction, i.e. in the direction of straining. Most of the fibres from softwood that grows in the Nordic countries have though a fibril angle below 15° thus being more or less elastic. Juvenile wood fibres probably show somewhat of a ductile behaviour with a fibril angle in the range of 15 to 30°, while the behaviour of compression wood fibres with a fibril angle reaching up to 30 to 45° may be different due its high lignin content and highly different structure of the cell wall. The variation of the fibril angle, *Figure 2.15* (Bergander 2001).

The elastic modulus of fibres in its length direction is directly dependent on the fibril angle of the S_2 -layer as seen in *Figure 2.16* (Salmén and de Ruvo 1985). It is also obvious that this modulus is very well predicted from the properties of the individual wood polymers considering the cell wall as a laminated composite, fibre reinforced material. The reason may be attributed to the high dependence in the longitudinal direction of the properties of the cellulose fibrils and that the elastic properties of cellulose have been determined with rather high accuracy.

For the properties in other directions of the cell wall data are scarce. The transverse elastic modulus of the fibre wall is highly dependent on the properties of the hemicelluloses (Bergander and Salmen 2002) but is hardly at all affected by the fibril angle of the main secondary wall the S_2 -wall as seen in *Figure 2.17* (Salmén 2001). The reason for this is of course that in the transverse direction the cellulose fibrils of the S_2 -wall is directed along the fibre due to the low fibril angle implying that the transverse forces are acting more or less in the cross direction to the cellulose fibrils.



Figure 2.16. The elastic modulus of chemically pulped softwood fibres in the longitudinal direction as a function of the fibril angle in the S_2 wall (Page et al 1977). The curves in the figure are based on model calculations considering the cell wall as a laminate built up of cellulose reinforcements in a matrix of lignin and hemicelluloses using the mechanical properties of the wood polymers as established for isolated materials (Salmén and de Ruvo 1985).



Figure 2.17. The transverse elastic modulus of softwood fibres as calculated considering the cell wall as a laminate built up of cellulose reinforcements in a matrix of lignin and hemicelluloses using the mechanical properties of the wood polymers as established for isolated materials plotted as a function of the fibril angle in the S₂-layer for some cases of defined composition of the cell wall (Salmén 2001). V_{cell} refers to the relative amount of cellulose in the fibre, S₂ to the relative volume of this cell wall and S₁ to the fibril angle of this layer. Also data from measurements on radial sections of the cell wall tested in the transverse direction on a micro-tensile stage in an ESEM are included (Bergander and Salmén 2000).

The morphological differences between earlywood and latewood fibres are of course most obviously related to the differences in cell wall thickness. Thus latewood fibres have a higher tensile stiffness and a higher breaking load than earlywood fibres. Generally also the elastic modulus and the breaking stress (quantities which take the cross sectional area in consideration) are higher for the latewood fibres as a consequence of a smaller fibril angle and a higher percentage of the S_2 -layer. As a consequence the elastic modulus in the transverse direction is lower for latewood fibres than for earlywood fibres.

When straining a fibre to high degrees it will tend to twist due to its helical fibrillar structure. This is a well-known phenomenon for tubular helical structures where the axis of the loading in its length direction is not coinciding with the main symmetry axis of the material. Thus a free fibre subjected to high tensile forces will twist and buckle to a shape as illustrated in *Figure 2.18*. Within the paper sheet structure such deformations are not possible but instead forces are built up from this tendency of the fibre structure to twist.



Figure 2.18. A helically wound tube, a fibre, subjected to high tensile forces will tend to deform by buckling and twisting as the material symmetry axis do not coincide with the loading direction.

2.3.2 Effects of Moisture and Temperature

With increasing temperature the wood polymers softens and this is of course reflected in the mechanical properties of the fibres as seen for the decrease of the torsional stiffness of Kraft fibres in *Figure 2.19* (Kolseth and Ehrnrooth 1986). The overall decreasing stiffness reflects the loss in hydrogen bond and van der Waals forces between the molecules with the increasing temperature and in relation to those the effect of the hemicellulose softening in the region of 150 to 200 °C is very small. This however reflects the fact that in the wood fibre it is the cellulose fibrils that are the load taking components.



Figure 2.19. Relative rigidity, relative torsional stiffness, (unfilled symbols) and logarithmic decrement (filled symbols) versus temperature for two high-yield Kraft pulp fibres; triangles = 50 % yield, 8 % lignin content, circles = 63.5 % yield, 21.4 % lignin content (Kolseth and Ehrnrooth 1986).

As moisture functions as a softener for the wood polymers it is not surprising that increased moisture content, or relative humidity leads to a decreasing stiffness of the wood fibre, *Figure 2.20* (Kolseth 1983). The magnitude of the loss in stiffness is very much what can be expected as an effect of the loss of stiffness of the hemicelluloses.

It is noteworthy that the magnitude of the decrease of the fibre stiffness caused by the softening of the hemicelluloses is within reasonable limits independent of the fibre composition as both shown experimentally and by theoretical calculations (Kolseth and Ehrnrooth 1986; Salmén et al 1985). The increased damping (logarithmic decrement) reflecting the viscous contribution from hemicellulose softening shows only a moderate increase at the higher relative humidities which also is a consequence of the strong dependence of the cellulose fibrils in the wood cell wall structure. The relative modulus decrease can anyhow very well be modelled from the data on the drop of stiffness of the hemicellulose polymer, a drop amounting to several decades in stiffness, with consideration of the laminar, reinforced structure of the fibre wall. As seen in *Figure2.21* the decrease in stiffness is much higher in the transverse direction of the fibre than in its longitudinal direction, which reflects the orientation of the cellulose fibrils. Along the fibre the cellulose fibrils have a stronger reinforcing capability than in the transverse direction of course as a reflection of the orientation of the fibrils, the low fibril angle in the S₂-layer.



Figure 2.20. The relative rigidity (torsional stiffness) and logarithmic decrement (damping) versus relative humidity for two high-yield Kraft pulp fibres; triangles = 50% yield, 8% lignin content, circles = 63.5% yield, 21.4 % lignin content (Kolseth 1983).