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Physicochemical characterization of papermaking fibres

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INTRODUCTION

The purpose of this paper is to present as complete as possible, a picture of our present knowledge about papermaking fibres and their physico-chemical characteristics. The properties of the papermaking fibres are, in most cases, significantly influenced by the morphology of the wood fibres, but, from one and the same kind of wood fibres, paper can be produced with widely different properties as a result of different pulping and papermaking processes. Dissolution of material from the fibre wall and the middle lamella, structural changes of the polymeric material, and mechanical work on the fibrous material (defibration, refining, and to a certain extent undesired mechanical damage to the fibres in the pulp mill machinery) combine to produce the fibre properties required in the papermaking process.

Starting from the structure of the wood, a survey is given of the pattern of dissolution of different important pulping processes and the resulting bulk composition of the pulps. Characterisation of papermaking properties should include effects of both bulk and surface of the fibres and for that reason they are both discussed. The bulk composition has been studied for many years and we have a fairly good knowledge of the main features, although there is still a need for more detailed knowledge. The properties of the fibre surface are less known, but they have been the subject of several recent studies. They are therefore dealt with in more detail, particularly the problem of making reliable and relevant measurements.

Dissolution of lignin and other components in the pulping process is also important for the chemical composition of the surface. Mechanical removal of the remaining middle lamella and the outer layers of the fibre wall (the primary wall and S1 of the secondary wall) substantially change the surface composition and create fines with a large surface area, which may interact with the wet-end chemicals in the paper mill and decrease the over-all effects of these chemicals. Removal of the outer layers will also change the fibre properties as a whole since, for instance, the S1 layer restricts outward swelling of the main part of the secondary wall, S2, and preserves fibre rigidity.

Swelling of the fibres influences the refining behaviour of a pulp. For lignin-containing pulps, swelling facilitates refining. For bleached pulps with a very low content of residual lignin, the effect of swelling on refining is rather difficult to predict, as will be briefly discussed. This leads to the following contents of this paper:

- * The wood fibre
- * Changes in chemical composition in different pulping processes
- * Chemistry of the fibre surface
 - Interactions between fibres in the wet state and between dry paper and other substances
 - Surface energy of the chemical constituents of the fibre wall, fibres and paper
 - Surface energy determined by contact angle measurements Surface energy determined by inverse gas chromatography
 - Chemical characterisation of the fibre surface
 - Charge determination of fibres
- * Structure and swelling of the fibre wall
 - Swelling of the fibre wall
- * Fibre swelling in relation to refining/beating
- * Consequences for papermaking
- * Conclusions

THE WOOD FIBRE

Wood fibres are composites of organic polymers, cellulose, hemicelluloses and lignin, which form a complex, highly ordered material with distinctive structural and mechanical properties, see for example Parham (1969).

Cellulose is the skeletal or framework substance of the cell wall. It is the main strength-bearing component in wood (and in pulp) and the least accessible, due to its high degree of crystallinity. The hemicelluloses form a matrix, which penetrate and encase the cellulose framework. The presence of hemicellulose is considered to regulate the pattern of aggregation of cellulose in wood, as discussed by Atalla (1995). Lignin is manufactured by maturing cells and permeates the fibre walls

and the intercellular regions (middle lamellae). It gives the wood tissue as a whole rigidity and cohesiveness.

The cellulose is a straight-chain, unbranched, hydrophilic polysaccharide composed of repeating β -D-glucopyranose monomer units which are linked together by (1-4)-glycosidic bonds. The degree of polymerisation (DP) is considered to average about 10 000 in wood (considerably lower in the primary wall, the thin outer layer of wood fibres). Cellulose has a strong tendency to form intra- and intermolecular hydrogen bonds, which stiffen the straight chain and promote aggregation into a crystalline structure, see Fengel (1989) and Sjöström (1993^a). The cellulose is hence found in lattices with ordered regions and with regions where the lattice is slightly disturbed and has a lower degree of order ("amorphous cellulose"). The state of order can probably not be divided into two absolute parts as crystalline and amorphous; several degrees of intermediate or semicrystalline order exist.

A large percentage of the so-called "amorphous cellulose" corresponds to the molecules on the surface of elementary fibrils, which are the smallest morphological units of ordered native cellulose, with sizes of about 35 Å in diameter, as discussed by for instance Fengel (1970) and Lennholm (1994). The different elementary fibrils aggregate to form larger microfibrils with different sizes depending on the source of the material and fibrils. How the cellulose chains are arranged in the elementary fibrils and microfibrils is not known in detail. Mechanical damage to the wood fibre produces dislocations in the cellulose lattice ("disturbed zones") which decreases the order and makes the cellulose more available for chemical attack.

The supramolecular state of the cellulose, its crystalline as well as its fibrillar structure is of great importance for the mechanical properties of both wood fibres and papermaking fibres. The characteristic pattern of fibrils through the fibre wall influences both swelling behaviour and mechanical properties. The presence of crystalline cellulose, with regions of less order, and the size of the elementary fibrils work together to produce an interesting combination of contrary properties such as stiffness and rigidity on the one hand and flexibility and toughness on the other.

Crystalline cellulose has a very limited accessibility to water and chemicals see Parham (1969). Chemical attack can therefore be expected to occur primarily on

amorphous cellulose and on crystallite surfaces. The borderline between available and not available cellulose is not fixed. Changes may occur due to reorganisation of the cellulose chains.

Hemicelluloses differ substantially from cellulose, although both are polysaccharides of similar molecular chain structure. They contain different building-stones; the DP is in the range of only 50-300, Parham (1969) and Sears (1978); possess side groups on the chain molecule, and are essentially amorphous. The main hemicelluloses in softwood are galactoglucomannans and arabino-glucuronoxylan. The primary wall as well as the middle lamella contains considerable amounts of pectic materials (largely polygalacturonic acid, to a large extent methylated), see for instance Parham (1969) and Westermark (1995). Swelling of the pectic materials may play a significant role in connection with mechanical and chemimechanical pulping. Chemical pulping can, however, be expected to degrade and dissolve the pectic materials so that they are of little consequence in chemical pulps.

The main hemicellulose in hardwood is glucuronoxylan. There are two important differences between glucomannans and xylans. Xylans contain acidic groups (glucuronic acid) and have a molecular structure which is similar to that of cellulose when the xylans are stripped of their branches. Hemicelluloses are very hydrophilic and play a major role in the fibre's ability to absorb water. They promote internal lubrication, leading to improved flexibility. During pulp drying, they tend to stiffen the fibre.

Lignin is an amorphous, crosslinked, three-dimensional phenolic polymer. The crosslinks consist of fairly stable covalent bonds, such as C-C bonds and ether bonds, and less stable hydrogen bonds.

Lignin is much less hydrophilic than either cellulose or hemicellulose, almost to the point of being hydrophobic as discussed by Goring (1971). Unless hydrophilic groups are introduced into lignin during pulping, it has a general effect of inhibiting water absorption and fibre swelling. Since lignin is thermoplastic, it possesses a characteristic that can be used to advantage in mechanical pulping, where high temperature softens the lignin.

In addition to the major chemical components, wood contains small amounts of various extraneous, low molecular mass organic materials, normally referred to as "extractives" or in papermaking systems as "pitch", and inorganic material. The

inorganic material is of little importance for the papermaking fibres but may be a serious problem for instance in the chemical recovery system in closed pulp mills. The extractives, on the other hand, are a source of serious disturbances in papermaking, in spite of the usually rather low content in wood.

In addition to the polymeric components of wood, water plays an important role in giving wood its characteristic elastic properties through swelling of the more or less amorphous matrix material. The presence of water is particularly important in mechanical pulping.

CHANGES IN CHEMICAL COMPOSITION IN DIFFERENT PULPING PROCESSES

The bulk chemical composition of different pulps with interesting properties is illustrated in **table 1**. The table is mainly based on SCA data obtained for wood in central Sweden. The carbohydrate composition has been checked against data given by Annergren, Rydholm and Vardheim (1963) and Sjöström (1993b) since the analytical level shows some drift and certain adjustments therefore have to be made. Particularly in the case of birch from which some xylose is easily lost in the determination of carbohydrate components because of incomplete separation from glucuronic acid in the hydrolysis to monomeric sugars. The table gives about the right magnitudes to illustrate the differences but should not be taken as an absolute truth.

| Pulp | Kappa number | | Yield | Chemical composition. % | | | % |
|---------------------------------------|--------------|----------|-------|-------------------------|----------|--------|---------------------------------------|
| | | | | DCM | | | |
| | unbleached | bleached | % of | extract | Lianin | Cellu- | Hemi- |
| | | | wood | tives | | lose | cellulose |
| | | | | | | | |
| Spruce pulpwood | | | 100 | 1,5 | 27 | 40,5 | 31 |
| Birch pulpwood | | | 100 | 3 | 21.5 | 30.5 | 36 |
| Liplesched groundwood pulp | | | | | 21,5 | | |
| soruce freeness 90-100 CSF | | | 98.5 | 10 | 27 | 41 | 31 |
| Unbleached TMP, spruce | | | 00,0 | .,0 | | | |
| freeness 100 CSF | | | 98.0 | 1.0 | 27.5 | 41.5 | 30 |
| Peroxide-bleached TMP. | | | - 510 | | | | |
| spruce, freeness 35-50 CSF | | | 96,5 | 0,5 | 27 | 42 | 30,5 |
| Peroxide-bleached CTMP, | | | | | | | · · · · · · · · · · · · · · · · · · · |
| spruce, freeness 750 CSF | | | 92 | 0,1 | 25,8 | 44,0 | 30,1 |
| | | | | | | | |
| Unbleached NSSC pulp, birch | | | 83 | 0,5 | 17 | 47,5 | 35 |
| Unbleached bisulphite pulp, | | | | | | | |
| spruce | | | 70 | 0,5-1,0 | 20 | 58 | 21- |
| | | | | | | | 21,5 |
| Unbleached high yield kraft | | | | | | | |
| pulp, pine | 90 | | 56 | 0,1 | 13 | 67,5 | 19,4 |
| Unbleached chemical kraft pulp, | | | | | | | |
| pine/spruce | 35 | | 48,5 | 0,1 | 5 | 76 | 18,9 |
| · · · · · · · · · · · · · · · · · · · | | | | | | | |
| ECF-bleached kraft pulp, birch | 18 | 1,0-1,5 | 50,6 | 0,1 | 0,2 | 70,5 | 29-29,5 |
| TCF-bleached kraft pulp, birch | 18 | 3 | 50,3 | 0,1 | 0,3-0,4 | 71 | 28,5 |
| TCF-bleached acid sulphite | | | | | | | |
| pulp, spruce | 15 | 0,5 | 47,5 | 0,3 | 0,1 | 84,5 | 15 |
| Conventionally bleached kraft | | | | | | | |
| pulp, pine/spruce | 35 | 0,5 | 45,2 | 0,1 | 0,1 | 82 | 17,5-18 |
| ECF-bleached kraft pulp, pine/ | | | | | | | |
| spruce | 25 | 0,5-1,0 | 44,5 | 0,1 | 0,1-0,15 | 82,5 | 17-17,5 |
| TCF-bleached kraft pulp, pine/ | | | | | | | |
| spruce | 20-25 | 1-2 | 43,5 | 0,1 | 0,15-0,3 | 83 | 16,5-17 |
| TCF-semibleached kraft pulp, | | | | | | | |
| pine/spruce | 15 | 4 | 42 | 0,1 | 0,6 | 84,5 | 14,5-15 |

Table 1. Chemical composition of different pulps from spruce, pine, pine/spruce (about 60/40), and birch pulpwood grown in Middle Sweden

The low-molecular mass lipophilic extractives may be very important as disturbing material in the papermaking fibres in spite of their low content. We have therefore assumed in our compilation that they are removed as efficiently as the pulping process permits. This is not always the case in practical operation, and this may cause major disturbances both in the pulp mill and in the paper mill. Modern process techniques can, in most cases, bring the extractives content down to a low level by effectively solubilising or dispersing the extractives. An effective solubilisation must be followed by effective washing. Even small amounts of solubilised pitch which are not removed in the washing stage constitute a considerable risk of forming disturbing deposits since they are not firmly attached to the fibres.

With the exception of mechanical pulps, the main objective in pulping is delignification, in many cases together with a modification of the swelling properties of the residual lignin. Delignification in the kraft process occurs mainly through fragmentation and creation of phenolates into the lignin fragments and the residual lignin. Since phenolates does not exist at a pH below about 10 they do not affect the swelling ability of residual kraft lignin. The rather low swelling of kraft lignin is due mainly to a low amount of carboxyl groups. The resistance towards swelling of the kraft lignin is a serious problem in the paper mill refining operation.

Bleaching solubilises the lignin primarily through the introduction of carboxyl groups. The very small amount of residual kraft lignin in bleached pulp can be expected to have an increased amount of carboxyl groups and hence a considerably stronger swelling power. In fact, it should be noted that a fair amount of the COOH-groups in fully bleached pulps could be attributed to the usually very small amounts of residual lignin, as shown by Gellerstedt (1991). In pulps predominantly bleached by means of oxygen and alkaline peroxide, 4-deoxy-4-hexenuronic acid is reported by Buchert (1995) and Laine (1996^a) to dominate the acidic groups in the pulp.

Treatment with sulphite in CTMP processes, neutral or alkaline sulphite processes and different kinds of acid sulphite processes introduces sulphonate groups, which exist as charged groups over the whole pH range applied in papermaking. Together with a decrease in crosslinking in the case of the residual lignin, sulphite lignin has a considerably increased swelling ability, Goring (1971), and does not resist the refining of fibres in the paper mill as does kraft lignin. The properties of unbleached CTMP are strongly affected by sulphonate groups in the residual lignin. In peroxide-bleached CTMP, the bleaching process has introduced a considerable amount of carboxyl groups, which significantly increase the swelling ability of the lignin further, as shown by Engstrand et.al. (1991).

Cellulose is dissolved to some extent in the kraft process, primarily through socalled "peeling" of the reducing end group of the cellulose. Material balances indicate that other dissolution mechanisms must also be considered for instance dissolution of short cellulose fragments liberated through alkaline hydrolysis. A typical cellulose yield for chemical kraft pulp is reported by Sjöström (1993b) to be about 90 %.

The rather small dissolution of cellulose is combined with a much more drastic degradation of the cellulose through alkaline hydrolysis, in bleached kraft pulps down to DP levels of about 1000 to 1500, according to the recommended translation of intrinsic viscosity measurements (SCAN-C 15:62), with even lower values under unsuitable process conditions. It is likely that the amorphous cellulose is more exposed to these changes than the crystalline cellulose and this should lead to an increased crystallinity of the remaining cellulose. The process may, however, also affect the degree of order of the crystalline cellulose somewhat.

The high cellulose yield in the pulping process leads to successively increasing cellulose content up to a high level in bleached pulp. In general, cellulose is the most important strength-bearing component in pulp fibres. The zero-span strength of different pulp fibres has been shown to be strongly correlated with the cellulose content, Page (1985). Above a certain level, an increase in cellulose content does not produce better strength. It might be speculated that it is partly because of the increased cellulose degradation which eventually passes a critical level, and partly because some hemicellulose is needed for proper stress distribution in the fibre wall.

In extended delignification in modified kraft cooks down to very low kappa numbers (well below 20 for softwood and below about 15 for birch) a considerably increased cellulose dissolution occurs and at the same time an increased cellulose content is obtained. This has led to such high cellulose contents that it has become extremely difficult to develop strength in paper mill refining (Annergren 1994). From strength characterisations of different pulps it can be concluded that the cellulose degradation is not homogeneous in kraft pulping, although it is more homogeneous than in acid sulphite pulping. For unbleached kraft pulps with low kappa numbers and bleached kraft pulps, there is a strong correlation between fibre tensile strength properties (for instance wet zerospan tensile strength or tear strength at a given tensile strength) and intrinsic viscosity and its corresponding DP. But the strength effects seem to be related to a local weakening of the fibre wall rather than to a general weakening of the fibres, which can be expected to be more directly related to an average DP.

Acid sulphite cooks give only negligible cellulose dissolution down to fairly low pulp yields. This means that the originally amorphous cellulose is not significantly removed. Nevertheless, it has been reported by Jayme (1973) that sulphite pulps have a higher proportion of crystalline cellulose than kraft pulps, which may be interpreted as indicating a secondary crystallisation of the cellulose. The cellulose degradation is also strong in these sulphite cooks, but compared at a given lignin content, the intrinsic viscosity of the sulphite pulps is somewhat higher than that of the kraft pulps. In spite of the higher viscosity level, the negative effects of cellulose degradation are much more pronounced in sulphite pulps, probably due to greater heterogeneity. A classical example of such a heterogeneous attack is the strong effect on pulp strength in the case of acid sulphite pulping of wood with considerable compression damage on the wood in the chipping operation, Hartler (1963). The variations in strength of chemical acid sulphite pulps are usually dominated by such compression damage.

Hemicelluloses are dissolved and degraded to a large extent in the pulping processes. It is mainly the most resistant hemicelluloses, glucomannan and xylan, which remain in the chemical pulps. Glucomannan is initially very sensitive to kraft cooking conditions and is dissolved to a large extent already in the beginning of the kraft cook whereas xylan is more resistant. This means that the content of xylan in chemical softwood kraft pulp becomes almost the same as that of glucomannan or sometimes even higher, in spite of the considerably higher content of glucomannan in wood. Yield-increasing measures, however, primarily affect glucomannan. Hemicellulose in hardwood kraft pulp is dominated by xylan.

The dissolution of hemicelluloses is at least as strong in acid sulphite pulping as in kraft pulping and the degradation is even stronger, as pointed out by Annergren, Rydholm and Vardheim (1963) as well as by Sears et.al. (1978) and Kettunen

et.al. (1982). In this case, a considerably higher yield of glucomannan is obtained so that typically about 2/3 of the hemicellulose in chemical pulp is glucomannan. Further cooking affects mainly glucomannan whereas the remaining xylan seems to be somewhat more resistant.

Of considerable importance are the acidic groups on xylan, mainly 4-O-methylglucuronic acid groups, which are retained to a somewhat greater extent in the kraft cook but seem to a large extent to be transformed to 4-deoxy-4-hexenuronic acid groups, see Teleman (1995). Normal bleaching removes a large portion of the acid groups whereas certain TCF-bleaching performed mainly with peroxide leave a considerable but varying portion of these groups, Buchert (1996). The acidic groups affect swelling and retention conditions in papermaking and are discussed in more detail later in this paper.

Xylan seems to combine with cellulose in more ordered structures in kraft pulping as indicated by Mitikka (1995), probably due to the stripping off of branches from the xylan chain and a kind of crystallisation on the cellulose surfaces. In general, kraft pulp hemicellulose is less accessible to extraction with for instance alkali than hemicellulose in different acid sulphite pulps. This can be interpreted as a higher degree of order in kraft pulp hemicellulose, which should be important for the toughness of the kraft fibres. A somewhat higher degree of order is obviously also obtained in the two-stage acid sulphite pulping of softwoods through the deacetylation of the glucomannan, which considerably increases the yield of glucomannan in pulp but does not increase the resistance towards alkaline extraction of this glucomannan, Annergren (1959).

Hemicelluloses play an important role in promoting swelling and refining. Excessive amounts of hemicelluloses are a disadvantage since they do not contribute to strength but produce brittleness. Normal kraft pulps seem to have a fairly well balanced ratio of cellulose to hemicelluloses, with quite high cellulose content. For pulp with a high lignin content, for instance high yield kraft pulp for linerboard, a somewhat higher hemicellulose content may, however, be beneficial to decrease the refining resistance (i.e. swelling resistance) that the high lignin content gives.

Considerable work has been devoted to establishing relationships between the gross chemical composition of fibres (as discussed above) and the properties of the finished paper, see for instance Annergren, Rydholm and Vardheim (1963).

Complicating factors are the increasing complexity of papermaking furnishes and some paper machine variables which are difficult to interpret. The behaviour of the fibrous material in the papermaking process (runnability) and its relation to the chemical composition of the fibres, on the other hand, are still not particularly well established, the reasons being that mapping of the critical phases of the process is in general insufficient, that one must also consider individual characteristics of each paper machine, and that relevant laboratory methods for predicting the behaviour on the paper machine are scanty. For the present fastrunning paper machines, the runnability seems to be the critical issue in the evaluation of papermaking fibres. Consistent properties are no doubt one of the most important issues for good runnability, particularly in the most modern paper machines where bottlenecks have been removed through more sophisticated process solutions.

CHEMISTRY OF THE FIBRE SURFACE

Interactions between fibres in the wet state and between dry paper and other substances

The surface chemistry of the fibres and its importance for the surface chemistry of the paper has been given a lot of attention during recent years. This interest has been focused mainly on the interaction between paper and other materials, see for example Berg 1993^a, but the surface chemistry is also important for the interaction between the fibres in the wet state during the consolidation of the paper. During this process it has earlier been shown that the state of swelling of the fibre wall and the apparent modulus of the fibre wall will determine the deformation of the fibres in the fibre/fibre contacts (see for example Lindström 1986 and Scallan and Tigerström 1992). Before entering into a more detailed overview of the work conducted to determine both the surface energy of the fibres and fibre swelling it is necessary to review the detailed interaction between the fibres during consolidation of the wet fibre web in order to clarify why the chemistry of the fibres surface is so important. A short description will also be given on how the surface energy of the paper will determine the dry paper and other solids or liquids.

Two fibres coming into close contact with each other can as a first approximation be represented by the interaction between two crossed cylinders as illustrated in **figure 1.** When water is removed, capillaries are formed in the fibre/fibre contact and capillary forces pull the fibres together.



Figure 1. Schematic representation of the interaction between two fibres during water removal. The radius of the fibres is R, the distance between the fibres D and the affected area in the contact zone is A

The forces acting between the fibres, apart from the capillary forces, are the wellknown electrostatic forces, van der Waals forces and polar type of interactions often referred to as acid/base interactions. For cellulose fibres, the electrostatic interactions are dominated by carboxylic groups or sulphonic acid groups (see for example Sjöström 1989). The origin of these groups will be discussed in more detail below. Naturally this view of the fibres as crossed cylinders is a rough approximation and is used here to demonstrate the influence of different factors on the interaction between the fibres. In a real situation, the fibres are deformed as the capillary forces pull the fibres together and in the dry state the fibres have a shape which more resembles two ribbons brought close to each other. For crossed cylinders the total potential energy (W_{cyl}) between the cylinders can be represented by the equation:

$$W_{cyl} = \frac{128\pi \operatorname{Rn} \operatorname{kTY}}{\kappa^2} \exp\left(-\kappa \cdot D\right) - \frac{A \cdot R}{6D}$$
[1]

where

R = Radius of the cylinders (i.e. Fibres)

 κ = Debye length

A = Hamaker constant of the cellulose/water system

D = Distance between the cylinders

$$Yo = \frac{\exp(ze\psi_o/2 kT) - 1}{\exp(ze\psi_o/2 kT) + 1}$$

 ψ_0 = Surface potential

 n_0 = Number of ions per unit volume in solution

z = Valency of the counter ion

By inserting appropriate values for the surface charge and Hamaker constant for the cellulose (in the present calculations a surface charge of 25 μ eq/g, a specific surface area of the external surface of the fibres of 1 m²/g, a Hamaker constant of cellulose of 6.7 • 10⁻²⁰ J, Winter (1987), and a Hamaker constant of water of 3.82 • 10⁻²⁰ J) the results presented in figures 2a and 2b were obtained.



Figure 2a. Interaction energy between two crossed cylinders, i.e. fibres, calculated from eq.1. A salt concentration of 10⁻⁴ M NaCl was used for these calculations and different degrees of neutralisation of the surface charges were chosen to demonstrate how this influences the interaction between the cylinders. The vertical line shows the Debye length.



Figure 2b. Interaction energy between two crossed cylinders, i.e. fibres, calculated from eq.1. A salt concentration of 10² M NaCl was used for these calculations and different degrees of neutralisation of the surface charges were chosen to demonstrate how this influences the interaction between the cylinders.

It is evident in these figures that:

- a) the electrostatic repulsion is very large in deionised water and the charge has to be significantly reduced to allow for the fibres to come close enough together to form the bond necessary for paper strength to develop. The forces created by this electrostatic repulsion are naturally counteracted by the capillary forces existing in the contact zone, as is discussed below.
- b) at higher ionic strengths this repulsion is naturally reduced, but values of about $1 \cdot 10^5$ kT are still found at 0.01 M NaCl.

In figures 2a and 2b it is also seen that very large surface potentials are achieved. In reality counterion binding leads to a decreased surface potential, but this has not been taken into account in these very simple calculations.

At the same time, the capillary pressure, caused by the water meniscus formed in the contact zone between the fibres, draws the fibres together. To overcome the repulsion between the fibres, a sufficiently small capillary radius has to be formed before molecular contact between the fibres can occur. A contact zone between the fibres is then formed and the size of this contact zone is very dependent on the elastic modulus of the fibre wall, which in turn is very dependant on the degree of swelling of the fibre wall. The true nature of the surface of the cellulosic fibres in the contact zone determines to what extent there will be molecular contact or not between the fibres. It is strongly believed that the flexibility of the outer surface layers of the fibres, as discussed by Pelton (1993) is very important for the degree of bonding between the fibres.

This discussion shows that the electrostatic charge, the Hamaker constant and the swelling of the cellulosic fibre wall are very important for how the interaction between the fibres takes place. The swelling forces within the fibre wall are not however sufficient to create a flexible fibre with a large bonding ability to other fibres. In order to achieve this, it is necessary to delaminate the fibre wall and thereby remove some of the swelling restraints created by the interlamellar bonds within the fibre wall. This delimitation is brought about by the beating operation which is thus indirectly essential for the swelling of the fibre wall. A knowledge of the size of these entities, i.e. electrostatic charge, Hamaker constants and fibre swelling, and the factors controlling their magnitude is hence very important in order to understand the development of bonding between the fibres and the creation of paper strength.

Another important factor, which has to be considered, is how the pressing operation influences these interactions. To have a complete view of the interaction, the force-balance between the fibres should be with the force complemented with the force applied during pressing. The pressing force will naturally compress the fibres, i.e. flatten the "cylinders", and help the capillary forces to overcome the electrostatic repulsion. On the other hand, the pressing naturally removes more water and the size of the contact zone (i.e. smaller capillaries are formed directly) between two fibres will hence become smaller when more water is removed. All this shows that the model of the fibres as two interacting cylinders must be used with caution.

According to Fowkes (1962 and 1964) and as described in detail by van Oss (1994) and Berg (1993^b) there are additional polar interactions between substrates, i.e. fibres, in aqueous media and currently there is a large scientific debate on how these interactions should be determined and also summarised theoretically. Without entering this debate, it can be stated that there will be additional forces between the fibres in the wet state depending on the acid/base properties of the fibres, and these will naturally add to the forces already mentioned. Today the change of the acid/base interaction with distance between the fibres is not known and these forces have therefore not been included in the calculations.

When the dry paper is contacted with other types of substances, the interaction will be controlled by the van der Waals interactions and the acid/base interactions. This was described for example by Berg (1993^a) and the total work of adhesion between two different materials can be described by the equation:

$$W_{total} = W^{LW} + W^{AB}$$
where
$$W^{LW} = Lifshitz-van der Waals interactions$$

$$W^{AB} = Acid-Base Interactions$$
[2]

The Lifshitz-van der Waals interactions can in turn be described by the following relationship.

$$W^{LW} = 2 \cdot (\sigma_s^{LW} \cdot \sigma_l^{LW})^{1/2}$$
[3]

where

 σ_{c}^{LW}

= Lifshitz-van der Waals contribution to the surface energy of the solid

$$\sigma_1^{LW}$$
 = Lifshitz-van der Waals contribution to the surface energy
of the liquid

and

$$W^{AB} = 2 \cdot ((\sigma_{s}^{+} \cdot \sigma_{l}^{-})^{1/2} + (\sigma_{s}^{-} \cdot \sigma_{l}^{+})^{1/2})$$
[4]

where $\sigma_s^+, \sigma_l^+ =$ Acid contribution to the surface energy of the solid and liquid respectively

 σ_s, σ_l = Base contribution to the surface energy of the solid and liquid respectively.

There are several ways of calculating the acid/base interaction between the surfaces and the van Oss approach (van Oss 1995) was chosen here to illustrate how the composition of the fibre and paper surface influences the interaction with other materials. From equation [2] - [4] it is clear that

- a) the van der Waal interactions are always important for the total interaction between different materials.
- b) polar interactions are also important for many materials the type of polarity of the materials is important. If both materials have electron donor properties there will be no polar interaction, despite the fact that both materials have polar properties.

Berg, (1993^{a, b}) also gave several examples of how differences in the acid-base properties of different materials really influence the interaction with liquids and solids.

It is obvious that a knowledge of the chemical composition of the fibre surface is important in order to optimise the interaction of the fibres in the wet state, to enhance fibre/fibre bond formation and to optimise the surface chemistry of papers for use in different practical applications. The following sections will therefore be devoted to a summary of what is known about

- a) the surface chemical properties of the constituents of the fibres
- b) the surface chemical properties of different fibres (pulps) and papers.

Surface energy of the chemical constituents of the fibre wall, fibres and paper

Before starting the detailed description of the available data on the surface chemistry of different materials it may be appropriate to mention that the results are naturally very dependent on the techniques used to collect the data. The most easily available technique for surface energy determinations is contact angle measurements with different liquids. This technique makes it possible to determine both the LW-part of the surface energy and the acid/base part. However, there are severe drawbacks and no satisfactory method has been defined for determining contact angles on porous substrates such as paper. Another popular method for the determination of surface energy and the different components of the surface energy is Inverse Gas Chromatography (IGC) where the retention times of different probe molecules are measured. The evaluation techniques for the data collected by this method often give results different from those given by the contact angle methods and the reason for this is still not exactly known. As a further complication, there are different evaluation principles for the data collected with both contact angles and IGC. These problems are discussed in the different sections below, but due to the large variation in the techniques used, the data in the tables must be treated with caution.

Surface energy determined by contact angle measurements

The origin of the use of contact angle measurements is the Young equation which gives a relation between the surface energy of the solid, the surface energy of the liquid, the interaction between the solid and the liquid and the contact angle of the liquid on the solid.

$$\sigma_{s} = \sigma_{1} \cos \theta + \sigma_{s,1}$$
^[5]

| where | σ_{s} | = | Surface energy of the solid in the environment used in the |
|-------|--------------|---|--|
| | | | experiments |

- σ_{e1} = Surface energy of the interface between the solid and the liquid
- σ_1 = Surface energy of the liquid in the environment used in the experiments

It is also commonly known that σ_{s1} can be characterised by the relationship:

$$\sigma_{s,l} = \sigma_s + \sigma_l - I^d - I^p$$
[6]

where

 I^{d} = Contribution of the dispersive forces to the surface energy of the interface

 I^{p} = Contribution of the polar forces to the surface energy of the interface

It must here be emphsized that the dispersive contribution in equation [6] is <u>not</u> the same as the Lifshitz- van der Waals term mentioned in e.q. [2]. In the treatment given in equation [6], the dispersion forces include only the London dispersion forces and the dipole-dipole, induced dipole- dipole interactions and hydrogen bonding interactions are all included in the polar term. The treatment in equation [4] is based on the work by Chaudhury (1984) who showed that the Lifshitz- van der Waals component is simply a sum of the London dispersion forces, the induction forces (Debye) and the dipole forces (Keesom). This means that it is not possible exactly to compare the results from evaluations by equation [6] and equation [4] even though they should give the same trends when characterising different surfaces.

It has been shown for example by Wu (1982), that the term I^{d} in equation [6] can be written as

$$I^{d} = 2 \cdot (\sigma_{s}^{d} \cdot \sigma_{1}^{d})^{1/2}$$
[7]

By inserting equations [7] and [6] into equation [5] the following useful relationship is obtained:

$$\sigma_{l}(1 + \cos \theta) = 2 \cdot (\sigma_{l}^{d} \cdot \sigma_{s}^{d})^{1/2} + I^{p}$$
[8]

By using different liquids with known properties, it is possible to determine σ_s^d and I^p and, knowing how to resolve the I^p term mathematically, it is also possible to determine the polar properties of the solid surface. The derivation of equation [8] has been included since a fair amount of work was conducted before the acid/base concept was introduced. Some of the earlier contact angle data has been transformed into a dispersive component of the surface energy and a polar

interaction with the liquid in question, since the mathematical form of the polar interactions was not known. However, later work has made use of equation [4] and liquids characterised from the Lifshitz- van der Waals and acid-base concept and therefore these data are also used in the summary below.

Sandell and Luner (1969) prepared films from cellulose and hemicellulose, Lee and Luner prepared films from lignin (1972) and Winter (1987) prepared films from different cellulose materials and the results of their work are given in **table 2.** In this table, the critical surface tension of the hemicellulose films has also been included. This entity is achieved by measuring $\cos \theta$ of a liquid on the sample for different apolar liquids, extrapolating to $\cos \theta = 1$ and reading the surface tension of the liquid at this position. This value can then be taken as a rough estimate of the dispersive part of the surface energy of the solid. It should be stated that this treatment holds true for nonpolar solids but for polar solids, it must be treated with much caution (Wu 1982).

 Table 2.
 Summary of the dispersive component of the surface energy of films from lignin, cellulose and hemicellulose. In the table, the polar interaction with water has been included as well as the critical surface energy of some materials. The data was used by applying equations [6] - [8]. No full chemical characterisation of the materials was given by the authors.

| Material | σ_{s}^{d} (mNm/m ²) | l ^p (mNm/m ²) | σ _c (mNm/m ²) |
|---|--|---|---|
| Lignin (hardwood) Cellulose (Avicel) * Cellulose (Rayon) ** Cellulose (MCC) *** Hardwood xylan **** Softwood xylan ***** | 41 45 25.1 37.2 - - | 50 78.6 89 78 - - | 36 36 - 34 35 |

* Sandell and Luner (1969), from commercial microcrystalline (MCC) cellulose

** Winter (1987), from a non-extracted commercial rayon material

*** Winter (1987), from specially prepared microcrystalline (MCC) cellulose

**** Sandell and Luner (1969) extracted with DMSO

***** Sandell and Luner (1969) extracted with water

The lignin film was prepared by Lee and Luner (1972) from a commercially available kraft lignin.

Table 2 shows that the dispersive part of the interaction between cellulose, hemicellulose and lignin and different liquids is always important and that the greatest difference between the cellulose and the lignin can be found in the polar interactions with water. This difference means that more polar liquids will wet the cellulose much more easily than they will wet the lignin. To illustrate this more the I^P term in table 2 was recalculated into a σ_s^P by using a geometric average as in equation [9], also for the polar part of the surface energy. This is naturally not correct but it can be used to illustrate the difference between cellulose and lignin.

$$I^{P} = 2 \cdot (\sigma_{I}^{P} \cdot \sigma_{s}^{P})^{\frac{1}{2}}$$
[9]

With this treatment the data given in task 3 were obtained.

Table 3. Summary of the surface energy data for lignin and cellulose from the work of Felix (1993)*, Westerlind (1988)** and Lee and Luner (1972)¹⁾. The data in row 1 and 3 have been calculated by applying a harmonic mean equation according to Wu (1982) instead of the geometric mean used for the rest of the data in the table. The data from the work by Felix and Westerlind were collected from measurements with single fibre wetting whereas the rest of the data were collected from goniometric measurements.

| Material | Liquids | σ_s^d (mNm/m ²) | σ_s^p (mNm/m ²) | σ_{s} (mNm/m ²) |
|---|---|------------------------------------|------------------------------------|------------------------------------|
| Cellulose * Cellulose(cotton) ** Cellulose(cotton) ** Cellulose (Avicel) ¹⁾ | Water/CH ₂ ₂ Water/CH ₂ ₂ Water/CH ₂ ₂ Water/αBr.N | 25.5 27.5 31.0 42.2 | 43.2 41.0 47.0 26.5 | 68.7 68.5 78.0 68.7 |
| Cellulose ¹⁾ | Glycerol/aBr.N | 42.2 | 17.6 | 59.8 |
| Lignin ¹⁾ | Water/aBr.N | 43.5 | 10.9 | 54.4 |
| (Hardwood) Lignin ¹⁾ (Hardwood) | Glycerol/αBr.N | 43.5 | 2.4 | 45.9 |

These results show more clearly that the polar component is considerably smaller for the hardwood lignin, which means that polar liquids will wet the cellulose more easily. It also means that, when fibres with surfaces covered with lignin are brought into contact with other polar materials there will be a much lower interaction between these materials than between fibres containing only cellulose and the material in question.

Another factor, which will influence the interaction, is naturally the hemicellulose, but no comparable data are available for hemicellulose.

The results in **table 3** also show that there is a large scatter in the data, probably due both to the nature of the material used and the method used for evaluation. There is hence a great need for comparative investigations of the different methods and a standardisation of the measurements, in order to be able to compare the data on a quantitative and not just a qualitative basis.

Later work conducted after the introduction of the acid-base concept includes this type of evaluation of the fibres or films. A large volume of data has been prepared by van Oss (1994) and these data also include cellulose, but the origin of this cellulose material is not defined. Work by Berg (1993^a) and by Toussaint and Luner (1993) also include fibres and films respectively. Berg (1993^a) used single fibre wetting with different liquids and Toussaint (1993) used cellulose films prepared from cellulose acetate and subsequently deacetylated. The results of these investigations are summarised in **table 4**.

 Table 4.
 Summary of the surface energy of a number of different cellulosic materials.

 Apart from the Lifshitz-van der Waals component of the surface energy the acid base properties of the materials, calculated according equations [3] and [4] are summarised.

| Material | σs ^{LW} (mNm/m²) | σ_{s}^{+} (mNm/m ²) | σ _s (mNm/m²) | σ _s ^{ab} (mNm/m²) | σ _{total} (mNm/m²) |
|-------------------------|------------------------------|--|----------------------------|--|--------------------------------|
| SWBK ^{a)} | 41.8 | 0.2 | 24.5 | 4.4 | 46.2 |
| HWBK ^{a)} | 43.2 | 0.4 | 16.3 | 5.1 | 48.3 |
| CTMP ^{a)} | 30.8 | 1.0 | 67.8 | 16.5 | 47.3 |
| Cellulose ^{b)} | 44 | 1.6 | 17.2 | 10.5 | 54.5 |
| Cellulose ^{c)} | 39.1 | 2.0 | 39.7 | 17.8 | 56.9 |

a) Berg, J. (1993)^a

b) van Oss. (1994)

c) Toussaint, A.F. and Luner, P. (1993)

The Lifshitz-van der Waals components of these materials have approximately the same values except for the CTMP fibres. This is also expected since these fibres are covered with lignin. The result is not however in accordance with the data in table 3, where it was shown that the dispersive component of the surface energy was about the same for lignin and cellulose. The data are not however fully comparable, since the Lifshitz van-der Waals component by definition is different from the σ_s^{c} as determined according to equation [7]. Another explanation can be that the lignin materials in the two investigations are not the same, since the CTMP fibres contain hydrogen peroxide bleached lignin whereas the sample reported in table 3 was not peroxide bleached.

Another factor, which was not given by the authors, was the content of sulphonic acid groups, which has a large influence on the properties of the fibres. Considering all this, it can only be concluded that the samples cannot be compared thoroughly, since the characterisation of the samples is not sufficiently good. In order to make a satisfactory comparison, it is necessary to know

- 1) the concentration of extractives.
- 2) the types and degree of modifications of the lignin in the pulps and also whether there is a difference between softwood and hardwood lignin.
- 3) how the fibres have been defibrated, which parts of the cell wall are exposed.
- 4) even when rayon was used it is necessary to know how the rayon has been produced, since the process may leave contaminates which in turn may be very important for the surface properties of the rayon films.

The table also shows that samples, which should be similar, i.e. the SWBK, HWBK and the cellulose samples still have very different properties. This might be caused by some flaws in the method but it is probably only a sign that the materials have different properties. This statement is based on the results presented by Toussaint and Luner (1993) who showed that the measured changes in the surface energy and its separate components could be used to predict the interaction between cellulose and synthetic polymers.

Another result presented in table 4 is that the fibres have a basic character, which is rather unexpected since the fibre surface, at least of the CTMP, should have a

lot of acidic groups. It is not only the sulphonic and carboxylic acid groups that can contribute to the interactions as defined by the definition of the Lewis acid/base concept, but also these groups are believed to play a dominating role for this material. On the other hand, the occurrence of a basic nature of the fibres is not surprising, since the method used to determine these properties (Berg 1993^a) often results in surfaces with basic properties, and Berg (1993^b) also claims that this is a sign that this evaluation principal is not totally correct. Without going into too much detail on this topic, it should also be mentioned that the properties of the different liquids used to determine the contact angle have been determined under the assumption that the electron donor and electron acceptor properties of water are the same, i.e. 25.5 mNm/m^2 . Recent publications have shown that the Lewis acid component for water should be 34.2 mNm/m² and that the Lewis base component should be 19 mNm/m², (Lee 1996). This results in lower values for the Lewis base component for all surfaces, but not sufficiently to change the properties to acidic properties. As for the results in table 4, it must again be concluded that further investigations are needed where the surface properties of the fibres are systematically changed and then characterised with these methods.

In view of this, the large base component of the surface energy of the CTMP is difficult to discuss without any further information, but this large value indicates that it should be possible to find certain specific properties of these fibres.

It is also interesting to note that there are no systematic characterisations of extractives available in the literature regarding Lifshitz-van der Waals components and acid base properties of the pure components. This is surprising, since these components are believed to have a profound effect on the adhesive interaction between fibres and other materials. It was shown by Aberson (1970) that the existence of low amounts of benzene extractives (< 0.1 %) resulted in drastic changes in the contact angle of water on these fibres. This is shown in **figure 3** where the contact angle is shown as a function of the extractives content.



Figure 3. The influence of extractives content on the contact angle of bleached sulphite fibres against water. In the figure results from both "fresh" fibres and aged fibres are shown. Reprinted from Aberson (1970)

Aberson (1970) also showed that this difference in contact angle between different pulps had a very large effect on the absorption properties of pulps containing these fibres. The same type of results has also been found in later investigations by Hodgson and Berg (1988).

The ageing effect shown by Aberson (1970) in figure 3 has been discussed in terms of vapour phase migration of extractives, as originally shown by Swanson (1959). Without going further into the discussion of extractives it should be stated that further investigations of pure extractives components regarding both Lifshitz-van der Waals parts of the surface energy and acid/base properties of the surface energy are definitely needed to understand the complete interaction between fibres and other materials.

As a final comment on the surface energy evaluation of cellulosic fibres through contact angle measurements, it should be mentioned that the fibres are very difficult to characterise both since they have a heterogeneous surface with a mixture of lignin, cellulose, extractives and hemicellulose and since even fairly clean surfaces of bleached chemical sulphite fibres for viscose production have moisture- and temperature; dependant surface properties. This was shown in early work by Borgin (1961) where it was shown that the water contact angle could be changed from 35° C to 55° C by heat treatment at 140°C and 0 %RH for 7 hours. This was interpreted as being due to a reorientation of the hydroxyl groups at elevated temperatures towards the interior of the fibres. This changes the properties of the fibres and also shows that a definition of the ground state used for evaluation of surface energy of the fibres is also very important. A word of caution is needed for this interpretation, however since the heat treatment used during the drying might have caused a migration of extractives, which are probably present in these fibres.

In summary, it must be concluded that despite the large efforts made by different researchers, it is striking to note that the chemical characterisation of most materials investigated is not thorough enough to allow for unambiguous interpretations of the results. The same is also true of the different techniques and it is obvious that a standardisation of how the contact angle can be and should be used is very important for future research in this area.

Surface energy determined by inverse gas chromatography

The discussion so far has been focused on the acid/base concept as defined by van Oss et.al. (1994) and the evaluations of the acidbase properties have also been focused on different concepts of this evaluation principle. Since the techniques are very different for the evaluation of the acidbase properties and since the entities achieved with the different evaluation principles are also very different, the following text is fairly detailed in order to compare the different data in a clear way.

As proposed by Fowkes (1978), the acid/base part of the work of adhesion, W^{AB} as defined in equation [2], is a direct function of the enthalpy of the formation of an acid/base linkage between different materials according to:

| WAB | $d = fn (-\Delta H^{AB})$ | [10] |
|-----|---------------------------|------|
| | | |

| where | n f | Number of acid/base linkages per unit area Conversion factor to equate the Gibbs free energy with an |
|-------|-----------------|---|
| | _ | enthalpic quantity |
| | ΔH^{AB} | = Enthalpy of the acid/base linkage formation |

One common way of determining the enthalpy of an acid/base linkage formation is that of Drago as described by Jacob and Berg (1994). However, this approach not has been applied to cellulose to any great extent since the Drago approach cannot handle probe molecules with both acidic and basic sites it. Another approach which can handle probes with both acidic and basic sites is the Gutmann (1966) approach which can be written in the following form.

$$(-\Delta H^{AB}) = (DN_{S}AN_{L})/100 + (DN_{L}AN_{S})/100$$
[11]

where $DN_s = Electron-donating ability of the solid$ $<math>DN_L = Electron-donating ability of the probe molecules$ $AN_L = Electron-accepting ability of the probe molecules$ $AN_s = Electron-accepting ability of the solid$

This equation means that it is possible to determine the electron-donor and electron-acceptor properties of the solid by determining ΔH^{AB} for different probes and by plotting $\Delta H^{AB}/AN_L$ as a function of DN_L/AN_L . The slope of this graph gives AN_s and the intercept gives DN_s . It was found by Dorris and Gray (1980) that the Gibbs free energy of interaction between a probe molecule and a solid could be determined by Inverse Gas Chromatography (IGC) from the relationships:

$$W_{A} = -\Delta G_{ads} / a_{mol}$$
[12]

 W_{A} = Work of adhesion between a probe molecule and a solid

where

 ΔG_{adc} = Gibbs free energy of adsorption

 a_{mol} = Molar area of the probe molecule on the solid

$$-\Delta G_{ads} = RT ln V_N + C$$

where

R = Gas constant

T = Absolute temperature

 V_N = Retention volume in the IGC equipment

C = Constant

Dorris and Gray (1980) also showed that the Lifshitz-van der Waals part of the surface energy could be determined by combining equations [3], [12] and [13] into the equation:

$$RT \ln V_{N} = 2a_{mol} \left(\sigma_{s}^{LW} \cdot \sigma_{l}^{LW}\right)^{1/2} + C3$$
(14)
where $\sigma_{s}^{LW} = Lifshitz$ -van der Waals component of the surface energy of

 $\sigma_1^{L''}$ = Lifshitz-van der Waals component of the surface energy of the probe molecule

By using probe molecules having only London dispersive interactions with the solid and by plotting $RTlnV_N$ as a function of $amol(\sigma_l^{LW})^{1/2}$, it is possible to determine σ_s^{LW} from the slope of this graph. In order to determine the acid/base interaction between a probe molecule and the solid, a probe molecule with a known molecular area on the solid is injected in the IGC equipment and its distance from the reference line according to equation [14] is then a measure of the acid-base contribution to the Gibbs free energy of adsorption. In mathematical terms this can be written as:

$$-\Delta G^{AB} = RT \ln \left(V_N^{Probe} / V_N^{alkane} \right)$$
 [15]

From these equations, it is possible to determine both the Lifshitz-van der Waals component of the surface energy of the solid and the acid-base contribution to the energy of interaction between a probe molecule and the solid by using IGC. By performing calorimetric measurements with different probe molecules and by applying the approach of Gutmann (1966) it is also possible to separate this acid-base interaction into an electron donor and an electron-acceptor property of the solid.

This is very tedious work and only a few publications available where the electron; acceptor and electron; donor properties of cellulosic fibres have been determined with the described technique. More publications are available where the Lifshitz-van der Waals components of the surface energy of the solid have been determined and where the acid-base interaction between the fibres and a probe molecule has also been determined. In **table 5**, data from some fairly recent publications have been summarised and σ_s^{LW} , ΔG^{AB} (with different probe molecules), K_a and K_d (constants describing the electron-acceptor and electron-donor properties of the solid respectively) values have been collected.

Table 5. Summary of surface energy determinations of different cellulosic fibres, and Micro Crystalline Cellulose (MCC), with the aid of IGC. Both data for σ_s^{LW} , constants describing the electron acceptor (K_a) and electron donor (K_d) properties of the materials and $-\Delta G^{AB}$ for interaction with different probes are included in the table. There is no full chemical characterisation of the different pulps used.

| Material | σs ^{LW} (mNm/m²) | Ka | K _d | -ΔG ^{AB} (mNm/m²) Probe (acid/base) |
|---|------------------------------|------|----------------|---|
| 60% Beechwood 40% Birchwood (1*) | 44.0 | 0.31 | 0.24 | Several |
| $CTMP(2^*)$ | | 5.7 | -5 | Several |
| SWBK (2*) | | 4.0 | 0 | Several |
| MCC (2*) | | 4.0 | 0 | Several |
| Whatman filter paper (4*) | 48.4 | 0.41 | 0.26 | Several |
| Softwood | 47.0 | | | 5.0/27.6 |
| ClO ₂ Bleached(3*) | | | | chloroform/ p-dioxane |
| Softwood | 43.5 | | | 3.9/29.5 |
| H ₂ O ₂ Bleached (3*) | | | | chloroform/p-dioxane |
| Softwood | 42.1 | | | 3.7/28.9 |
| O₃ Bleached (3*) | | | | chloroform/p-dioxane |
| Hardwood | 46.5 | | | 5.8/25.8 |
| CIO ₂ Bleached (3*) | | | | chloroform/p-dioxane |

1* = Felix (1993), 2* = Jacob (1994), 3* = Lundqvist (1996), 4* = Lee (1989).

It is very difficult to obtain a clear picture of the acid-base properties of the fibres. If the data of Felix (1993) and Lee (1989) are compared with the data of Jacob (1994), it is found that the absolute values differ and so does also the trend of the data. The data of Felix (1993) and Lee (1989) are in fairly good agreement and they show that paper are both acidic and basic with a dominance for the acidic properties. This is also found in the work of Lundqvist (1996) where the interaction energies with the basic probes is much larger than the interaction with the acidic probe, which again indicates that materials from bleached chemical pulps with a dominating content of cellulose have a predominantly acidic character. In contrast, Jacobs data (1994) show that both fibres containing mainly cellulose and MCC have a monofunctional acidic nature and that lignin-containing fibres (CTMP) give anomalous results with negative basic properties (!). Since Jacob (1994) also points out that the interpretation of her data, which is made at a surface coverage of 2 % and not at infinite dilution, as for the rest of the data in

table 5, is not straightforward these data must be treated with some caution. The common picture emerges that fibres are both acidic and basic in nature but that they have a predominantly acidic character and the constants given in the table are then also in fairly good agreement. It is also clear that the different investigations give fairly comparable results with regard to the Lifshitz-van der Waals components of the surface energy of the fibres containing mainly cellulose. This kind of fibre always contains hemicellulose and the data in table 5 are therefore typical for fibres containing both cellulose and hemicellulose.

When these data are compared with the data in table 4, it is clear that there is a fairly good agreement between the different methods regarding the Lifshitz-van der Waals components, with the minor difference that the contact angle approach gives values slightly lower than the IGC method. This indicates that the different methods are measuring the same entity and that this entity is probably the Lifshitz-van der Waals component of the surface energy. A similar comparison has also been made by Lundquist (1996) who compared different laboratory-prepared fine paper sheets. The sheets consisted of 50 % bleached softwood pulp, 50 % bleached hardwood pulp, and when filler was added it was added at an amount of 20.5 % and, regardless of pH, kaolin was used as filler. Furthermore, the sheets were either sized with rosin dispersion size (and alum and the sheets were prepared at a pH of 4.5) or with alkylketene dimer size. The results of this comparison are shown in **figure 4**.



Figure 4. The Lifschitz-van der Waals part of the surface energy for different laboratoryprepared fine paper sheets obtained by IGC and contact angle measurements. Reprinted from Lundquist (1996)

As can be seen in this figure, the contact angle data are generally lower than the IGC data but the trend for the different sheets is the same and it is also clear that the difference in the case of the more hydrophobic sheets, i.e. sheets containing sizing agents, is lower than the difference for the more hydrophilic sheets. This same trend was found by Felix (1993) where contact angle measurements (single fibre wetting in a Cahn balance) were compared with IGC measurements. These measurements showed that the dispersive part of the surface energy was 25.5 mNm/m^2 as determined with contact angle measurements and 44.0 mNm/m^2 as determined with contact angle measurements and 44.0 mNm/m^2 as determined with contact angle measurements and 44.0 mNm/m^2 as determined with a coverage whereas the contact angle measurements measures the surface at zero surface coverage whereas the contact angle measurements in the surface at a zero surface properties "through" a multilayer of the contact liquid on the adsorbate. This statement is however contradicted by the results in table 3, where it is shown that it is mainly single fibre wetting which gives very low values for the dispersive part of the surface energy of the fibres. The reason for this is not known.

However, from these comparisons, it may be concluded that there is a good agreement between the contact angle method, from goniometric measurements, and the IGC method when the dispersive part of the surface energy is considered and that the difference is larger the higher the surface energy of the solid.

As has already been mentioned, the discrepancy is larger when the acid-base properties of the fibres, as determined by the two methods, are compared. In the IGC method the determination yields virtually acidic fibres whereas the contact angle method yields almost totally basic fibres. This discrepancy has not been resolved at present but a recent publication, (Lee 1996), has shown that the division of the polar properties of water in equal acidic and basic parts is probably not correct and that a more realistic value would be a Lewis acid component value of 34.2 mNm/m² and a Lewis base value for water of 19.0 mNm/m². As was discussed in connection with table 4, this will result in a lower Lewis base component for the tested surfaces but it will not be enough to change the basic properties to acidic properties.

Since there are, today, unexplained differences between the methods, systematic investigations are needed to clarify the reasons. Until this is done the acid-base properties as determined with the two methods must be treated with considerable caution. In this respect, a very interesting investigation has recently been published, (Lundquist 1996), where fibres have been carboxymethylated to

different degrees and then measured with the IGC technique. Unfortunately, contact angle measurements were not published, but the IGC data clearly show that the fibres become more and more acidic with an increasing degree of carboxymethylation and as shown in **figure 5**, there is an almost linear relationship between D.S of the fibres and the interaction energy with a basic probe, p-dioxane.



Figure 5. The interaction energy between carboxymethylated bleached softwood cellulosic fibres and a basic probe, p-dioxane, as a function of degree of substitution of the fibres (Lundqvist 1996)

This shows that the IGC method can be used to determine correctly a change in the acid-base properties of the fibres. Lundquist (1996) also showed that a modification of the fibres with a basic component, i.e. a commercial diethylaminoethyl cellulose was used, resulted in a cellulosic surface with a predominantly basic nature. This gives further support to the belief that the IGC method can be used not only to determine the Lifshitz-van der Waals component of the surface but also by using well characterised probe molecules, to detect correctly changes in the acid-base properties of the surface.

Chemical characterisation of the fibre surface

The chemical composition of the fibre surface can be significantly different from the bulk composition of the fibres. Due to the lack of suitable techniques, it has however been very difficult to study the surfaces of the fibres separately from the bulk of the fibres. The development of the ESCA (Electron Spectroscopy for Chemical Analysis)-technique opened up new opportunities and several workers have used this technique to study fibre surfaces over the last 20 years. The following section gives a short review of how this technique has been applied and a summary of the results achieved in these investigations.

Apparently Dorris and Gray (1978^1) were the first to study fibres with the ESCA technique. They used the C(1s) and the O(1s) peaks to characterise the chemical composition of the surfaces of the fibres and they claimed that the escape depth was 1-5 nm and that this was a typical measure for the depth of the analysis in their investigation. They worked on the assumption that the carbon atoms could be divided in different classes depending on the chemical surroundings of the atoms according to the following:

- 1) carbon atoms bonded only to carbon and/or hydrogen (C C)
- 2) carbon atoms bonded only to a single oxygen other than a carbonyl oxygen (C O)
- 3) carbon atoms bonded to two non-carbonyl oxygen's or to a single carbonyl oxygen (O C O, C = O)
- 4) carbon atoms bonded to a carbonyl oxygen and to a non carbonyl oxygen (O = C O)

but in the early paper they worked only with the ratio between O(1s) oxygen atoms and C(1s) atoms, N_0/N_c . It was first in a later paper, (Dorris and Gray 1978³) that they showed how the C(1s) peak could be deconvoluted into peaks corresponding to the different groups and, in this later work, they also showed that the results with only the relative intensities used in their first work were a good approximation.

By comparing calculated values for lignin and cellulose with measured values, they achieved the results given in **table 6**.

Table 6. Calculated oxygen-to-carbon ratios for different materials (from Dorris and Gray 1978¹). The different values for kraft pulps and Whatman filter papers correspond to different samples and should represent the scatter of properties for different materials.

| Material | N _o /N _c |
|--|--------------------------------|
| Cellulose (Calculated) Spruce millwood lignin (calculated) | 0.83 0.33 |
| Spruce dioxane lignin (calculated) Whatman filter paper | 0.36 |
| Bleached kraft pulp | 0.72, 1.14, 0.62 |
| Dioxane lignin on filter paper Dioxane lignin on glass | 0.36 0.31 |

The authors concluded that the difference between the calculated values and the measured values could be ascribed to the existence on the surface of organic compounds other than cellulose and lignin.

In a later work, the same authors, (Dorris and Gray 1978²) presented a way to calculate the weight fraction of cellulose and lignin on the surface of the fibres from the theoretical composition of cellulose (C_6O_5) and lignin ($C_{9.92}O_{3.32}$) according to the equations:

$$W_{L} = 1.132S_{L} / (1 + 0.132S_{L})$$
[16]

where

 W_{L} = Weight fraction of the lignin on the surface

S_L = Segment mole fraction of lignin on the surface (according to eq. 17 below)

$$S_{\rm I} = (5 - 6(N_{\rm O}/N_{\rm C})) / (1.68 + 3.92(N_{\rm O}/N_{\rm C}))$$
[17]

where N_0 and N_c are defined as above.

With these definitions, the authors characterised many different mechanical pulps and, by measuring both unextracted and Benzene/acetone/water-extracted pulps, it was possible to determine both the influence of the extractives and the weight fraction of lignin on the surface of the fibres, assuming that the extracted fibres contained only cellulose and lignin. The results given in **table 7** were presented by Dorris and Gray (1978^3) .

Table 7. Summary of the data for mechanical pulps characterised by Dorris and Gray (1978³). The table shows both the original data for the pulps as well as the values for the extracted sheets and the corresponding weight fraction of lignin on the surface according to eq. [16] and [17]

| Material | N _o /N _c | Solvent-Extracted (Benzene/acetone/water) | Lignin Weight fraction (on the surface) |
|-------------------------------------|--------------------------------|--|---|
| SGW (Mill deckers) | 0.47 | 0.63 | 0.32 |
| -"- (aged) | 0.32 | 0.62 | 0.34 |
| (fines free) | 0.49 | 0.58 | 0.41 |
| -"- (Aged) RMP (Mill deckers) | 0.50 | | |
| (fines free) RMP (Mill arinders) | 0.48 | | |
| (fines free) TMP (pilot plant) | 0.46 0.44 | 0.65 0.56 | 0.28 0.45 |

It is clear that the amount of lignin on the surface of the fibres corresponds approximately to the average bulk concentration of lignin of the fibres, i.e. all except TMP have values somewhat higher than the bulk concentration of lignin.

The table also shows that the TMP fibres seems to have a higher content of lignin on the surface, which may also be expected considering the process conditions used to produce these pulps. It is also clear that there is a large influence of the extractives despite the fairly low total amount of extractives in the sheets. This finding was supported by experiments with a single-stage high temperature TMP where the N_O/N_C ratio decreased from 0.47 to 0.39 when the energy was increased in the refining, indicating that the surfaces were covered with material rich in carbon. The authors were not able to determine the exact source of this material but the extractives were indicated as being mainly responsible for this decrease. This statement is also supported by later work by Katz and Gray (1980). It may thus be concluded that ESCA proved to be a very useful tool to characterise the
outermost surface of the fibres and, using simple mathematical formulae and careful extractions of the pulps, it was possible to determine the weight fraction of cellulose and lignin on the surface and also the influence of the extractives on the N_c/N_c ratios detected.

Several workers continued to apply ESCA to different pulp grades and a good summary, see **table 8**, of this work was given by Carlsson (1996) who summarised both own work and similar work conducted by others. This summary also follows very closely the summary given by Laine (1994).

Table 8.The N_O/N_C ratio for different materials and a summary of the distribution of
how the carbon atoms are linked to oxygen (in % of total). From Carlsson
(1996) but the summary follows very closely the summary given by Laine
(1994). The bleached chemical pulp was extracted with DiChloroMethane
(DCM).

| Material | No/Nc | C-C (%) | C-O (%) | O-C-O (%) | O-C=O (%) |
|---------------------------|-------|---------|---------|-----------|-----------|
| | | | | | |
| Cellulose (theoretical) | 0.83 | 0 | 83 | 17 | 0 |
| Extr. Bleached kraft | 0.80 | 6 | 75 | 18 | 1 |
| Galactoglucomannan | | | | | |
| (theoretical) | 0.81 | 3 | 78 | 16 | 3 |
| Arabinoglucuronoxylane | | | | | |
| (theoretical) | 0.81 | 0 | 78 | 19 | 3 |
| Xylan (Laine 1994) | 0.83 | 5 | 67 | 24 | 4 |
| Lignin (theoretical) | 0.33 | 49 | 49 | 2 | 0 |
| Kraft lignin (Laine 1994) | 0.32 | 52 | 38 | 7 | 3 |
| Kraft lignin | | | | | |
| (Mjöberg 1981) | 0.40 | - | - | - | - |
| Oleic acid (theoretical) | 0.11 | 94 | 0 | 0 | 6 |
| Extractable mtrl. | 0.12 | 93 | 5 | 0 | 2 |

This table shows that the extracted bleached pulps are very close to the theoretical value for cellulose but some C - C linkages are nevertheless found in this pulp indicating the existence of remaining lignin and/or extractives. However, according to Laine (1994), the C - C linkages found in the extracted pulp are probably due to a strongly adsorbed extractive, which it is not possible to remove with the DCM treatment.

It is also clear in the table that the lignin data of Laine (1994) fit the theoretical data, according to Freudenberg, very well, whereas the data of Mjöberg (1981)

showed a considerably higher value. Both investigations used lignin isolated from spent liquors from kraft cooks and the reason for the difference between the investigations seems to be linked to the existence of small amounts of carbohydrates in the samples tested by Mjöberg, according to Carlsson (1996). The results also show the importance of the extractives for the N_0/N_c ratio on the fibres, since the value of the ratio for the extractives is so much lower than for example for cellulose.

Ström and Carlsson (1992) introduced a simple way of calculating the surface coverage of the fibres of extractives and lignin using the N_0/N_c ratios for the original pulps, extracted pulps and pure carbohydrates according to the equations

$$\Phi_{\text{extr}} = \frac{\frac{N_{\text{o}} / N_{\text{c}} (\text{after extraction})^{-N} \text{o} / N_{\text{c}} (\text{before extraction})}{N_{\text{o}} / N_{\text{c}} (\text{after extraction})^{-N} \text{o} / N_{\text{c}} (\text{extractives})}$$
[18]

$$\Phi_{\text{lignin}} = \frac{\frac{N_{o} / N_{c} (\text{after extraction}) - N_{o} / N_{c} (\text{carbohydrates})}{N_{o} / N_{c} (\text{lignin}) - N_{o} / N_{c} (\text{carbohydrates})}$$
[19]

These equations assume that the depth of analysis is lower than the depth of the covering layer. This is naturally a fairly rough assumption and, as was pointed out by Carlsson (1996), the thickness of extractive layers may be smaller than the depth of analysis in the ESCA equipment and this means that the surface coverage of extractives as determined with equation [18] is underestimated. Carlsson (1996) also claims that the depth of analysis in the ESCA experiments was 5 - 10 nm, which is fairly thick in relation to a monolayer coverage of for example extractives. The influence of the depth of analysis was also discussed by Laine (1994) who found, using ESCA analysis with different angles of emission, that the thickness of the surface layer of lignin was very thin. With these assumptions in mind, the summary presented in table 9 can be made regarding the surface coverage of carlsson (1995):

Table 9. Summary of composition of a number of different pulps (total amounts of DCM and lignin) (evaluated from the kappa number of the pulps and appropriate conversion factors) and the surface coverage of extractives and of lignin (on extracted pulps). From Carlsson (1995) and Carlsson (1996)

| Material | DCM extractives (%) | Bulk Lignin (%) by weight | Φ _{extractives} (surface composition) | Lignin/carbohydr. (surface composition |
|---|--|--|--|---|
| Highyield kraft -"-, aged Unbleached kraft -"-, aged Bleached kraft -"-, aged Unbleached sulphite | 0.2 0.2 0.09 0.04 0.04 0.04 | 12 12 3.3 3.3 < 0.1 < 0.1 | 13 11 9 11 2 0-5 14 | 66/34 66/34 30/70 30/70 14/86 14/86 28/72 |
| -"-, aged | 0.6 | 4.3 4.3 | 28 | 28/72 |

This table shows that the ESCA technique is a very powerful tool to characterise different pulps and the influence of ageing and extraction on the surface properties of these pulps with regard to the interaction between fibres and fibres and other materials. It is also clear in the table that it is possible to determine the migration of extractives when sulphite pulps, i.e. pulps with a high extractives content, are stored. The table shows that the surface coverage increases from 14 to 28 % when the pulps are aged. Considering that the concentration of DCM extractives is only 0.6 %, it is astonishing to find a surface coverage of 28 %.

It is also obvious in table 9 that the surface concentration of lignin is considerably higher than the bulk concentration of the lignin. As was mentioned earlier, this was also found by Laine (1994) using ESCA with different angles of emission, which means different depths of analysis of the fibres.

In a later work, Laine et.al. (1996^2) investigated how different bleaching conditions affected the surface composition of fibres from an unbleached chemical pulp with an initial (unbleached) kappa value of 25.9. In general the author found that after the cooking there is a higher content of lignin on the fibre surfaces and that this slows down the bleaching response of different bleaching chemicals. The investigation also showed that the fraction of surface lignin which is removed by

 O_2 and H_2O_2 bleaching is lower than the average removal of the lignin, whereas O_3 gives the same fractional removal of lignin regardless of the position of the lignin in the fibre wall. The influence of ClO_2 depends on the number of bleaching stages before the addition of the ClO_2 . This large investigation is summarised in **figure 6** which shows the fraction of surface lignin, calculated according to eq. [19], as a function of the total lignin content. The sequence of bleaching and not only the chemicals as such has a large influence on the results.



In this study, the surface coverage of the extractives was also investigated and it was found that the surface coverage varied between 2 and 9 % for the different bleaching conditions, whereas the total amount of extractives varied between 0.06 and 0.15 %. This is probably due to a reprecipitation of the extractives on the fibre surfaces. The bleaching studies also showed that the surface fraction of extractives decreases with O_2 and slightly with H_2O_2 whereas O_3 and ClO_2 bleaching had only a minor effect on the extractives on the fibre surface. In this respect it is believed that the neutral components of the extractives play a major role, but it must be kept in mind that bleaching operations represent two alkaline and two acidic treatments and that this, as such, has a large impact on the achieved results. By combining enzyme treatment of unbleached chemical pulps, Buchert et.al.

By combining enzyme treatment of unbleached chemical pulps, Buchert et.al. (1996) were able to draw some interesting conclusions regarding the relative location of the lignin, carbohydrates and extractives on the fibre surface. A xylanase treatment of a birch pulp, with a kappa number of 18.2, resulted in the removal of 29 % of the xylan originally present in the pulp and a simultaneous removal of 10 % of the lignin originally present in the pulp, but no change in the surface coverage of lignin, which indicates the existence of lignin/carbohydrate complexes. Treatment of the same pulp with a mannanase did not result in the same lignin removal. An analysis of the extractives of these pulps showed that the overall weight fraction of the extractives was 0.5 % but that the surface coverage was 35 %. The xylanase treatment reduces the surface concentration of the extractives from 35 to 20 % and this also indicates a link between the extractives and the xylan. A similar treatment of a pine kraft pulp with an initial kappa number of 25.9 did not give the same result. When treating these fibres with xylanase, 21 % the xylan originally present was removed and, at the same time, the lignin coverage of the surface increased from 17 to 28 % and only 2 % of the lignin was removed with the xylan. This indicates that the xylan is located outside the lignin on the surface of the fibres and also that the lignin is precipitated first before the xylan is reprecipitated on top of the lignin. In turn, these results also show, according to the authors, that there is no linkage between the lignin and the xylan as was found for the birch pulp. A treatment of the fibres with mannanase resulted in a decrease in the galactoglucomannan content by about 24 % of the material originally present. All these results show the very fruitful effect of combining selective removal of certain compounds from the fibres with an analysis of the difference with specific techniques such as ESCA. The investigation will probably lead to similar work in the future, even though some of the conclusions drawn are rather far reaching. Instead of cleavage of linkages between lignin and carbohydrates, pure washing can be used to explain the results. Nevertheless the combination of the techniques is very interesting.

Similar studies have been conducted by Heijnesson et.al. (1995^{1 and 2}) where the surfaces of different unbleached pulps were mechanically peeled with a novel procedure, and both the remaining fibres and the material peeled from the fibres were analysed. The results were essentially the same as those already mentioned, which means that the surfaces are richer in lignin-rich materials which can be peeled off with the described technique. A possible future application would be to combine the mechanical peeling methodology with the ESCA technique.

Another very interesting technique for chemical characterisation of the fibre surface is the Atomic Force Microscope (AFM) technique, where a very fine tip interacts with the fibre surface and either the force between the surface and the tip is detected or a topological map of the surface is drawn, Hanley (1992, 1994 and 1996). Fibres represent a very difficult task for this very sensitive technique with their extremely rough surfaces but, as was demonstrated by Hanley, both fibrillation, (Hanley et.al. 1992) and fibril angle (Hanley 1994) can be detected by the technique. Pereira et.al. (1995) also used the AFM technique to characterise the residual lignin in kraft pulps.

In order to achieve a more specific mapping of the fibre surface, a more well characterised tip is needed in the AFM and, in a recent work by Akari (1996), it has been demonstrated that by coating the tip with carboxyl groups it is possible to obtain an image of single polyethyleneimine molecules on polystyrene latices. With this technique, it should also be possible to investigate the distribution of anionic charges on fibres and by modifying the tip with different probe molecules it should be possible to study other types of interactions with high lateral resolution.

As a summary of this description of the use of ESCA to characterise the fibre surface, it may be mentioned that the surface composition of the fibres can be significantly different from the bulk composition. In the case of the lignin the differences are not very large, i.e. smaller than one order of magnitude, but for extractives the difference in composition between the bulk and the surface is even larger than an order of magnitude. It should also be emphasised that the results achieved with well characterised pulps and modern ESCA equipment are very interesting and that the combination of ESCA analysis and e.g. the effects of treatment with well characterised enzymes looks very promising for the future chemical characterisation of the fibre surface. Many of these conclusions are based on the assumptions in eq. [18] and [19], and model experiments are definitely needed to show the validity and limitations of these assumptions. The AFM techniques with chemically modified tips or latices are also very interesting techniques for the surface characterisation of fibres.

Charge determination of the fibres

The charges on the fibres and fines from the fibres are important for a number of different reasons. First the number of charges determines the consumption of cationic additives used in papermaking and secondly the charges are very important for both fibre swelling and the interaction between the fibres during consolidation of the fibres in the dryer of the paper machine. This was discussed earlier and it is obvious that a good knowledge of the exact charge on the fibres, its variation with pH and the availability of the charges, is essential for a good characterisation of the fibres. For this reason a lot of effort has been devoted to the determination of these entities over the last 20 years. In the following paragraph, a condensed summary of the different techniques used for determination of the charge, in μ moles/g, is given.

Different techniques for the determination of the potential of the fibre surface are not however covered. The work devoted to the conversion of the charge into potentials on the fibre surface is not considered either, since this would demand too large a focus on the different models used for the calculation, without providing any new information about the fibre surface.

As was mentioned in the introduction, the charges on the fibres originate both from the chemical composition of the materials in the fibre wall and from how these materials have been changed by different process steps during the preparation of the fibres. Sjöström (1989) showed that most of the charges in the wood emanate from the hemicelluloses in the wood and here there are large differences between softwood and hardwood. Most of the carboxyl groups in the hemicellulose are of the uronic acid type, (Sjöström 1981) and are found in the xylan. In the hardwood, the xylan is composed of O - acetyl - 4 - O-methylglucuronoxylan and, in softwood, the xylan consists mainly of arabino - 4 - Omethylglucuronoxylan. The degree of substitution of the acid side-chain groups is different for these different xylans. In birchwood xylan, one tenth of the xylose units are substituted with a methylglucuronic side chain and in pinewood xylan one fifth of the xylose units are substituted, (Timell 1967). On the other hand, the hemicellulose content of the birchwood is higher than in the pinewood and, as was pointed out by Sjöström (1989), the amount of carboxyl groups present in pinewood is 150 mmol/g and in birchwood the figure is 250 - 350 mmol/g. In spruce, the concentration of carboxyl groups is 150 - 250 mmol/g.

Sjöström (1989) also pointed out that phenolic groups as well as alcoholic and hemiacetallic group can be responsible for anionic charges on the fibres but these groups are ionised at higher pHs than those found during regular papermaking conditions.

The constituents of the fibre wall can undergo changes during processing and the lignin can, for example, be oxidised during cooking and bleaching, see for example Sjöström (1981), and this will naturally change the overall charge on the fibres. Some new carboxyl groups can also be created in the carbohydrates due to the peeling reaction which is stopped by the formation of metasaccharinic acid, (Sjöström 1981), but the amount is naturally dependent on the processing conditions.

Early methods for determining of charges in the fibres were mainly based on the adsorption of metal ions and/or the adsorption of dyes (Rydholm 1965). These methods often showed large scatter in the results due to the existence of non-ionic interactions between the dyes and the fibres and due to problems in eluting all adsorbed metal ions. In a paper by Katz (1984), it was however shown that conductometric titration could be used to determine the concentration of both sulphonic acid groups and carboxylic acid groups in one titration with sodium hydroxide. The dissociation patterns of these two acidic groups are very different and as the authors showed, it was fairly simple to determine the concentrations of both groups merely by monitoring the conductivity of the suspension of the fibres as a function of the added amount of sodium hydroxide.

The strong sulphonic acid groups were detected as fully dissociated, whereas the carboxylic groups were fully protonated at the beginning of the titration. To test the method, two other methods were used, potentiometric titrations and Mgelution, and a good agreement between the methods were found. A large range of materials was tested and the results from Katz (1984) are summarised in **table 10**.

| Table 10. | Summary of | the | e determi | inatic | on of both | sulpho | onic acid | groups | and carb | oxylic |
|-----------|-----------------------------|-----|-----------|--------|------------|--------|-----------|---------|-------------|--------|
| | acid groups Katz (1984). | in | different | raw | materials | using | conduct | ometric | titrations, | from |

| Material | Yield (%) | Amount of sulphonic acid groups (μmol/g) | Amount of carboxylic acid groups (μmol/g) |
|---|--------------|--|---|
| Wood sulphonated for 12.5 min at $pH = 7$ | 99 | 120 | 91 |
| Wood sulphonated for 35 min at pH = 7 | 97 | 181 | 125 |
| Wood sulphonated for 110 min at pH = 7 | 95 | 227 | 125 |
| CMP* from chips | 92 | 236 | 124 |
| Suprioriated at pH = 7 | 70 | 208 | 87 |
| High yield bisulphite | 47 | 28 | 43 |
| Low yield bisulphite | 42 | 6 | 24 |
| Low yield acid sulphite | 66 | 0 | 201 |
| Unbleached kraft | | | |

* = CMP = Chemimechanical pulp

It is obvious in this table that the different materials have very different charges and that they, will therefor show vastly different properties regarding the consumption of chemicals and strength properties. Another conclusion from the results in the table was that sulphonic and carboxylic acid groups could be separately determined by conductometric titration, whereas the other methods could give only a total measure of both types of charges. As will be discussed later, it is also possible to determine different ionic groups with accurate potentiometric titrations.

Scallan has also in several recent papers showed that the conductivity of the fibre suspension is a very accurate method for determining the concentrations of charged groups both within the fibre wall and on the surface of the fibres since the conductivity of the suspension is largely influenced by the charged groups within the fibre wall, (Scallan 1988, Scallan 1989).

Wågberg et.al. (1985) also compared the conductometric titration technique with a technique where they used cellulosic fibres, which had been carboxymethylated with ¹⁴C-labelled monochloroacetic acid. Their results showed that there was a very good agreement between the charges determined with the two methods, which indicates that the conductometric titration method can be used to determine the charges on cellulosic fibres.

In the paper by Wågberg et.al. (1985), it was also shown that it was possible to use polyelectrolyte adsorption to determine the total charge on the fibres provided the fibres were highly charged and sufficiently swollen to allow the polyelectrolyte molecules to enter the fibre wall. For the non-substituted fibres there was a fairly large difference between the results of conductometric titrations and polyelectrolyte adsorption, indicating that the polymer could not enter the fibre wall of these less charged and less swollen fibres. These results have also been supported by later work, (Wågberg 1987) where it was shown that the adsorption of highly charged cationic polymers was an ion-exchange process and that it was consequently also possible to determine the charge on the external surface of the fibres if the molecular mass of the polymer was large enough. This was also shown in a paper by Wågberg (1989) where different polymers with different molecular masses, were used to detect the total charge and surface charge of the carboxymethylated fibres. Some of the results of these measurements are shown in **figure 7**.



Figure 7. Charge on the carboxymethylated cellulosic fibres (D.S. = 0.025) from polymer adsorption, as a function of pH. Both surface charge and total charge are included in the figure as well as an experimental series in deionised water. The ionic strength for the rest of the measurements was 0.01 M NaCl. The 3.6. -ionene had a molecular mass of 5.9 • 10³ and was used to determine the total charge and the poly-DiMethyl/DiAllylAmmoniumChloride had a molecular mass 3.8 • 10⁵ and was used to determine the surface charge of the fibres. From Wågberg (1989)

As can be seen in this figure, the surface charge is about 20 % of the total charge for this type of fibre, but the ratio of surface charges to total charges can vary, as will be discussed later in this paper. The low pH dependence of the surface charges was ascribed to a very efficient competition of the high molecular cationic polymer for the protons on the carboxyl groups, and it was suggested by Wågberg (1989) that the pH dependence of the charges determined with the high molecular mass polymer should be treated with caution. The final level reached is, however, believed to be a good measure of the surface charge of the fibres. With the combination of these techniques, it is hence fairly easy to determine the total charge of the fibres, which is important for fibre swelling, and the surface charge, which is very important for predicting the consumption of cationic wet end additives by the fibres. Swerin (1994) also showed that polymers with different molecular mass could be used to determine how the availability of the fibre wall for the polyelectrolytes was changed when the yield of unbleached kraft pulps was changed and these results are summarised in figure 8. The authors do not, in detail, discuss the trends in charge ratio as the yield is decreased and there is a difference in trends found in figure 8 and in figure 10. However, since the results in figure 8 give a combined measurement on charge distributions and availability of charges within the fibre wall, the data in the two figures are not directly comparable.



Figure 8. The charge ratio, i.e. the ratio of adsorbed polymer charges at the plateau-level in the adsorption isotherms to the total charge of the fibres, as a function of weight average molecular mass of the polyelectrolytes used (3.6. -ionene and different poly-DMDAAC's) for laboratory-cooked unbleached pine kraft pulps of different yield. From Swerin (1994)

A combination of conductometric titrations and polyelectrolyte adsorption has also been used by Zhang et.al. (1994) to determinate the charge of mechanical and unbleached sulphite and sulphate pulps. A short summary of their results is given in **table 11**.

 Table 11.
 Summary of the data presented by Zhang et.al. (1994) regarding sulphonic acid groups and carboxylic acid groups determined directly by conductometric titration.

| Pulp | Sulphonic acid groups (μmol/g) | Carboxylic acid groups (µmol/g) |
|---|-----------------------------------|--|
| Unbleached TMP Bleached TMP (H ₂ O ₂) Unbleached CTMP Bleached CTMP (H ₂ O ₂) Unbleached sulphate | 40-70 40-70 | 80-110 150-250 80-110 150-250 |
| (Kappa number <32) Unbleached sulphite (kappa number <32) Bleached sulphate | - 100-120 - | 50-80 50-60 10-25 |

The corresponding data for the surface charge, as determined with a poly-DMDAAC with a weight average molecular mass of $2.2 \cdot 10^5$, is summarised in **table 12**.

Table 12. Summary of the data presented by Zhang et.al. (1994) regarding total surface charge of different pulps as determined with the polyelectrolyte adsorption method using a poly-DMDAAC with a weight average molecular mass of 2.2•10⁵.

| Pulp | Total surface charge (µmol/g) |
|---|-------------------------------|
| Unbleached CTMP Unbleached TMP Bleached CTMP (H_2O_2 , start pH = 12) Bleached CTMP (H_2O_2 , start pH = 13) Bleached CTMP (H_2O_2 , pH = 12, 40 % | 12.6 10.7 28.2 33.0 |
| pulp conc. during bleaching) | 32.8 |

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As can be seen in table 11 the total charge due to carboxylic acid groups of the unbleached spruce-based TMP and CTMP is rather close to the values of 150–250 mmol/g previously mentioned for the carboxylic acid content of the hemicellulose in this species. Considering that there is certainly a yield loss during the preparation of these pulps, the values in table 11 are very close to this value. For the CTMP it can again be noted that there is a fairly large contribution of sulphonic acid groups to the total charge. Table 11 also shows that the bleaching can considerably increase the concentration of carboxylic acid groups, mainly due to an oxidation of the lignin with this type of bleaching.

A comparison of table 11 and table 12 shows that the surface charge is about 10% of the total charge for these types of pulps and that the relative increase in the surface charge upon bleaching is larger than the relative increase in the total charge upon bleaching.

This is also consistent with the earlier remark that peroxide bleaching causes an oxidation of the lignin and, since the CTMP is rich in lignin on the surface, this result is expected.

As a final example on conductometric titrations, the interesting work by Pu and Sarkanen (1989) must be mentioned. These authors used conductometric titrations with both sodium hydroxide and sodium bicarbonate. In this way it was possible to detect the influence of different groups in the wood on the charge as determined with sodium hydroxide titration alone. They tested both unbleached Western Hemlock and black Cottonwood meals that had been extracted in order to remove all influence of extractives. In the experiments, they first conducted the titrations with sodium hydroxide, which means that they will detect free carboxylic groups, possible esters and also some influence from phenolic groups, depending on how high the pH was at the end of the titrations. In order to remove the influence of phenolic groups they treated the wood meals with diazomethane and then repeated the titration with sodium hydroxide. They also titrated diazomethane-treated woodmeals with sodium bicarbonate and with this measurement they claim that they detected only the free carboxyl groups. By subtracting the value achieved with the bicarbonate titration from the value achieved with the sodium hydroxide, on the diazomethane-treated wood meals, it was then possible to detect the carboxyl esters in the materials. By using the results from all these measurements, it was possible to separate the influences of all the different groups mentioned above. A summary of the results obtained is given in table 13.

Table 13. Summary of the results by Pu and Sarkanen (1989) showing the influence of different chemical groups in the wood on the charge of the material. Wood meals from both Western Hemlock and Cottonwood were tested and they were carefully extracted before the measurements in order to remove the influence of extractives.

| Functional group | Charge (µeq./g) Western Hemlock | Charge (µeq./g) Cottonwood |
|---|------------------------------------|-------------------------------|
| Sum of free and esterified carboxyl groups Free carboxyl groups Carboxyl esters Phenolic groups * | 158 31 127 260 | 127 66 61 147 |

- Determined by NaOH equilibration between pH = 8.5 and pH = 12 - 12.5 on borohydride reduced wood meals

Pu and Sarkanen (1989) concluded that the charge is about what could be expected with regard to the chemical compositions of these materials. It can be seen that a high relative amount of carboxyl esters was found and it would be necessary to repeat these measurements on different well-characterised pulps in order to test whether this methodology is safe for separating the influence of different groups.

The authors, nevertheless, refer to earlier work by Johansson (1977) stating that a large proportion of the 4-O-Methylglucuronic acid groups in birch xylan is esterified and that the results are not therefore unexpected. Lloyd (1993) also used this technique and found large differences in the results of the bicarbonate titration and the NaOH titrations. These large differences were ascribed to the partial ionisation of the phenolic groups in the lignin in the NaOH titration. The technique is very interesting, but further experiments are needed to verify that the evaluation principle is accurate enough and that the different treatments of the wood meals in the work by Pu and Sarkanen (1989) do not introduce artefacts in the materials.

The last technique for the detection of electrostatic charges on fibres, which will be discussed here, is potentiometric titrations. These measurements are based on titrations with mainly sodium hydroxide and a very accurate determination of the pH and the difference between a blank and a sample containing cellulosic fibres. Herrington et.al. (1984) published a very detailed description of the technique and the evaluation of the results. They also in two later publications used the same evaluation principle (Budd 1989, Herrington 1992) to determine the charge of different pulps. Herrington (1992) presents a new way of determining an accurate starting point of the titrations where the hydrogen ion concentration of the clear water phase is determined before the titration, and the authors claim that this technique gives even more accurate results. A summary of the results of these three publications is given in **table 14**. When preparing this table, the results corresponding to a NaCl concentration of 0.1 M have been used and the charge determined at pH = 7 has been used as an estimate of the total charge of the fibres.

Table 14. Summary of the charge determination from potentiometric titrations from Herrington (1994), Budd (1989) and Herrington (1992). The values correspond to measurements conducted at 0.1 M NaCl and the charges are the charges detected at pH = 7. No chemical characterisation of the pulps was given by the authors, so a direct comparison internally in the table and with other data is difficult to conduct exactly.

| Type of pulp | Charge (µeq. /g at pH=7) 0.1 M NaCl |
|---|--|
| Cotton linters ¹ Bleached sulphate pulp (pine) ¹ Unbleached sulphate pulp ¹ Bleached softwood sulphate pulp ² Bleached hardwood sulphate pulp ² Bleached eucalyptus grandis sulphate pulp ² Bleached softwood sulphite pulp ² Bleached Eucalyptus globulus sulphate(dried) ³ Bleached Eucalyptus grandis sulphate(dried) ³ Bleached Betula Verrucosa sulphate (dried) ³ Bleached Betula Verrucosa sulphate (dried) ³ Bleached pine/spruce sulphate (dried) ³ | 5.28 30.5 99.4 30.5 69.4 49.2 90.1 35.2 87.0 45.0 52.0 66.0 31.0 |

From Herrington (1984)

² From Budd (1989)

³ From Herrington (1992)

In this table it is obvious that bleached hardwood pulps have a higher charge than bleached softwood pulps and that the bleaching reduces the charges of the pulps, which is rather different from the results in e.g. table 11. This is not unexpected though, since the bleaching of the chemical pulps summarised in table 14 leads, by definition, to a large lignin removal, whereas the situation is quite different for the mechanical pulps summarised in table 11. In this respect it should be pointed out that, when the charge of the lignin is increased the solubility of the molecule increases and eventually the lignin is dissolved into the surrounding solution as described by e.g. Swerin (1994). The charge on the fibres will therefore pass through a maximum when the charge of the lignin is increased, but for the chemical pulps shown in table 14 the maximum is long since passed and the decrease in charge for the bleached pulps is therefore expected. The authors make no difference between sulphonic acid groups and carboxylic acid groups for the sulphite pulps, since this is difficult to interpret from the data, but this is a drawback compared with the results of Katz (1984). The chemical characterisation of the materials tested and summarised in table 14 is very limited and the value of the data for future quantitative comparison with other materials is therefore limited, but they have been included in this summary since they have a value as such for qualitative purposes.

In recent work by Laine et.al. (1994^2) , the results of very accurate potentiometric titrations and an evaluation of the data with different theoretical models, assuming the existence of different charged groups in the fibres, were published. Unlike the previous data presented in this section, this paper contains both accurate titration data and a good characterisation of the unbleached pulps used in the investigation. The titrations were furthermore conducted at constant ionic strength and the hydroxyl groups were generated coulometrically. The authors achieved the best fit between the measured values and the model used when the existence of two different ionic groups in the surface was assumed. These groups had intrinsic stability constants of approximately 3.4 and 5.5. The first group, with an intrinsic pK-value of 3.4, was linked to the hemicellulose in the sample, whereas the weaker acidic group was linked to charged groups in the lignin. This latter result is summarised in **figure 9**.



Figure 9. The amount of weaker acid groups in unbleached kraft pulps as a function of the lignin content of the unbleached kraft pulps used in the experiments. From Laine (1994²)

The conclusions of the authors that the weaker acid groups could be found in the lignin of the pulps are strongly indicated by the experimental results in this figure. The rest of the results regarding the charge on the unbleached pulps are summarised in **table 15**.

 Table 15.
 Summary of the charge data from Laine (1994²) where both the total charge and the distribution of this charge on different groups with different intrinsic pK-values have been included.

| Kappa number | Total charge (μeq./g) | % group 1 pK = 3.4 | % group 2 pK = 5.5 |
|--------------|-----------------------|-----------------------|-----------------------|
| 17.7 | 65 | 82 | 18 |
| 19.0 | 55 | 82 | 18 |
| 34.7 | 75 | 78 | 22 |
| 56.6 | 115 | 76 | 24 |
| 56.7 | 110 | 75 | 25 |

In this table, it can again be seen that there is a clear correlation between the kappa number and the concentration of weaker acidic groups, but it is also clear that the amount of stronger acidic groups decreases when the kappa number decreases from 56.7 to 17.7. This is probably linked to a decrease in the hemicellulose content when the cooking is extended.

In a later work, Laine (1996^{1}) investigated the charge of an unbleached birch kraft (kappa number = 18.2) and unbleached pine kraft (kappa number = 25.9) pulp, both by potentiometric titration and, by polyelectrolyte adsorption with the previously mentioned 3.6. -ionene, and how this charge was changed by enzymatic treatment with both xylanase and mannanase. The results showed the existence of two different acidic groups and the relative amount of the weaker acid in the softwood and hardwood pulps was respectively 20 % and 10 % of the total amount of acidic groups. Upon treatment with the mannanase, there was no significant change in the ratio between the two different charged groups but the xylanase treatment decreased the relative amount of the stronger acid. The results of the measurements are given in **table 16**.

Table 16. Summary of the charge data from Laine (1996¹) showing the charge of the fibres as determined by both polyelectrolyte adsorption and potentiometric titration. The table also includes data for pulps, which had been treated with pure and well-characterised enzymes.

| Pulp type | | Treatment | Total charge(µeq/g) from 3.6ionene ads. | Acidic groups (μeq./g) from pot. titration |
|--|---|---|---|--|
| kapp Pine kraft Pine kraft Pine kraft Birch kraft Birch kraft | ba number 25.9 25.9 25.9 18.2 18.2 18.2 | Ref. Xylanase Mannanase Ref. Xylanase | 100 90 100 150 100 | 85 75 85 125 90 |

There is a good correlation between the adsorption method and the potentiometric titration data showing the applicability of the adsorption method. The data in Laine (1996¹) also showed that the xylanase treatment removed 30 % of the xylan in both pulps and 22 % of the acid groups in hardwood but only 8 % of the acid groups in the softwood. This indicates that the amount of uronic acid groups in the accessible xylan is lower in softwood than in hardwood.

In summary, it can be stated that all the methods described in this section can be used to detect charges in fibres but that they have to be used with caution. In particular they have to be used in different ways with different pulps. The same trend mentioned before about poor characterisation of the used pulps is true also for the charge determinations, but the results of the different methods are very consistent. The work by Laine (1994^2) and (1996^1) also shows that a combination of good characterisation of the pulps and very careful charge determinations opens up a new dimension in fibre charge characterisation.

STRUCTURE AND SWELLING OF THE FIBRE WALL

When the swelling of the cell wall of the fibres is 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 then go on to discuss how the water is held within the wall and how the presence of the water affects the fibres.

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 (1965)¹ 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 drving 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 $0.3 \text{ cm}^3/\text{g}$. Stone and Scallan (1965²) 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 m²/g at a yield of 95.4 % for kraft pulps to 274 m²/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, macro-molecules 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 17**.

 Table 17. 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)

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

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 10.



Figure 10. 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 cm 'g. The macro-pore water is defined as the volume of N₂ adsorption and the micro-pore water is defined as the volume of 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 1968¹) 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 (1968¹) 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 1996) has shown that the absolute value of the pore size may be different from the values given by Stone and Scallan (1968¹).

Stone and Scallan (1968^2) 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, Scallan (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 11**.



Figure 11. 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 1968²). 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 12**.



Figure 12. 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 protofibrils are associated in the radial direction, with a size of 35-70 Å, whereas 3-4 protofibrils 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.

The pore structure of different fibres has also been studied more recently with NMR techniques, (Li et.al. 1993), and by Inverse Size Exclusion Chromatography (ISEC), (Berthold 1996), and the results from these measurements agree very well with the earlier measurements. With the NMR technique (Li 1993) found that the pores in the fibre wall of fibres from unbleached kraft pulps had a radius (note that these values should be doubled in order to be comparable with the pore width published by Stone and Scallan) of 2.5-30 nm which is comparable to earlier published data. An extra advantage of the NMR technique is that the diffusion of water molecules in different directions in the fibre wall could be detected, and it was found that the pores extend from a few µm up to tens of µm in the fibre direction whereas the extension in the cross direction is "rather small" (Li 1993). Berthold (1996) investigated how the delignification changed the distribution of pores in different size ranges by using ISEC where different pullulane standard polymers were used to characterise the pores in the fibre wall. With this technique, the author claims that only the pore water is measured and not the water in any gel phase of the fibre wall. Bertholds results, (Berthold 1996), show that the volume of pores in the size range from 70 to 150 Å increases when the lignin is removed whereas the volume of pores in the range from 5 to 40 Å decreases. This is in fairly close agreement with the data presented by Stone and Scallan (1968^{1}) despite the difference in the methods although it must again be stated that the use of solute exclusion and ISEC cannot give any absolute value of the pore size distribution unless the shape of the pores is known. It is also obvious that ISEC is very similar to the solute exclusion method. However, the general agreement between the different methods definitely show that the micro-pores in the fibre wall associated with a gel phase close to the cellulosic microfibrils is in the size range between 5 and 25 Å, and that the size of the interlamellar macro-pores is the size range in 25-300Å. However, an absolute determination of the size of the pores in the fibre wall is still needed.

Swelling of the fibre wall

Once the structure of the fibre wall is determined, it is easier to discuss the swelling of the fibre wall. The water held in the micro-pores, in the size range between 5 and 25Å, and macro-pores in the size range between 25 and 300 Å, is termed inaccessible water and may also be termed gel water as suggested by Lindström (1986) who followed a definition by Tieman (1906) regarding the concept of fibre saturation point. This definition is critical since it may be used to further extend our understanding of the fibre wall if it is correct. It is therefore necessary to investigate the dimensions found in other better-characterised gels.

Silberberg (1977) described the structure of acrylamide gels and found, from permeability measurements, that a proper dimensional characterisation of the gel should be the ratio, l/a, of the chain length of the constituting polymer (1) to the dimension of the crosslinked region (a) at a certain volume concentration. In crosslinked systems, he found that the ratio was between 10 and 100 and that the dimension of the crosslinked region was between 15 Å and 70 Å depending on the degree of neutralisation of the carboxyl groups in the gel. The same type of comparison has also been made by Arvanitidou (1992) and Attwood (1988) with virtually the same conclusions. This means that the dimensions are of the same order of magnitude as the dimensions found in the characterisation of the fibre wall and that the definition of the fibre wall as a gel is at least not in contradiction to the definition of synthetic gels, at least from a structural point of view.

However, it is not clear how the similarity should be interpreted on a molecular level. In a synthetic gel the single molecular chains are the smallest entities of the gel, but in a fibre wall it is the protofibrils rather than the single cellulosic chains that should be regarded as the smallest entities, as discussed by Kerr (1975). A further complicating factor for the fibre wall is the remaining lignin and hemicellulose, which form linkages between these protofibrils. The open structure between these protofibrils and the volume within the amorphous regions of the cellulose microfibrils should this constitute the gel phase of the cellulosic fibre wall together with the remaining lignin and hemicellulose. When anchored to the fibre wall, they contribute to the swelling forces in the gel but, once they start to dissolve, i.e. when their linkages to the fibre wall are broken, they are by definition no longer a part of the fibre wall. This means that there is a dynamic equilibrium within the fibre wall, which has to be considered when the similarity between a synthetic gel and the fibre wall of the cellulosic fibres is discussed. Nevertheless, with support from the geometric considerations and the fact that the fibre wall holds a considerable amount of charges and hydrophilic material, it seems justifiable to regard the fibre wall of a cellulosic fibre as a gel and to use this view to understand fundamental phenomena associated with the ability of the fibre to hold water, to be flexibilised and to interact with other fibres.

The swelling of a gel is controlled by the elastic free energy of the gel, ΔG_{elast} , the free energy of mixing of the gel components and the swelling medium, ΔG_{mix} , and the electrostatic free energy, ΔG_{elctr} (Flory 1953, Katchalsky 1954, and Yin 1992). In equilibrium, the total free energy is 0 and the following equation is hence valid:

$$\Delta G = \Delta G_{\text{electr.}} + \Delta G_{\text{elast.}} + \Delta G_{\text{mix}} = 0$$
^[20]

The following is a brief description of the contributions of the different terms in equation [20].

 ΔG_{mix} : This term emanates from the fact that the molecules constituting the network of the gel interact with the solvent and form a mix of polymer molecules and solvent molecules. It is hence composed of both an enthalpic terms described by the χ parameter, which is a dimensionless quantity characterising the interaction energy per solvent molecule divided by kT, and an entropic term taking the molar volumes and the number of molecules into consideration. In turn these results in an osmotic pressure within the gel compensating for this interaction between the solvent molecules and the molecules of the gel. Apart from cellulose, uncharged hemicellulose is believed to contribute significantly to this term.

 $\Delta G_{electr.}$: This term, which emanates from the charges within the gel can, according to e.g. Flory (1953), be deduced in two different ways. Either the total electric potential difference between the interior of the gel and the surrounding solution is determined and the osmotic pressure to this gives rise is determined, or the distribution of small ions over the gel boundaries is determined and the osmotic pressure to which this gives rise is calculated. The concentration of mobile ions will always be larger in the gel phase due to the charges in the gel.

As Flory (1953) points out, these two approaches yield identical results. Flory (1953) also mentions that the osmotic pressure created by the large number of small ions in the gel, i.e. counterions to the charges in the gel, is for most gels much larger than the osmotic pressure created by the ΔG_{mix} term. Katchalsky (1954) pointed out however that the activity coefficient of the counterions to the charges within the gel is much smaller than unity and, when determining the swelling forces of the gel from the distribution of ions between the free solvent and the solvent within the gel, this fact has to be considered. This means that the ideal osmotic pressure created by the large number of small ions in the gel, i.e. counterions to the charges in the gel, be decreased in relation to this change in activity coefficient of the counterions. Katchalsky (1954) also introduced another correction to the Flory (1953) equation for the swelling of polyelectrolyte gels which takes into consideration the change in electrostatic energy with stretching of the gel-network. The charges are found both in lignin and in xylan in the fibre wall.

 $\Delta G_{elast.}$ This term emanates from the restraining action of the compounds that constitute the fibre wall. It can be either the arrangement of protofibrils in the different cell wall layers or the combined action of these fibrils and the remaining lignin in the fibre wall. This term counteracts the osmotic forces described by the other terms mentioned above.

Taking all these factors into consideration, Katchalsky proposed the following equation for the description of swelling pressure of polyelectrolyte gels.

$$P = \left(\pi - \left(\partial G_{\text{electr.}} / \partial \kappa\right)_{V} d\kappa / dV\right) - \left(P + \left(\partial G_{\text{electr.}} / \partial V\right)_{\kappa}\right)$$
[21]

where

| π | = | Ideal osmotic pressure created both by the number of small ions within the gel and by the interaction between the solvent and the chain molecules of the gel network. |
|---|---|---|
| $\left(\partial \mathbf{G}_{electr.} / \partial \kappa\right)_{V} \mathrm{d}\kappa / \mathrm{d}V$ | = | Correction for the decrease in osmotic pressure due to the interaction between the counterions and the ionised molecules in the gel. κ is the Debye length of the solution and V is the volume of the gel. |
| Р | = | Ideal contractile pressure from the restraining action of the polymeric chains of the gel. |
| $\left(\partial \mathbf{G}_{electr.} / \partial \mathbf{V}\right)_{\kappa}$ | Ξ | Change in electrostatic free energy with the stretch of the network. |

Katchalsky (1954) also introduced simplified equations for the determination of the swelling pressure of synthetic gels, but to our knowledge these equations have not been applied to cellulosic fibres, although it would definitely be worth while to try this approach.

The theories mentioned have been developed further by e.g. Hasa $(1975^{a})^{b}$. These extensions will not be further discussed here, but the references are included for those interested in further reading on the topic.

The basic concepts of these theories of swelling of polyelectrolyte gels have been applied to cellulosic fibres and fines by several workers (Farrar 1952, Lindström 1980. Lindström 1982^{a and b}, Carlsson 1983, Scallan 1979, Grignon 1980, Scallan 1992 and Laivins (1996) to mention just a few. They have all found that the fibre wall of cellulosic fibres behaves in a manner similar to a polyelectrolyte gel, and they have also seen that the swelling behaviour of the fibre wall has very important implications for the behaviour of the fibre as a papermaking raw material.

Farrar (1952) found that the cations, i.e. counterions to the charges in the gelphase of both cellophane and cotton fibres, showed an accumulation in the gelphase at least at low salt concentrations according to the Donnan theory. It should however be noted that they did not use the term gel phase probably because the polyelectrolyte gel theories were not available at the time of publication of their data. This approach was also followed by Grignon (1980) who developed a simple model for the distribution of ions between a gel phase of the fibres and the external solution and the implications this has for the swelling of the cellulosic fibre wall when it is considered as a gel. Grignon (1980) developed the following equation describing the osmotic pressure, or at least an entity, which was proportional to the osmotic pressure, of the gel:

$$\mathbf{E} = ((\lambda - 1)/(\lambda + 1) \,\mathrm{c}\alpha$$
^[22]

where

- = Entity directly proportional to the osmotic pressure in the gel caused by the E high concentration of small ions in the gel.
- = $(Na^+)g/(Na^+)_s$ which is a distribution constant of the ions across the gel. λ

Boundary, where σ denotes gel phase and ς denotes solution phase.

 $c\alpha$ = concentration of dissociated charged groups within the gel.

The calculated ion distributions follow the same trends as were found experimentally by Farrar (1952) when the salt concentration was increased. The approach of Grignon also provides an estimate of the relationship between the pH within the gel and the pH of the external solution. It was also possible to calculate how the ion distribution changed with this model. It should be pointed out however that the model neglects the change of activity coefficient of the

counterions since concentrations are set equal to activities and there is no proper treatment of the restraining action of the network. Regardless of this, the work by Grignon and Scallan (1980) gave the first possibility to at least semi-quantitatively describe the swelling of cellulosic fibres and its change with pH and a relation between the pH in the interior of the gel and in the external solution.

In a later work by Scallan (1992), the author used the van't Hoff equation which states that the osmotic pressure within the fibre wall is RT (n/V) where R is the gas constant, T the absolute temperature, n the mole of charged groups per kg oven dried pulp and V the volume of the swollen cell wall. Assuming that Hook's law can be applied to the swelling of the cellulosic fibre wall and that the hydrogen form of the charged groups of the fibres can be taken as a reference state, the following equation was postulated as a kind of bulk modulus of the fibre wall:

$$K = \frac{RT(n/V)}{(V - V_0)/(V_c + V_0)}$$
[23]

where

- K = Bulk modulus of the fibre wall
- V = Volume of water in the swollen fibre wall
- V_0 = Volume of water in the fibre wall when the charged groups are in their hydrogen form
- V_c = Specific volume of the material in the fibre wall assuming the density to be $1.5 \cdot 10^3 \text{ kg/m}^3$

The amount of charged groups was determined by conductometric titrations and the volume of water in the fibre wall was determined by the solute exclusion procedure where the fibre saturation point was determined with a high molecular mass dextran polymer. With this fairly simple approach, Scallan (1992) determined the elastic modulus of the fibre wall of different fibres. Some of his results are shown in **figure 13**.



Figure 13. The elastic modulus of never-dried and dried and re-wetted fibres calculated according to equation [23]. From Scallan (1992)

The elastic modulus of the fibre decreases as the yield decreases indicating that the fibres are less able to withstand swelling when the lignin is removed from the fibre wall. The same trend is seen when the fibres are beaten showing that the combined action of swelling forces within the fibre wall and mechanical action is needed to flexibilise the fibres. These results show that simple relationships based on the concept that the fibre wall can be regarded as a gel can be used to understand and predict the behaviour of cellulosic fibres. It should be added that in equation [23] the relative influence of ΔG_{mix} is totally neglected.

In earlier work by Lindström (1978), Scallan (1979), Lindström (1980) and Lindström (1982^a and b), it was also shown how the chemical environment around the fibres influenced the swelling of the fibres and the properties of the paper made from these fibres. These papers show that the fibres showed swelling behaviour typical of polyelectrolyte gels and, by increasing the salt concentrations of the solution or by adding cations with higher valency, the swelling of the fibres decreased and the strength of the papers produced from these fibres decreased. Lindström (1982^a) also presented photomicrographs showing the deswelling of fibres upon addition of NaCl, which again gives support to the assumption that the

fibre wall can be regarded as a gel. The sensitivity to ions of higher valency has also been investigated by other authors, and Ampulski (1989^{a and b}) presented ion exchange equilibrium for the exchange of sodium ions by calcium ions in cellulosic fibres.

Lindström (1982^b) also showed that the fibre wall is partly irreversibly closed upon drying and, in order to overcome this so-called, "hornification", the number of charged groups had to be increased over a certain value as shown in **figure 14**, provided the charged groups had been kept in their sodium form during drying.



Figure 14. Swelling of never-dried and dried carboxymethylated fibres as a function of the concentration of charged groups in the fibre wall with different counterions to the charged groups during drying. From Lindström (1982^b)

This enables the restraining forces of the fibre wall to be calculated, but this was not done by the author, (Lindström 1982^{b}). However, the results elegantly show the balance between swelling and restraining forces within the fibre wall and that fibre walls are indeed similar to polyelectrolyte gels.

Carlsson (1983) also showed that for the swelling of chlorite-delignified spruce fibres there was a balance between swelling forces, i.e. charges within the fibre

wall, and the restraining forces caused by the structure of the cellulosic fibrils and remaining lignin in the fibre wall. As the degree of delignification increased, the swelling of the fibre wall increased due to the increasing number of charges in the fibre wall. Another factor, which allowed a larger swelling, was the removal of the lignin, which together with the hemicellulose and the cellulosic fibrils holds the fibre wall together. Since the charges of the fibres are to a large extent found in the chemically treated lignin, a maximum in swelling with increasing lignin removal should be detected due to the presence of these two counteracting factors. This was not found by these authors but in a later investigation of kraft pulps with different yields, this was found by Swerin (1994). This again shows the polyelectrolytic character of the fibre wall. Carlsson (1983) also showed that the swelling of the delignified fibres increased as the degree of dissociation of the carboxyl groups of the fibres increased, i.e. as the pH increased. When the salt concentration was increased there was a decrease in the degree of swelling of the fibres.

All these investigations show that the swelling of cellulosic fibres can be regarded as a swelling of a polyelectrolyte gel, but there is a need for further investigations where the swelling forces are calculated more rigorously and where the restraining forces of the fibre wall are determined. So far, only Scallan and co-workers have tried to estimate the magnitude of these forces in fibres. When these forces can be determined and also how they are changed by different process conditions, the concept of the fibre wall as a gel can be fully utilised.

FIBRE SWELLING IN RELATION TO REFINING/BEATING

Beating or refining (in the following called only beating) is a very important preparatory papermaking process, which is influenced by both morphological and physico-chemical characteristics of the fibres. It involves an intense mechanical treatment of a more or less diluted fibre suspension between bars, usually with a small clearance. The complex character of the process has made it very difficult properly to describe the mechanisms involved in the process, (Atack 1977), and to control the different effects on the fibres, both positive (mainly internal and external fibrillation) and negative (increased drainage resistance and fibre shortening) from a papermaking point of view (Page 1989). The heterogeneous nature of most industrial beating operations complicates the picture further and makes it less efficient. Hence, much of the industrial development in beating has been based on empirical approaches.

Beating should make the fibres sufficiently flexible and should promote fibre-fibre contacts so that, for example, a target tensile strength can be reached without too great an increase in the drainage resistance and without too great a deterioration in other properties of the finished paper. Internal and external fibrillation are effects which best satisfy this. Fibrillation depends on the breakdown of the hemicellulose-lignin matrix between cellulose fibrils by means of forces applied during beating so that a marked delamination occurs. The pores in the fibre wall which are obtained through swelling and dissolution during pulping are not sufficiently large to bring about the required flexibility of the fibre wall, (Page 1989), but can be expected to facilitate the development. Lignin usually makes beating more difficult, particularly in the case of kraft pulps.

The readiness of the matrix to break down should be regarded in relation to the general strength of the fibre wall. On the one hand, it is of great interest to have a matrix, which is easily broken down. On the other, it should retain a sufficient ability to distribute the required stresses between the less elastic fibre wall lamellae so that the strength-bearing elements are not unduly damaged. In general, swelling of the matrix material facilitates beating and improves the effects on the fibres. This is demonstrated by the difference in beating requirement between never-dried pulps rich in exceedingly amorphous and broken down hemicellulose, such as certain two-stage acid sulphite pulps, and high yield kraft pulps rich in low-swelling lignin or dried pulps with a hornified matrix. In the case of fully bleached pulp, the positive effect of swelling is not as obvious.

Disruption of the outer layers of the fibre wall, the primary wall and the S1 wall, influences swelling but is also of importance in determining the surfaces available for fibre-fibre bonding. For good fibre-fibre bonding, the reduction of fibre rigidity, produced by e.g. internal fibrillation, must be combined with a softening of the fibre surface layer, (Page 1989). This relates to the chemical composition of the fibre surface, to swelling, and at prolonged beating also to secretion of plastic material on the surface. Fines on the surfaces may also promote fibre-fibre bonding, which is particularly important for mechanical pulp fibres due to their high content of low-swelling lignin and lack of elasticity, (Nordman 1987).

Fibre-fibre bonding depends on both the bonded area and the bond strength. The bonded area has been determined as the area of fibre-fibre crossings without light scattering. Since optical contact between fibres is necessary before strong forces can be developed between the fibres, such a determination may exaggerate the size of the bonded area and underestimate the actual bond strength, as discussed by Clark (1978). The concept of bonded area is naturally correct. But today there is no good method available to estimate a correct value for this bonded area. More work in this area is definitely needed.

CONSEQUENCES FOR PAPERMAKING

The actual outcome of beating depends on several different factors of which the chemical composition (contents of mainly crystalline cellulose and of less-ordered hemicelluloses and of lignin) and swelling (mainly regarding the matrix of hemicelluloses and lignin) are of considerable importance. **Table 18** illustrates the beating required in a PFI mill in order to reach a certain apparent density of standard laboratory sheets for the different pulps shown in table 1. The mechanical pulps and pulps with very high yield have however been excluded since they cannot be brought to the chosen density levels under normal conditions. It is also difficult to reach the highest chosen density with the semi-chemical pulps, in spite of the very mild beating process used and the fact that these pulps.

 Table 18.
 Characterization of pulps according to SCAN-C 24:67 (beating in PFI mill) as well as SCAN C 26:76 and 28:76 (sheet formation and testing), cf. Table 1 for chemical composition.

| Pulp | Density | Beater revolutions | Tensile index | Tear index |
|--|--------------------|-----------------------|------------------|---------------|
| | kg/ m ³ | | kNm/kg | Nm²/kg |
| Never-dried pulps | | | | |
| Unbleached bisulphite pulp, spruce,yield 70 % | 750 | 3300 | 93 | 6,3 |
| Unbleached high yield kraft pulp, pine, kappa No. 90 | 750 | 11000 | 90 | 9,3 |
| Unbleached chemical kraft pulp, pine/spruce, kappa No. 35 | 750 800 | 4500 9500 | 92 101 | 10,9 9,0 |
| Dried pulps | | | | |
| Unbleached chemical kraft pulp, pine/spruce, kappa No. 35 | 750 800 | 5500 12000 | 90 100 | 11,2 9,3 |
| ECF-bleached kraft pulp, birch, intrinsic viscosity 1080 dm ³ /kg | 750 800 | 900 1750 | 64 79 | 8,7 8,3 |
| TCF-bleached kraft pulp, birch, intrinsic viscosity 900 dm ³ /kg | 750 800 | 700 1550 | 58 74 | 8,2 8,0 |
| TCF-bleached acid sulphite pulp, spruce | 750 800 | 1900 4100 | 62 74 | 8,4 7,0 |
| Traditionally bleached kraft pulp, pine/spruce, intrinsic viscosity 1000 dm ³ /kg | 750 800 | 3800 8200 | 87 97 | 10,8 9,1 |
| ECF-bleached kraft pulp, pine/spruce, intrinsic viscosity 875 dm ³ /kg | 750 800 | 4000 8500 | 86 95 | 10,5 8,9 |
| TCF-bleached kraft pulp, pine/spruce, intrinsic viscosity 850 dm ³ /kg | 750 800 | 4000 7800 | 86 98 | 10,9 8,9 |
| Ditto, intrinsic viscosity 725 dm ³ /kg | 750 800 | 3950 8000 | 82 93 | 10,1 8,6 |
| TCF-semibleached kraft pulp, pine/spruce, intrinsic viscosity 800 dm ³ /kg | 750 800 | 3975 8100 | 86 95 | 11,0 8,8 |
The chemical pulps on the other hand, have been tested after drying, corresponding to what applies to a market pulp. For comparison, the test results for a never-dried chemical softwood kraft pulp are shown, to illustrate the effect of drying. Dry pulp requires more beating but, if the beating is sufficiently mild, the strength level at a given density does not deviate significantly from that of a never-dried pulp although for instance the drainage resistance according to the Schopper-Riegler method is considerably higher for dried pulp. In industrial beating, the dried pulp almost always gives a lower strength than the never-dried pulp because the tougher beating conditions impair the results in general, the deterioration being greater the more powerful the beating is.

The data in the table give about the right proportions between the pulps, but there may be minor differences depending on difficulties in maintaining stable test levels over the long period, which has been required to cover all the different pulps. There are indications that the difference in tensile index between unbleached chemical softwood kraft pulps and bleached may be somewhat too small, and that the tear strength of the bleached pulp should be increased correspondingly. Bleached sulphite pulp strength varies considerably. The test results shown are somewhat above the average for this kind of pulp.

When the required beater revolutions are compared with the chemical composition in table 1, a rather complex picture is obtained. Without doubt, lignin makes the beating more difficult, but the high lignin content of high-yield bisulphite pulp has not been particularly hindering, compared for instance to the more or less ligninfree bleached kraft pulps. The greater swelling capacity of the sulphonated lignin should be of great importance in this case. A very high cellulose content should also make the beating more difficult, but that is seen in the table only for the bleached softwood kraft pulp with the lowest yield and the effect is even slight. However, in this case the difference becomes greater in industrial beating. The effect indicates that the amount of swelling matrix material is of some importance.

Compared at a given density, the tensile index values of the softwood pulps vary relatively little, with the exception of the bleached sulphite pulp and to some extent also the bleached kraft pulps with the lowest intrinsic viscosity's, i e with the most degraded cellulose. Tear index, on the other hand, varies considerably because of differences in the number of fibres per unit weight, cellulose content and fibre strength.

The birch pulps show a different pattern. Because of their smaller fibres and very high hemicellulose content, they are extremely easy to beat so as to produce the desired densities. The resulting strength levels are in general lower than those of the corresponding softwood kraft pulps, although they are quite competitive compared to those of the corresponding softwood sulphite pulp.

A general conclusion is therefore that swelling is important but that it does not dominate the beating process and its effect on the fibre properties. Obviously the response of the pulp to beating depends on a balance between the mechanical forces applied on the pulp and the softening of the fibre wall which is achieved through swelling of the matrix material. Swelling as such is not sufficient to produce the desired flexibility of the fibres. Delimitation of the fibre wall is required to considerably decrease the rigidity of the wall, as was discussed in connection with figure 11. This is attained by means of the mechanical forces in beating, unfortunately in practice accompanied by other, less desirable effects on the fibres.

CONCLUSIONS

This review has shown that the current understanding of the chemical composition of the fibre wall and how it changes with different treatments is fairly good. What could be improved is the chemical and physicochemical characterisation of the carbohydrates in the fibres. A lot of effort has been focused on lignin and extractives, from a chemical analysis point of view, despite that fact that cellulose and hemicellulose are the main constituents of a fully bleached chemical pulp.

Much effort has during the last 15-20 years been focused on a surface chemical characterisation of fibres, since the external surface is the part of the fibre, which is directly involved in the interaction between fibres and between fibres and other materials. Techniques such as charge determinations, ESCA, IGC, and contact angle measurements have been used and lately all these techniques have been refined to give even higher resolution in the characterisation of the fibre surface. However, there is still a need to use these measurement techniques on well-defined materials in order to see how different treatments influence the composition of the fibre surface. There is also a need to develop measurement techniques which can be used to determine how these changes in surface chemical composition influence the interaction between fibres and between fibres and other materials.

There is a close relationship between the structure of the fibre wall and the swelling of the fibres. Much work has been carried out to determine the structure of the cell wall and the swelling of the fibres. Today the generally accepted view is that there are micropores in the size range between 5 and 25 Å and macropores in the size range between 25 and 300 Å. Even though the experimental work behind this conclusion is good, the methods are still indirect and some work is needed to determine directly the structural dimensions in the fibre wall. Another interesting gap in our knowledge is whether the changes in the volumes of the pore sizes can be used to predict changes in the fibres from a paper-making point of view. There are experimental results indicating that a description of the structure in size ranges larger than 300 Å is necessary to give a full picture of the structure of the fibre wall.

There is a large volume of experimental results available showing that the fibre wall can be regarded as a polyelectrolyte gel and that this has considerable significance for the swelling properties of beaten fibres. What is not available in the literature, to the knowledge of the authors, is data concerning the relative importance of the charges in the fibre wall and the hydrophilic material in the fibre wall, i.e. hemicellulose, on the swelling of the fibres under realistic papermaking conditions. There is also a need to clarify how the swelling forces and mechanical treatment in the beating operation work together to flexibilise the fibre wall. It is clear, however, that the swelling forces in the fibre wall in the case of, normal papermaking fibres, are not sufficient to flexibilise the fibre wall can be looked upon as a polyelectrolyte gel, there are very few investigations available where the fundamental properties of the "gel" have been determined. This is definitely an area, which can be very fruitful in future investigations where fundamental fibre properties are linked to fundamental paper properties.

Last but not least, this paper has shown that despite fairly large initial differences between the fibres it is possible to change those properties with an appropriate mechanical treatment of the fibres. This also shows that a fundamental understanding of the relationship between fibre properties (both chemical and physical), papermachine runnability and paper properties is still lacking. This research area has a large potential for future research progress.

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LITERATURE

Aberson, G.M.: Tappi STAP No.8 (1970)pp.282

Akari, S., Schrepp, W. and Horn, D.: Langmuir 12,4(1996)857

Alince, B.: Tappi J. 11(1991)200

Ampulski, R.S.: Nordic Pulp Paper Res. J. 4,1(1989)38^a

Ampulski, R.S. and Högfeldt, E.: Nordic Pulp Paper Res. J. 4,1(1989)42^b

Annergren, G., Rydholm, S. and Vardheim, S.: Svensk Papperstidn. 66(1):1 (1963)

Annergren, G.E. and Rydholm, S.A.: Svensk Papperstidn. 62(20):737 (1959)

Annergren, G., Unpublished results (1994)

Arvanitidou, E., Klier, J. and Aronson, C.L.: In "Polyelectrolyte Gels - Properties, Preparation and Applications", R.S. Harland and R.K. Prud'homme (Eds.), ACS Symposium Series 480, American Chemical Soc., Washington, D.C., 1992, pp.190

Atack, D.: Advances in beating and refining in "Fibre-Water Interactions in Paper-Making", Transactions of the Symposium held at Oxford: September 1977, volume 1, p.261

Atalla, R.H.: Cellulose and the Hemicelluloses: Patterns for Cell Wall Architecture and the Assembly of Lignin, The 8th International Symposium on Wood and Pulping Chemistry, Helsinki 1995, Proceedings, p.77

Attwood, T.K., Nelmes, B.J. and Sellen, D.B.: Biopolymers 27(1988)201

Berg, J.C.: In "Wettability" "Surfactant science series v.49", J. Berg Ed., Marcel Dekker Inc., New York, Basel and Hongkong, 1993, pp.75^b

Berg, J.C.: Nordic Pulp Paper Res. J. 8,1(1993)75^a

Berthold, J.: PhD Thesis, The Royal Institute of Technology, Dept. Pulp and Paper Chemistry and Techn., Stockholm, Sweden, 1996

Buchert, J., Teleman, A., Harjunpaa, V., Tenkanen, M., Viikari,L. and Vuorinen, T.: Tappi J. 78 (11) : 125 (1995)

Buchert, J., Carlsson, G., Viikari, L. and Ström, G.: Holzforschung 50(1996) 69

Buchert, J., Tenkanen, M., Ek, M., Teleman, A., Viikari, L. and Vuorinen, T.: Effects of Pulping and Bleaching on Pulp Carbohydrates and Technical Properties, 1996 International Pulp Bleaching Conference, Washington D.C:, Proceedings, Book 1, p.39

Budd, J. and Herrington, T.M.: Colloids Surfaces 36(1989)273

Carlsson, G.: PhD Thesis, Royal Institute of Technology, Stockholm, Sweden, 1996

Carlsson, G., Kolseth, P. and Lindström, T.: Wood Sci. Technol. 17(1983)69

Carlsson, G., Ström, G. and Annergren, G.: Nordic Pulp Pap. Res. J. 10,1(1995)17

Chaudhury, M.K.: "Short-range and long-range forces in colloidal and macroscopic systems", PhD Thesis, SUNY, Buffalo, USA, 1984

Clark, J. d'A.: Pulp Technology and Treatment for Paper, Miller Freeman Publications, Inc., San Francisco, 1978, p.147

Dorris, G.M. and Gray, D.G.: Cell. Chem. Techn. 12(1978)721²

Dorris, G.M. and Gray, D.G.: Cell. Chem. Techn. 12(1978)735³

Dorris, G.M. and Gray, D.G.: Cell. Chem. Techn. 12(1978)91

Dorris, G.M. and Gray, D.G.: J. Colloid Interface Sci. 77,2(1980)353

Engstrand, P., Sjögren, B., Ölander, K., Htun, M.: Significance of carboxylic groups for the physical properties of mechanical pulp fibers", 6th International Symposium on Wood and Pulping Chemistry Proceedings, Appita, Parkville, Victoria, Australia, 1991, vol. I, p.75

Farrar, J. and Neale, S.M.: J. Colloid Sci. 7(1952)186

Felix, J.: PhD Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1993, pp.39

Felix, J.M. and Gatenholm, P.: Nordic Pulp Pap. Res.J. 8,1(1993)200

Fengel, D. and Wegener, G.: Wood. Cernistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin, New York, 1989, p.66

Fengel, D.: Tappi 53(3):497 (1970)

Flory, P.J.: "The Principles of Polymer Chemistry", Cornell University Press, Ithaca and London, 1953

Fowkes, F. and Mostafa, M.A.: Ind. Eng. Chem. Prod. Res. Dev. 17(1978)3

Fowkes, F.: Ind. Eng. Chem. 56(1964)40

Fowkes, F.: J. Phys. Chem. 66(1962)382

Fowkes, F. and Mostafa, M.aA: Ind. Eng. Chem. Prod. Res. Dev. 17(1978)3

Gellerstedt, G. and Lindfors, E.-L.: "On the structure and reactivity of residual lignin in kraft pulp fibers", International Pulp Bleaching Conference 1991, Stockholm, Sweden, June 11-14, 1991, Proceedings, vol. 1, p.73

Goring, D.A.I.: In Lignings, Ocurrence, Formation Structure and Reactions (K.V. Sarkanen and C.H. Ludwig Ed.), Viley-Interscience, New York, London, Sydney, Toronto, 1971, p.695

Grignon, J. and Scallan, A.M.: J. Appl. Polymer Sci. 25(1980)2829

Gutmann, V., Steininger, A. and Wychera, E.: Monatsh. Chem. 97(1966)460

Hanley, S. and Gray, D.G.: Holzforschung 48(1994)29

Hanley, S., Giasson, J., Revol, J.-F. and Gray, D.G.: Polymer 33,21(1992)4639

Hanley, S.: PhD Thesis, McGill University, Montreal, Canada, 1996

Hartler, N.: PhD Thesis, Royal Institute of Technology, Stockholm, Sweden, 1963

Hartler, N.: Svensk Papperstidning, 66(11):443(1963)

Hasa, J., Ilavsky, M. and Dusek, K.: J. Polym. Sci. 13(1975)253^a

Hasa, J. and Ilavsky, M.: J. Polym. Sci. 13(1975)263^b

Heijnesson, A-C., Simonsson, R. and Westermark, U.: Holzforschung 49(1995)313¹

Heijnesson, A-C., Simonsson, R. and Westermark, U.: Holzforschung 49(1995)75²

Herrington, T.M. and Midmore, B.R.: J. Chem. Soc. Faraday Trans. 1, 80(1984)1525

Herrington, T.M. and Petzold, J.C.: Colloids Surfaces 64(1992)97

Hodgson, K.T. and Berg, J.C.: Wood Fibre Sci. 20(1988)3

Jacob, P.N. and Berg, J.C.: Langmuir, 10,9(1994)3086

Jayme, G. and Islam, M.A.: Papier 27(3):81(1973)

Johansson, M.H. and Samuelson, O.: Sven. Papperstidn. 80(1977) 519

Katchalsky, A.: In "Progess in Biophysics and Biophysical Chemistry, Volume 4", J.A.V. Butler and J.T. Randall (Eds.), Academic Press Inc., New York and Pergamon Press Ltd., London, 1954, pp.1

Katz, S. and Gray, D.G.: Sven. Papperstidn. 83(1980)226

Katz, S., Beatson, R.P. and Scallan, A.M.: Svensk Papperstidn. 87(1984)R 48

Kerr, A.J. and Goring, D.A.I.: Cell. Chem. Techn. 9(1975)563

Kettunen, J., Laine, J.E., Yrjala, I. and Virkola, N.E.: Aspects of strength development in fibres produced by different pulping methods", Paperi ja Puu, 4,205(1982)

Laine, J., Buchert, J., Viikari, L. and Stenius, P.: Holzforschung 50, 3(1996^a)208

Laine, J., Lövgren, L., Stenius, P. and Sjöberg, S.: Colloids Surfaces 88(1994)277²

Laine, J., Stenius, P., Carlsson, G. and Ström, G.: Cellulose 1(1994)145

Laine, J., Stenius, P., Carlsson, G. and Ström, G.: Nordic Pulp Pap.Res. J.11,3(1996)201²

Laivins, G.V. and Scallan, A.M.: J. Pulp and Paper Sci. 22,5(1996)J178

Lee, L.H. and Luner, P.: Nordic Pulp Pap. Res. J. 4,2(1989)164

Lee, L-H.: Langmuir 12,6(1996)1681

Lee, S.B. and Luner, P.: Tappi 55,1(1972) 116

Lennholm, H.: "Investigation of Cellulose Polymorphs by ¹³C-CP/MAS-NMR Spectroscopy and Chemometrics", Diss. Royal Institute of Technology, Department of Pulp and Paper Chemistry and Technology, Stockholm 1994

Li, T.-Q., Henriksson, U. and Ödberg, L.: Nordic Pulp Paper Res. J. 8,3(1993)326

Lindström, T.: Das Papier 34(1980)561

Lindström, T.: In "Paper- Structure and performance", A. Bristow and P. Kolseth, Eds., Marcel Dekker, Inc. New York, Basel, 1986, pp.75 and pp.99

Lindström, T. and Carlsson, G.: Proceedings EUCEPA Conf., Warzaw, 1979, pp.32

Lindström, T. and Carlsson, G.: Sven. Papperstidn. 85,3(1982)R14^a

Lindström, T. and Carlsson, G.: Sven. Papperstidn. 85,3(1982)R146^b

Lloyd, J.A. and Horne, C.W.: Nordic Pulp Paper Res. J. 8,1(1993)48

Lundqvist, Å.: Lic. Thesis, Royal Inst. Techn., Stockholm, Sweden, 1996 Luner, P. and Sandell, M.: J. Polymer Sci. Part C, 28(1969)115

Mitikka, M., Teeaar, R., Tenkanen, M., Laine, J. and Vuorinen, T.: The 8th International Symposium on Wood and Pulping Chemistry, Helsinki 1995, Proceedings, 3: Poster Presentations, p.231

Mjöberg, J.: Cell. Chem. Techn. 15(1981) 481

Nordman, J.: In Pulp and Paper Manufacture, Volume 2. Mechanical Pulping. Joint Textbook Committee of the Paper Industry of the United States and Canada, CPPA/TAPPI, Montreal, Atlanta, 1987, p.272

Page, D.H.: Beating of Chemical Pulps - the Action and the Effects, in "Fundamentals of Papermaking", Transaction of the Research Symposium Held at Cambridge : September 1989, Volume 1, p. 1

Page, D.H., Seth, R.S. and El Hosseiny, F.: Strength and Chemical Composition of Wood Pulp Fibres", Transactions of the Eight Fundamental Research Symposium held at Oxford, September 1985, p.77

Parham, R.A.: In Pulp and Paper Manufacture. Volume 1. Properties of Fibrous Raw Materials and their Preparation for Pulping, Joint Textbook Committee of the Paper Industry of the United States and Canada, CPPA/TAPPI, Montreal, Atlanta, p. 35

Pelton, R.: Nordic Pulp Paper Res. J. 8,1(1993)113

Pu, Q. and Sarkanen, K.: J. Wood Chem. Techn. 9,3(1989)293

Rydholm, S.A.: Pulping Processes. Interscience Publishers, New York, 1965, pp.1115

Scallan, A.M. and Tigerström, A.; J. Pulp Paper Sci. 18,5(1992)J188

Scallan, A.M., Katz, S. and Argyropoulos, D.S.: In "Cellulose and Wood- Chemistry and Technology", C. Schuerch, Ed., Proceedings of the Tenth Cellulose Conference, John Wiley & Sons Inc., 1988, pp.1457

Scallan, A.M.: In "Fibre-Water Interactions in Paper-Making", Transact. Sympos. at Oxford, Tech. Div. Br. Paper Board Ind. Fed., London, UK, 1978, pp 9

Scallan, A.M. and Grignon, J.: Sven. Papperstidn. 82.3 (1979)4

Scallan, A.M. and Grignon, J.: Sven. Papperstidn. 82,3(1979)40

Scallan, A.M.: Tappi J. 72,11(1989)157

Scallan, A.M.: Wood Sci.: 6,3(1974)266

Sears, K.D., Alexander, W.J., Goldschmid, O. and Hamilton, J.K.: Tappi 61(9):105 (1978)

Sjöström, E.: Wood Chemistry, Fundamentals and Applications, Academic Press, New York, 1981

Sjöström, E.: Nordic Pulp Paper Res. J. 4,2 (1989)90

Sjöström, E.: Wood Chemistry, Fundamentals and Applications, Academic Press, New York, 1981

Sjöström, E.: Wood Chemistry. Fundamentals and Applications, second edition, Academic Press, Inc., San Diego, 1993^a, p.54

Sjöström, E.: Wood Chemistry. Fundamentals and Applications, second edition, Academic Press, Inc., San Diego, 1993^b, p.133

Stone, J.E. and Scallan, A.M.: Cellulose Chem. Techn. 2,3(1968)343²

Stone, J.E. and Scallan, A.M.: In "Consolidation of the Paper Web", F. Bolam, Ed., Transact. Symp. at Cambridge, Tech. Sect. Brit. Paper Board Makers Assoc., London, UK, Vol. 1, 1965, pp.145³

Stone, J.E. and Scallan, A.M.: J.Polym. Sci.: Part C 11 (1965)13²

Stone, J.E. and Scallan, A.M.: Pulp Paper Mag. Canada 66,8(1965)T407¹

Stone, J.E. and Scallan, A.M.: Pulp Paper Mag. Canada 69,6(1968) T2881

Stone, J.E. and Scallan, A.M.: Tappi 50,10(1967)496

Ström, G. and Carlsson, G.: J.Adhesion Sci. Technol. 6(1992)745

Swanson, J.W. and Cordingly, S.: Tappi 42,10(1959)812

Swerin, A. and Wågberg, L.: Nordic Pulp Paper Res. J. 9,1(1994)18

Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., and Vuorinen, T.: Carbohydrate Research 272:55 (1995)

Terashima, N. and Atalla, R.: The 8th International Symposium on Wood and Pulping Chemistry, Helsinki 1995, p.69

Tieman, H.D.: U.S. Dep. Agric. For. Serv. Bull. No 70(1906)

Timell, T.E.: Wood Sci. Technol., 1,1(1967)45

Toussaint, A.F. and Luner, P.: In "Contact Angle, Wettability and Adhesion", K.L. Mittal, Ed., VSP Publications, (1993), pp.383

Van de Ven, T.G.M.: Private Communication 1996

van Oss, C.J.: "Interfacial forces in aqueous media", Marcel Dekker, Inc., New York, Basel and Hongkong, 1994

Weiss, N. and Silberberg, A.: In "Hydrogels for Medical and Related Applications", J.D. Andrade Ed., ACS Symposium Series 31, American Chem. Soc., Washington D.C., 1976, pp.69

Westerlind, B. and Berg, J.C.: J. Appl. Polym. Sci. 36(1988)523

Westermark, U. and Vennigerholz, F.: "Morphological Distribution of Acidic and Methylesterified Pectin in the Wood Cell Wall", 8th International Symposium on Wood and Pulping Chemistry, June 6-9, 1995, Helsinki, Finland; Proceedings, 1: Oral Presentations, p.103

Winter, L.: Lic. Thesis, Royal Inst. Tech., Stockholm, Dept. Paper Technology, 1987

Wu, S.: "Polymer Interface and Adhesion", Marcel Dekker Inc., New York, Basel and Hongkong, 1982

Wågberg, L., Winter, L. and Lindström, T.: Papermaking Raw Materials, Transactions of the Eight Fundamental Res. Symposium held at Oxford, Mechanical Eng. Publ. Ltd., London(1985)917

Wågberg, L., Winter, L., Ödberg, L. and Lindström, T.: Colloids Surfaces 27(1987)163

Wågberg, L., Ödberg, L. and Glad-Nordmark, G.: Nordic Pulp Paper Res. J. 4,2(1989)71

Yin, Y.-L., Prud'homme, R.K. and Stanley, F.: In "Polyelectrolyte Gels - Properties, Preparation and Applications", R.S. Harland and R.K. Prud'homme (Eds.), ACS Smposium Series 480, American Chemical Soc., Washington, D.C., 1992, pp.91

Zhang, Y., Sjögren, B., Engstrand, P. and Htun, M.: J. Wood Chem. Techn. 14,1(1994) 83

Transcription of Discussion

Review Paper: Physico-chemical Characterisation of Papermaking Fibres

Lars Wågberg, SCA Research AB, Sweden

Jim Luce, Paper Performance, USA

When you were discussing the distribution of chemicals to the cell wall I recalled an effect that wasn't mentioned. In the 1960s Yllner and Engstrom and others demonstrated the redeposition of hemicellulose on fibre surfaces during the later part of the kraft cook. Does this effect exist or has that work been superseded?

Lars Wågberg

I think Gören Annergren should answer this but I can try to start an answer. In the 1960s the reprecipitation was calculated from the average chemical composition of the fibres and not from the surface composition as discussed here. But naturally you redeposit some hemicellulose since you change the chemical structure of some hemicellulose in the cook.

Gören Annergren, SCA Fine Paper, Sweden

First of all Yllner and Engstrom didn't determine reprecipitation of glucomannan because that doesn't exist. The second thing is that modern kraft cooking uses a much higher alkalinity than in the old days so you get much less xylan redeposition on the fibres. But of course it exists.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

I would like to ask a question concerning the state when the inter-fibre bond is just about to be formed. You mentioned that as a result of refining you were creating some particular structures on the external surfaces. I am a little bit bothered that we too often consider the bonded interfibre surfaces as lap joints. Should we start to consider them as jungles or entanglements of various sizes of fibrillar materials. How do we characterise this, prove or disprove this kind of 3-D fibrillar in which state you get this type of entangled fibrillar bond before the consolidation of the actual bond. How much Fibrillar entanglement do we have between the various units, lamella, macrofibrils, microfibrils, elementary fibrils and individual molecules.

Lars Wågberg

Naturally we have the same conclusion, ie that somebody should bring order into this, to determine the relative influence of the difference processes you are mentioning. Here the work at the Institute of Surface Chemistry in Stockholm and STFI have made a big step forward starting to produce pure, molecularly smooth cellulosic surfaces. If you can get a clean cellulose surface you can see how that starts to interact with other materials. You can see what is important for the pure cellulose interactions and also by determining the influence of the swelling of the surface gel you can get an idea of the influence of the fibrillar part of the band. We also had an idea for what we call the ultimate beating trial. First we beat the pulp and take out the fines and make a sheet of that. Then take enzymes to polish the surface to take away the fibrils and then check the strength again and finally prepare sheets at high salt in order to determine the influence of the swelling. That's the kind of experiment we planned to do. The problem we have with the enzymes is that as soon as you start to remove the fibrils the enzymes start to decompose the cellulose molecules in the fibre wall, as noted by a decrease in D.P (Degree of Polymerization). That's the kind of investigations I would like to see in future.

Dr Theo van de Ven, Director, Paprican/McGill, Canada

I first want to make a comment about using the geometrical rule for acid/base interactions. There is absolutely no theoretical justification of this and I think that's the reason why you infer a basic character from surface measurements of the fibres, while when you do IGC, you obtain an acidic character. I think intuitively that IGC is a much more reliable technique than surface tensions.

Lars Wågberg

Can I comment on that first? Of course you are right that a simple geometrical mean is not correct. However, if you go through Chaudhury's thesis (reference in the review) he is working hard to reach the expression for the acid-base interaction so you have to be careful before you rule it out but naturally you are right about the shortcomings of geometrical averages for these kind of interactions. It is a problem. Another problem is that you assume that the acid and base properties of water is 25mN/m and 25mN/m respectively and that is what everything is based on. Prof Stenius brought forward to me a paper which I quoted in the summary about new derivations of the fact that this assumption is not true. That makes all these measurements very shaky.

Theo van de Ven

A second point is, I am somewhat surprised that you are quoting surface potentials of over -400 millivolts and obviously in order to obtain that number, you have to use some surface area. You can either use the external surface area of about 1m²/g or use a BET area which is 100 times as large. So there is a factor of two orders of magnitude difference. Which surface area did you take and why?

Lars Wågberg

This calculation was done just to symbolise the importance of the charges. That was my main purpose. We chose $1m^2/g$ as an external surface area because that's what the fibre exposes to other fibres. You can pick another number.

Theo van de Ven

Then you have to take the charges on the external surface only.

Prof Jacques Silvy, Universidade de Beira Interior, Portugal

Do you have a comment about the effect of the roughness of the fibres in respect to the value of entanglement made on the pure film of the cellulose.

Lars Wågberg

Yes I can speculate a bit. Other people have measured the importance of the roughness that I referred to. In the work by Stan Mason you can see the importance of the roughness and the microroughness of surfaces but I also think that you have to put it into the right dimensions when you, for example, are looking at contact angles. What you are seeing is a huge droplet on the surface and this will result in an averaging when determining surface properties. So for the contact angle as determined with a sessile drop you get an average but naturally that average is very dependent on the surface structure. We have looked at that a little in our research laboratory. The effects of roughness are there but they don't totally change the values that we are determining. But naturally small droplets of pitch on the fibres might alter the results of measurement totally. It's a good question but it's very hard to give a straightforward answer.

Professor Per Stenius, Helsinki University, Finland

Just a comment on the surface potential of fibres. From our titrations you can actually calculate the surface potential using a suitable double layer model¹ using the simplest possible model (constant capacitance), which seems to be justified at reasonably high ionic strength, the highest surface potential you ever come up with is about 70 millivolts. For bleached fibre I believe the potential should be about one tenth of that.

Lars Wågberg

Yes, I read those papers also. They also contain some assumptions but I usually believe in your work and so I do in this case. Coming back to what I said before our calculations were just an illustration to show that you shouldn't neglect electrostatic forces when the fibres come together.

Bruce Lyne, Senior Manager, International Paper, USA

There is a factor of about 10 difference between the base and acid components reported for the characterisation of paper surface chemistry. I don't think you can explain that simply by the use of the geometric mean. Do you have any final thoughts as to whether the surface chemistry of the fibres is really acidic in nature or basic in nature?

Lars Wågberg

To be quite honest I don't know. I become very sceptical when I read the literature. People tend to publish data without putting them into perspective and usually pretty crude assumptions are made. Even though I might lean a bit towards the IGC technique for determining acid/base properties of the fibres, this technique must be developed further to give the true acidic and basic surface properties of the fibres.

¹ Laine, J., Stenius, P., Lörgren, L and Sjöberg, S.: Potentiometric titration of unbleached kraft cellulose fibre surfaces: Colloids Surf, A:88:277-287: 1994