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# THE ROLE OF THE FIBRE IN THE

# STRUCTURAL HIERARCHY OF PAPER

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## ABSTRACT

In this review paper, the concept of structural hierarchy is applied to paper in an effort to establish the role of the fibre in the structure of paper. The structure of paper is partitioned according to the size or scale of the features of interest, and the basic nature of a generic paper physics research project is shown to be independent of the scale being considered. The literature dealing with paper structure and properties at each significant scale is briefly introduced, and the similarity of studies at quite different ends of the spectrum is highlighted. The prospects for an integrated model relating a mechanical property such as modulus to structural variables alone are discussed. Throughout the emphasis is on mechanical properties, and the central role of the fibre within the structural hierarchy.

## INTRODUCTION

Why are we interested in the structure of paper? In fact, as end users, we are not really interested in structure at all. In the purest sense, end users of a material are interested only in the collection of properties that the material represents. For example, if a thin sheet material is tough, durable, waterproof, and can be printed

on, it could be used in applications now reserved for paper regardless of whether or not it is made of aluminum, polymer film, or paper. The use of polymer films in banknote printing is proof of this point.

Producers of a material, however, understand that the properties of the material are entirely dependent on its structure. This fundamental concept is sometimes overlooked in the paper industry. It is sometimes implied that the process used to make a material determines the properties directly, and while this is true, it is also misleading. The raw materials are processed to make a structure, and it is this structure which controls the properties. Information about the process settings - the jet to wire ratio, the calender nip pressure, the drying conditions etc. - is conveyed to the end user only if it is somehow encoded in the final structure of the sheet. This principle is a fundamental tenet of materials science and was used as the basis for the organization of the Second Fundamental Research Symposium in 1961 (1). This symposium was critical in promoting the study of paper structure (2).

This review will deal with the structure of individual fibres and the influence of this structure on the properties and structure of the resulting sheet. Because so much of the basic information has been thoroughly reviewed previously, the focus will be on creating a rigorous framework which might be useful for categorizing the literature, and highlighting some of the key references and their place within this framework. The review will therefore provide a basic description of the paper physics literature as a whole, and may be particularly useful to those without a background in materials science.

## STRUCTURE AND STRUCTURAL HIERARCHY

### Some definitions

A simple definition of **structure** is "the arrangement of particles or parts of a body" (3). By definition then, structure is that which can, at least in principle, be directly observed. In practice, very fine structural details such as the exact placement of atoms within a lignin molecule cannot be directly observed, but this is only due to the lack of a suitable measuring instrument. A complete set of **material properties** describes the way in which the material *interacts* with the rest of the universe, i.e. with external loads, radiation, and so on. This is the basic

reason that end users cannot be interested in the structure of a material: the interaction between the user and the material is controlled by the properties of the material and not its structure, although the properties are determined entirely by the relative placement of the components. **Processing** of materials is all about achieving the optimum arrangement of such components at low cost.

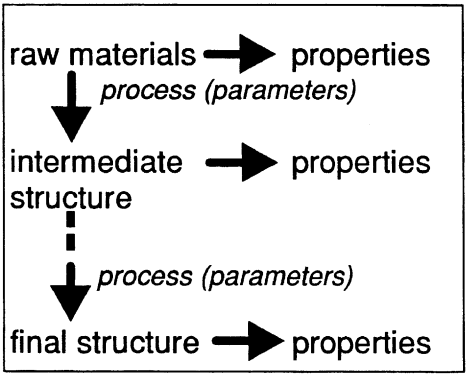


*Figure 1: A schematic of materials processing.*

The basic operation of materials processing can be considered in terms of a number of repeated operations in which a material is subjected to a process leading to a new structure. (see Fig. 1) Each structure determines the properties of the material, and each process is characterized by a set of process parameters. For example, the process of papermaking begins with tree growth, where chemical elements and compounds are turned into wood, and the associated process parameters are the tree genetics, soil conditions, and climate.

**Materials science** is the study of the structure of a material, its dependence on the process that created it, and its relationship to the properties.

In the paper science literature, the terms "structure" and "properties" are not always used according to the definitions provided above. For example, a recent paper identified seven "fibre properties" as the basic variables to describe a network: fibre strength, specific bond strength, light absorption coefficient, fibre length, fibre width, fibre coarseness, and relative bonded area (4). The first three parameters can indeed be considered to be properties of the fibre, dependent on its internal structure, but the width, length, coarseness are clearly structural variables. RBA is a variable describing the structure of the sheet. Nevertheless, this selection of variables is perfectly reasonable; for although the fibre strength is a function of the internal distribution of fibrils within the fibre, and cellulose crystals within the fibrils, etc., it is not necessary, or even desirable to consider the structure at this level of detail when modelling the properties of paper. In other words, we recognize that there is a **structural hierarchy** in paper, and we choose to ignore the structure below a certain scale. In a similar way, a civil engineer designing a bridge does not worry about the dislocation density or grain size in the steel I-beams, only the measured stiffness and failure loads of these beams. This does not mean that the structure below the scale of interest is not important in determining properties - the degree of polymerization of the cellulose in a paper fibre does have an influence on the strength of the sheet - only that the details of the small scale structure may be accounted for in a measured property. This approach is always used in paper physics, and a key objective of this review is to articulate the approach, its advantages, and its inherent pitfalls.

**Structural Hierarchy In Paper**

In a recent paper in *Nature*, Lakes discussed materials with structural hierarchy (5). All materials exhibit this hierarchy to a lesser or greater extent, but the concept of structural hierarchy is particularly important for paper. The term **structural hierarchy** describes the existence of structure at a variety of scales. Rance, in his introduction to the 1961 Fundamental research symposium, explicitly discussed the structure of paper at various scales, but suggested that the fibre was the most important structural element (1).

In nature, materials with a high degree of structural hierarchy are much more efficient than more homogeneous structures: wood and bone are excellent examples. Of course, engineers now use structural hierarchy to reduce the weight and cost of load bearing structures. Lakes cites the Eiffel tower as an example of a

very hierarchical structure (5); a high performance fibre composite structure such as a ski is a more modern example.

An example of the concept of structural hierarchy was given by Frey-Wyssling who discussed the various scales of structure in cotton (6). A similar table has been produced more recently by Emerton (7).

*Table I: Structural hierarchy in cotton fibres (after Frey-Wyssling (6)).*

| Scale | Area of cross-section | Number of cellulose chains on cross-section |
|---|---|---|
| **cotton hair** | 314 $\mu m^2$ | $1 \times 10^9$ |
| **macrofibril** | 0.16 $\mu m^2$ | $5 \times 10^5$ |
| **microfibril** | 625 $nm^2$ | $2 \times 10^3$ |
| **elementary fibril** | 30 $nm^2$ | $1 \times 10^2$ |
| **cellulose molecule** | 0.32 $nm^2$ | 1 |

Ashby and Jones produced a similar table for metals (8). Their introductory texts on materials science are highly recommended to those who want some basic background in the field (8, 9).

The concept of structural hierarchy is most useful if the scales do not overlap and the material can be considered to be homogeneous below the scale of current interest. In this case, *the structure at all scales below the scale of interest is ignored and instead represented by a set of* ***properties.*** These properties may be calculated from a model which considers the lower level structures, but more commonly they are simply characterized experimentally. This methodology is behind the choice of control variables adopted by Retulainen (4). The internal structure of the fibres is generally not of interest in the modelling of paper strength: most of the existing models use a combination of fibre properties, fibre morphology, and sheet structural variables as the basis for predicting sheet properties such as modulus and strength (10, 11, 12, 13, 14). Similarly, a model for fibre strength and modulus may consider the arrangement of the various cell wall components, but is likely to use the modulus of a cellulose crystal as an input parameter without being too concerned about the physics governing this modulus (15).

The rigorous treatment of a paper structure in terms of a distinct hierarchy is complicated by the fact that the important structural scales in paper do overlap. Nevertheless, in Table II, an attempt is made to identify the main structural levels, and to illustrate the relationship between structure and properties for each of these levels. The structure of individual atoms and the structure of the particles that make up these atoms are not included in the table, although in principle they should be, since the properties of paper ultimately depend only on the spatial distribution of, and interaction between the smallest indivisible particles of which it is composed.

*Table II: The hierarchical structure of paper.*

| **scale** | **structural component**<br>• various types at the level | **structural parameters**<br>• characterizing spatial distribution of mass only | **properties dependent on structure at this scale** |
|---|---|---|---|
| .1nm - 10 nm | **molecular structure and packing**<br>• cellulose<br>• hemicellulose<br>• lignin<br>• other components | • molecular weight (dop)<br>• stereoregularity<br>• chemical composition - (type and number of bonds, functional groups, etc.)<br>• degree of crystallinity<br>• crystal structure<br>• free volume<br>• aspect ratio of elementary fibrils (cyrstallites)<br>• fibrillar defects | • hydrogen bonding potential<br>• tensile modulus and strength of fibrils<br>• Tg of lignin<br>• influence of moisture on Tg, stiffness<br>• viscosity<br>• x-ray diffraction properties |
| 10 nm to 1 μm | **internal structure of the fibre**<br>• softwood tracheids<br>• hardwood fibres<br>• hardwood vessels<br>• ray cells<br>• compression wood<br>• tension wood | • volume fraction and position of the various components of the cell e.g. for softwood tracheid: P, S1, S2, S3, W<br>• wall thickness<br>• lumen diameter<br>• pit location and density<br>• fibril angle in each layer<br>• cracks<br>• internal fibrillation, porosity<br>• external fibrillation | • stiffness and strength of the fibre<br>• anisotropy<br>• distribution of weak spots along fibre<br>• bond strength<br>• moment of inertia of cell walls<br>• light scattering<br>• fibre saturation point<br>• swelling potential |

| | | | |
|---|---|---|---|
| 1 μm to 10 mm | **fibre morphology**<br>• different for different types of fibres: softwood tracheids, hardwood fibres, hardwood vessels, ray cells, fines | • length, width, thickness<br>• moment of inertia<br>• coarseness<br>• curl, kinks<br>• microcompressions<br>• specific surface area<br>• fines content and type ("quality") | • fibre strength, distribution of strength<br>• fibre modulus, stress/strain curve<br>• shear and torsional properties<br>• fibre flexibility<br>• collapsibility<br>• hygrothermal properties (transverse and axial) |
| 1 μm to 10 mm | **paper micro-structure** | • RBA<br>• fibre orientation distribution<br>• density<br>• fines distribution (location)<br>• porosity, pore size distribution<br>• surface texture<br>• shive content<br>• z-direction distributions - 2-sidedness | • local sheet properties - strength modulus, stress/strain curve<br>• tear strength and fracture toughness<br>• peel strength/delamination resistance<br>• viscoelastic properties<br>• printability<br>• linting<br>• opacity<br>• surface feel<br>• absorbency |
| 1 mm to 10 cm | **paper meso-structure** | • distribution of mass<br>• distribution of regions with net differences in microstructure such as average local fibre orientation, local density, or local relative bonded area | • optical formation<br>• printability<br>• tensile strength of the sheet |
| 5 mm to 30 m | **paper macro-structure** | • roll defects<br>• roll structure (density profiles etc.)<br>• md and cd variations in sheet and roll structure<br>• box structure<br>• multilayered structure | • converting performance<br>• end use performance |

Table II shows that the structure can be considered on many discrete but overlapping scales. Fibre morphology and paper microstructure are presented as separate lines in the table, but have the same basic size range, and therefore really should be lumped together.

A typical research paper will deal with the structure at one particular scale, and attempt to discuss the relationship between the processing, structure and the resultant properties at that scale. For example, Wong, et. al., discussed the effect of formation on paper properties, and treated the sheet itself as an homogeneous continuum with the local properties varying in direct proportion to the local mass (16). Similarly, Pommier et al. modelled the performance of a box by treating the constituent layers, linerboard and fluting, as homogeneous materials with known properties (17).

One apparent exception to this modelling philosophy, which deserves mention because it is widely known, is Nissan's Hydrogen Bond Theory. This theory relates the properties of paper directly to those of the hydrogen bonds within and between the fibres. Nissan concluded a recent paper with the statement that "...fundamentally, paper mechanics must be governed by the density and characteristics of the hydrogen bond, and no theory can be complete that is not based on this fact." (18). On this basis, one could equally assert that no theory can be complete without considering the density and characteristics of quarks in the nucleii of the constituent atoms. Clearly, Nissan simply followed the standard approach described here, ignoring the submolecular structure, and instead characterizing it by a **property**: in this case the force - displacement characteristics of an individual hydrogen bond. The unusual aspect of Nissan's theory is that it apparently ignores the structure at scales larger than the scale of interest. While this may be reasonable for a macroscopically homogeneous structure such as ice, it seems remarkable that it could produce a general theory in a structure as hierarchical as paper. However, the higher level structure can be partly accounted for through the parameter describing the effective number of hydrogen bonds. In random sheets this is taken as one third of the total, but is said to be higher in oriented sheets (19). If this parameter is dependent on the higher level structure, or microstructure, as suggested, then the apparent conflict between the H-bond theory and the philosophy described here is eliminated. In a discussion of the theory, Dodson and Herdman state that "Evidently the hydrogen bond model for cellulosic materials has factored out the macrostructure, and in paper this means

fibres." (20) A detailed criticism of Nissan's early work was presented by Page (21).

**Characterizing Structure at a Particular Scale**

The structure at a particular scale is nothing more than a description of the distribution of mass at that scale. This distribution is typically characterized by some sort of direct observation which involves the interaction of radiation with the material. Visible light is used in conventional and laser confocal microscopy, electrons are used in the scanning and transmission electron microscopy, x-rays are used to probe the crystal structure, and contact β-radiography is used to create mass maps for formation studies. Paradoxically, these methods of "direct" observation of structure are really only indirectly revealing structure, since the interaction of the material with radiation is actually a property of the material, according to the definition provided earlier. Nevertheless, we can accurately deduce the distribution of mass using these methods. Other methods are more clearly indirect: fibre orientation might be deduced by a zero-span tensile test or sonic modulus measurement for example.

We have established that a focus at a single structural level means that true structural variables alone are not enough to characterize the material. It is also necessary to measure (or model elsewhere) some key properties of the material which characterize the structure below the level of interest. Consequently most experimental and theoretical studies of structure/property relationships in paper actually mix a set of structural variables characterizing the level of interest with a set of properties from the next level down. Again, this does not mean that the smaller structural details are unimportant, only that they are sufficiently characterized by an appropriate set of measured or modelled material properties. In Table II, a typical set of "input parameters" or study parameters can be found by choosing the structural parameters from one line of the table, and the properties from the previous line. Of course, many experimental or theoretical studies are interested in only a subset of the complete set of parameters; only the effect of curl, or only the effect of fibril angle for example.
Table II is undoubtedly incomplete, and in any case must continue to evolve with advances in paper physics. Hopefully, the framework described by the table is useful enough to attract comment from the research community. Readers are welcome to contact the author with suggestions for improving and correcting the entries in the table.

## Processing/Structure Relationships

We have been focusing primarily on the structure/property relationships, but paper scientists are also interested in the relationship between processing and structure. For some processes, the effect of the process on the structure at one particular level can be isolated. For example, Chan et al. discussed the effect of fibre curliness on the grammage distribution (22), and Kibblewhite (23) considered the effect of pulping and refining on internal cell wall structure. It is far more common however, for a particular process to affect the structure on several levels. For example, Page suggested that the "molecular, supermolecular, and morphological structure of a wood pulp fibre" is important in considering the effect of beating (24). A failure to realize this has led to great difficulties in the study of paper physics. A classical materials science experiment involves holding all structural variables constant except for one, and relating the changes in properties to the changes in that one variable. It must emphasized that extreme caution must be used when such an approach is applied to the study of paper, since many processes alter more than one structural variable. Furthermore, the additional, and uncontrolled changes may be occurring at an entirely different structural level, one which is outside the researcher's field of expertise. Plots of property versus process variations must therefore be interpreted with great care.

## Structure/Property Relationships

By considering the structural hierarchy of paper and modelling the properties of the material based on the structure at one particular scale, we divide the task of materials modelling into manageable pieces. In principle, the models can be integrated to form a description of sheet properties based on the structure alone by feeding the output from each model into the model for the next largest scale. For example, Salmen started with the properties of cellulose, hemicellulose, and lignin, computed the properties of the cell wall based on fibril aspect ratio and volume fraction of cellulose, and then used these computed properties a composite laminate model to obtain some fibre properties (15). Although this integrated approach has great value, it is seldom used. Producers often have limited control over their raw materials, and from a practical viewpoint there is little need to model those aspects of the structure which cannot be changed. It is usually easier and more reliable, for example, to simply measure the typical fibre flexibility and strength from a particular pulp, rather than to predict these quantities based on

measurements of fibril angle and percentage crystallinity within the fibrils. This does not imply that studies of the effect of fibril angle on fibre strength are unimportant, simply that they may be partitioned off as a separate task.

Sometimes an attempt is made to bypass intermediate structural levels. For example, it a box manufacturer might try to relate swelling potential of fibre directly to box stability in a cyclic humidity environment. There might well be a strong positive correlation between this small scale structural variable and the macroscopic property of the box. Nevertheless, the relationship can only be an empirical one in the absence of a knowledge of the intermediate level structures.

Even if a single study by an individual researcher involves structural variables from several levels, or involves bypassing the intermediate level structure, it is still useful to understand the structural hierarchy, so that models can be constructed in a modular way, and that omissions are intentional and understood.

**Processing/Property Relationships**

Of course, many studies in the pulp and paper literature completely ignore the structure of the sheet and simply relate process parameters to end use properties of interest. This is common practice in a mill, which might monitor tear strength for example, and modify refining energy based on experience with the relationship between these two parameters. While this approach is fine as long as the pulp supply is stable, it tends to lead to problems when conditions change, because it is essentially based on empirical modelling. This type of approach does not generally lead to a good fundamental understanding of paper as a material.

The remainder of this article will concentrate on providing a few key references and information about the paper structure at each scale, beginning with the molecular level. We will attempt to show how individual studies can be seen in terms of their emphasis on processing/structure or structure/property relationships. By understanding the generic structure of a research paper and its position within the overall framework provided by Table II, it is possible to build a fundamental knowledge of paper behaviour more quickly than would otherwise be possible. Throughout, the emphasis is on mechanical rather than optical or printing properties. The classification approach used however, is quite general.

## MOLECULAR STRUCTURE AND PACKING

There are three main chemical components in pulp fibres: cellulose, hemicelluloses, and lignins. Each of these plays a different role in the structure of the cell wall and the overall fibre structure, but it is useful to have a working knowledge of the basic chemical structures of these components before proceeding to discuss fibrils, fibres and so on. The minor chemical components of wood -resins, waxes, tannins, pectins, and minerals - play a lesser role in the mechanical properties and will not be discussed further.

Cellulose is the name used for a linear polymer of β-D-glucopyranose (25). It is a long chain polymer with a degree of polymerization reported in wide range from 600 in wood pulps (26) to 8000 for undegraded cotton (27). The DOP is substantially reduced by the pulping process.

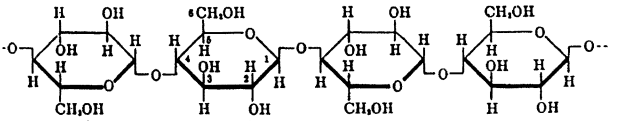

*Figure 2: The cellulose chain. Reprinted from Ranby (28)*

Hemicellulose is a term used to describe a set of low molecular weight polysaccharides which have hydroxyl groups allowing them to bond to cellulose (27, 29). They have a much lower molecular weight with a degree of polymerization in the range 100-200 (25).

Lignins are the third major constituent of wood. Their structure is based on highly branched aromatic rings with many substituted groups, and consequently they are amorphous. Recently, there have been a number attempts to understand the structure of lignin with computer simulations.(30). Lignins, together with the hemicelluloses, acts as a matrix for the cellulose microfibrils in a manner which has been copied by engineers in the construction of modern fibre composites. Lignin chemistry is discussed in detail in Ref. (31).

The chemical structures of cellulose, hemicelluloses, and lignins may are discussed by Emerton (7), Clark (26), Kolseth and deRuvo (25), and Casey (27). Atalla has studied the various molecular and crystalline arrangements in native cellulose (32). Work in this area is ongoing (33).

The proportion of each component in some typical woods is provided in Table III. Although the cellulose content of woods is quite stable, the relative amounts of hemicellulose and lignin varies from species to species and can even depend on when in the growing season the fibres were formed (34).

*Table III: Chemical composition of normal wood . Numbers are in % with range in brackets. (After Emerton, (7))*

| | **cellulose** | **hemicellulose** | **lignin** |
|---|---|---|---|
| **conifer** | 44 (41-47) | 27 (22-32) | 29 (26-32) |
| **broadleaf** | 44 (40-48) | 35 (28-42) | 21 (17-25) |

Because cellulose has a regular structure it will crystallize, with the unit cell the subject of some debate until recently. The cellulose molecules align in a parallel extended chain conformation, providing stiffness and strength in the longitudinal direction. In fibres of low fibril angle (defined below), experiments show that the fibre strength is directly proportional to the α-cellulose content, demonstrating that cellulose crystals are the prime load bearing elements in the fibre (35).

There is a hierarchy within the definition of cellulose structure, which consists of molecules, elementary fibrils, microfibrils, and fibrils. Table I provided some basic dimensions for each of these structural levels in cotton. Unfortunately, the transition between an elementary fibril, microfibril, and macrofibril is somewhat arbitrary and not generally well defined. A basic definition of an elementary fibril (sometimes referred to as a crystallite or micelle) is a structural unit of cellulose with a cross-sectional area that cannot be further reduced by mechanical means (36). The diameter of this basic unit is thought be approximately 3.5- 5 nm (6, 24). An elementary fibril represents a single ordered crystalline region of cellulose. The length of the elementary fibrils is unknown, but is probably three orders of

magnitude larger than the diameter. The definition of length is hampered by the presence of disordered zones along the length of the elementary fibrils (15, 25).

Elementary fibrils are organized into larger structural units: microfibrils and fibrils. The significance of the microfibril as a structural entity has been questioned, and it can only be defined as a proper structural entity if it has a unique structural feature which defines its boundaries. Fibrils, however, are the main sub-fibre structural feature, bounded by a matrix of amorphous material. Fibrils are embedded in a matrix of hemicellulose and lignin, although the details of possible covalent cross-links between the various components are unknown (24). The beating process is very dependent on the fibrillar distribution and the details of the links between fibrils.

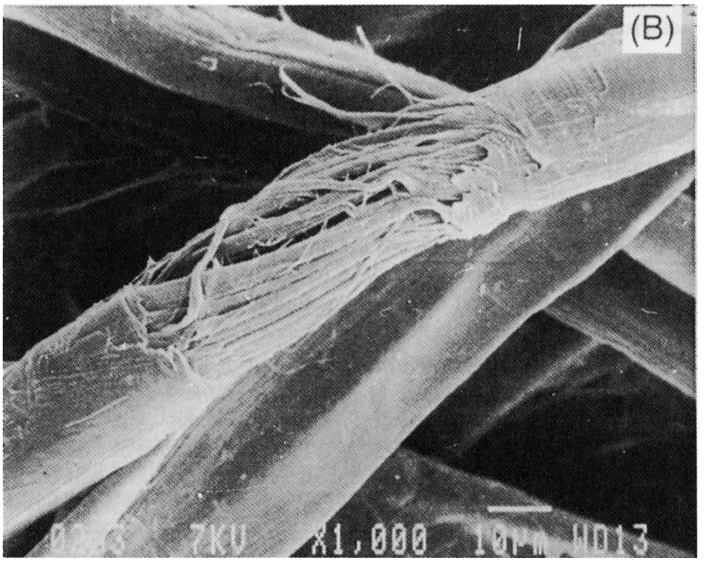


*Figure 3: SEM micrograph showing a fibrilated mechanical pulp fibre. Reprinted from Karnis (37) with kind permission from the Journal of Pulp and Paper Science.*

There is a natural division between the "chemists" who study structure at the molecular and supermolecular level, and "physicists" who study the higher level structure. The chemistry of the fibre affects its swelling and bonding potential, as well as the inherent fibre strength and modulus. These things are often simply measured for use in the physics models. Although it is acceptable and even desirable to partition the study of paper structure along these lines, all studies should at least consider the structure at other levels to ensure that factors having a major influence on the experimental outcome are not overlooked. This is particularly true for pulping studies which may have a profound effect on both fibre chemistry and morphology.

## INTERNAL STRUCTURE OF THE CELL

### Characteristics

The structure of the cell wall has been rather well documented over the years. In part of the discussion, we will concentrate on the internal structure of the cell wall only, leaving details such as the overall dimensions, lumen diameter, and so forth for the discussion of fibre morphology. This cell wall structure is sometimes referred to as the "ultrastructure" of the fibre.

There are many different types of cells in both hardwood and softwood trees. Of the various cells, the softwood tracheid has been the dominant papermaking element and thus has received the most attention in the literature. About 95% of the dry mass of softwood is made up of tracheids (34). The standard view of a softwood tracheid fibre is shown in Figure 4.

The softwood tracheid consists of five important layers, and an understanding of this layered structure is obviously critical if we are to understand the mechanical behaviour of the fibre. The middle lamella is made up primarily of lignin, which is amorphous and serves as the matrix to support and bind the fibres in wood. The primary wall is extremely thin and is made up of widely spaced microfibrils together with hemicelluloses and pectins. Chemical pulping typically removes the primary wall and middle lamella, which when considered together are referred to as the compound middle lamella. Although the primary wall is not load bearing in the finished product, it does have a significant effect during beating operations.

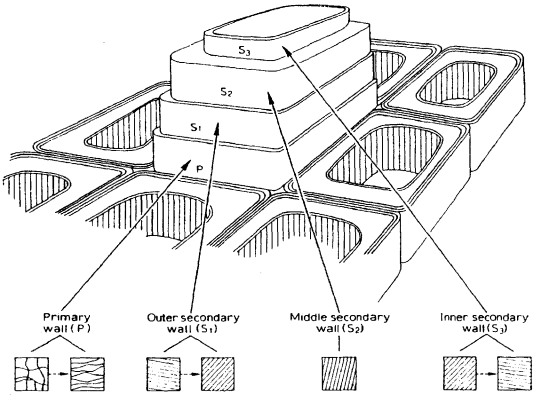


*Figure 4: Schematic cross-section of a softwood tracheid. Reprinted from Ref. (7) Emerton, H.W., "The fibrous raw materials of paper" in Handbook of Paper Science V1, ed. H.F. Rance, pp. 91-138 (1982) with kind permission from Elsevier Science -NL, Sara Burgerharstraat 25, 1055 KV Amsterdam, The Netherlands.*

The secondary wall and in particular the S2 layer, controls the mechanical properties of the fibre. The S1 or outer secondary wall is relatively thin, and is characterized by helically wound cellulose fibrils which are aligned close to the transverse direction. It is thought to consist of four to six lamellae (thin layers) with the helix angle gradually increasing toward the centre of the fibre (7). The S2 layer is perhaps two orders of magnitude thicker, 1-5 μm, and hence is the dominant structural component. The S2 layer is made up of helically wound cellulose fibrils in a matrix of lignin. The fibril angle is one of the key determinants of the ultimate mechanical properties of the fibres. Both the axial stiffness and strength depend on this angle to a large extent (15, 34, 54, 60). Low fibril angles lead to high modulus and strength, and lower strain to failure for the individual fibres. Although the direction of the helix is constant for a species, the angle does vary within a single species. Mark has provided a good review of the methods of determining fibril angle (34).

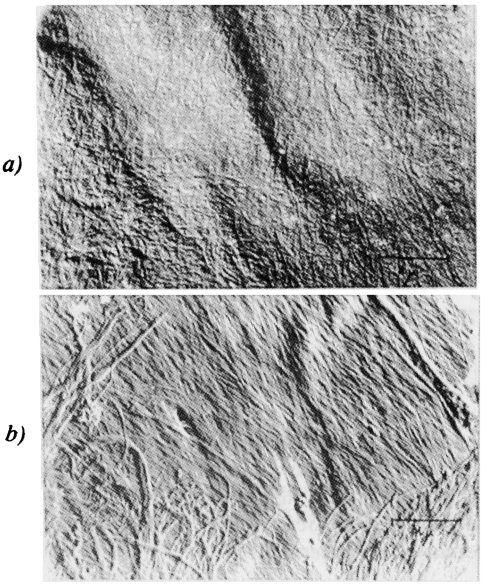


*Figure 5: Fibrillar structure of the a) primary wall in a pine tracheid, and b) outer secondary wall with remnants of the primary wall in a beaten spruce pulp. Reprinted from Jayme and Hunger (38).*

The S3 layer, or tertiary wall is distinguished from the S2 layer by a transition back to transverse fibrillar orientations, but this layer, and the so-called warty layer bounding the lumen are of little significance in papermaking.

**Processing/Ultrastructure Relationships**

The process that creates the cell wall structure in the original wood is tree growth, and this is governed by both genetics, and external factors such as the soil and climate. There is some measure of "control" over these process parameters, particularly for rapidly growing species where attempts are made to clone those trees which have intrinsically good papermaking fibres. To a large extent however, a particular mill must make the best of the existing raw materials available to it.

Fortunately, the structure of the cell wall can be altered by pulping and refining conditions, so a mill does have some control over the internal fibre structure.

The core of the papermaking operation is pulping, where wood chips are turned into fibres by mechanical or chemical means. A discussion of pulping and its effect on the fibres is beyond the scope of this review.

Another key operation is that of refining or beating of the fibres. In the case of thermomechanical pulps, refining at elevated temperatures is the basis of the pulping operation, but for other pulps, beating and refining are used to develop fibre properties by mechanically altering the structure of the fibre. The phenomenon of beating has been widely studied and a number of review papers are available. The influence of beating on the structure of the fibre, and in particular the structure of the cell wall has been studied and reviewed extensively (24, 38, 39, 40, 41, 45). There are also many of papers which relate beating directly to the final properties of the sheet without considering structural changes; beating is a common treatment in practice, and so has been used as a processing variable in many studies. Some of the early work relating beating to changes in mechanical properties was discussed by Steenburg (42).

Beating is known to produce two important structural effects at the cell wall level: internal fibrillation, and external fibrillation. Internal fibrillation is a term used to describe the separation and swelling of the cellulose fibrils in the cell wall. This separation reduces the effective moment of inertia of the cell wall and allows the fibre to become more flexible, conformable and collapsible. External fibrillation leads to the generation of fine material and leaves a gelatinous coating on the fibre which can influence the interfibre bond strength (43). The relative importance of these two effects was once the subject of intense scrutiny, and both are now thought to be important (24).

Many studies have concentrated on the cell wall porosity, swelling, and the influence of beating on these structural changes. Kibblewhite (23) showed evidence of wall delamination and found that undried kraft fibre walls delaminate and expand inward into the lumen upon refining, with the S1 layer preventing outward expansion. Page suggested that more emphasis should be placed on understanding the structure of matrix that links fibrils since it controls internal fibrillation (24). A commonly cited physical description of cell wall swelling and internal fibrillation was given by Scallan, and is illustrated in Figure 6.

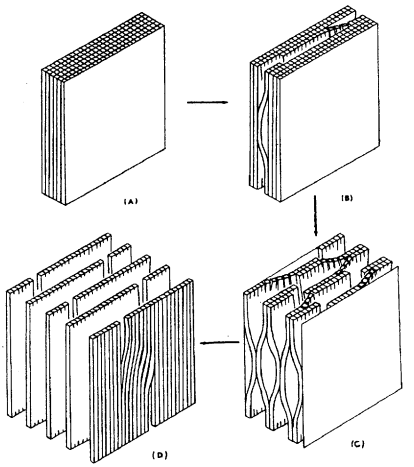


*Figure 6: Internal fibrillation with progressive cell wall swelling. Reprinted from Scallan (44) with kind permission from Wood and Fiber Science.*

There are other processes which influence the structure of the fibre wall. For example, drying is known to have a pronounced effect on distribution of microfibrils in the fibre wall (23, 45, 46). Weise and Paulapuro describe the effect of drying in terms of two sequential mechanisms: lamination or compaction of the cell wall material (the reverse of Scallon's swelling mechanism), and dehydration of the microfibril-matrix causing fibre cell shrinkage (47).

**Ultrastructure/Property Relationships**

There are a number of studies which have dealt with the relationship between the properties of the fibre and its internal structure. Experimental studies relating the internal structure of the fibre to its properties often rely on mechanical tests of individual fibres. This type of testing is rather difficult because of the small size of the fibres and the low loads involved, but in a number of studies single fibres have been loaded to failure in a tensile machine. A good summary of single fibre testing methodology has been provided by Mark and Gillis (48). A recent addition

to the methodology has been the introduction of strain mapping on the surface of a single fibre by a video image correlation technique (49). Of course, the average strength of individual fibres is also often inferred from zero-span tests of paper (10, 50).

Experimental studies of the mechanical properties of single fibres date back more than 100 years, and some of the earlier work is reviewed by Mark (48). Kallmes and Perez studied the interaction of tension and drying history on the load-elongation behaviour of single fibres and found that the application of load during drying could increase the elastic modulus by a factor of up to three, and to increase the strength by a factor of up two (51). The change in strength, in particular, indicates that the formation of hydrogen bonds within the cell wall during drying is a critical factor in determining the effective introduction of load into the crystallites. Alexander et al. examined the effect of beating and wet pressing on the properties of springwood and summerwood kraft spruce fibres and observed the introduction of defects into the cell wall, as well as changes in the fibrillar angle attending the pulping and refining processes (52). Hardacker studied the effect of loading rate, span and beating on the modulus and strength of a number of pulps (53). He observed that the tensile strength of a single fibre was reduced as the test span increased, indicating the presence of weak spots along the fibre length. Beating was found to increase the strength and modulus of the fibres, and this effect was attributed to a "working" effect which led to better stress distribution in the beaten fibres.

Page, El-Hosseiny, and colleagues published a series of papers about the mechanical properties of single wood fibres (54, 55, 56, 57, 58, 59, 60). They plotted both tensile strength (54) and elastic modulus (60) as a function of fibril angle and showed that both decreased as the angle between the fibrils and the fibre axis increased. Theoretically, the upper bound for the modulus of single fibres can be predicted reasonably well from the basic properties of the cellulose crystallites and a knowledge of the S2 fibril angle (15, 60). (See Figure 7) By repeating Hardacker's measurements of tensile strength with varying span, they were able to conclude that the fibres do contain defects along their length (57). Pits are obvious defects, and there is now direct experimental evidence of the stress concentrations close to the pit border (49). Provided the fibre was sufficiently swollen in the wet state, drying stresses were found to enhance strength by removing microcompressed regions in low fibril angle fibres, and by reducing the fibril angle in larger fibril angle fibres (56).

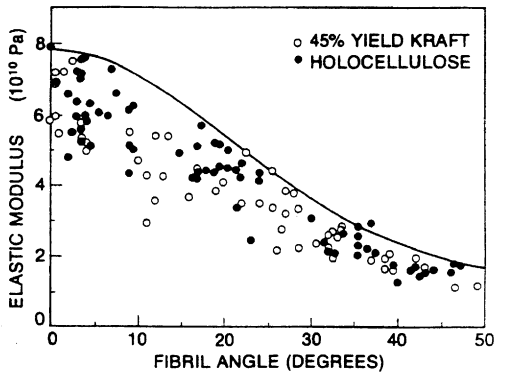


*Figure 7: Theoretical and experimental results for modulus as a function of fibril angle for spruce. Reprinted from Page (60) with kind permission from the Journal of Pulp and Paper Science.*

We can conclude the discussion of the internal structure of fibres (the "ultrastructure") by stating that the structure at this level has been well characterized in the past. There is a great deal of experimental work relating the processing of fibres to their internal structure, and in turn relating this structure to the mechanical properties of the fibres. The modelling of the mechanical properties of single fibres is not very well developed however, in part because of the great variations in structure found within a single pulp sample, and the presence of defects along the length of the fibre.

Since it is possible to measure the properties of individual fibres through tests on single fibres or by inference from paper tests such as the zero-span test, it is possible to ignore the internal fibre structure in models operating the microstructural level. This is commonly done, with fibre strength and modulus used as input variables. However, the complexity of the internal structure makes

this approach inherently risky, and this must be remembered during microstructural and higher level studies.

## FIBRE MORPHOLOGY/PAPER MICROSTRUCTURE

In this paper, the fibre morphology - length, width, thickness, curl etc. - will be discussed in conjunction with paper structural variables such as relative bonded area, density, fines distribution, etc. since they are both in the same approximate size range. In effect, the morphological variables are elements of microstructure of the sheet. A large fraction of the recent paper physics literature deals with the microstructure of paper, its effect on properties, and its dependence on processing.

Many experimental studies have focused on a single species, or a single process, and have produced a set of data relating process, structure, and properties. Unfortunately, while these studies may be useful to a mill faced with an immediate need for knowledge about a specific problem, they do not in general serve to enhance the fundamental understanding of paper as a material, because they are usually too narrow. Other studies, particularly those in which theoretical models are developed, have attempted to capture "all" of the important parameters governing these relationships. Rarely, however, can a model actually use all of the appropriate input parameters: models which attempt to do this lose their utility because they become too complex. Nevertheless, it is good to have a complete list of the variables which might be important, so that physicists are aware of the variables which are being ignored. This is particularly critical for the experimental study of paper because of the difficulty in performing a classical materials science experiment, where one variable is varied while all others are held constant. A study in which the flexibility of a fibre is altered by beating can be ruined if there is an undetected change in fibre curl, for example. Such effects are undoubtedly responsible for many of the apparently anomalous results in the literature.

In the following sections on microstructure, an attempt will be made to classify the individual papers on the subject according to their place in the hierarchical framework described by Table II.

### Principle Variables Describing "Microstructure"

As discussed above, the microstructure of the sheet is defined by a set of variables which include fibre morphology and the details of local fibre connectedness and

distribution. In addition to these geometric, or "structural" variables, taken from the third and fourth rows of Table II, we must add some fibre properties from the second row, since when we consider the microstructure of the sheet, we are generally no longer interested in the internal workings of the fibre.

The variables describing structure at this scale are reproduced below. This list only includes the variables which influence the mechanical properties of the sheet. There are other variables which are relevant for the optical, thermal, and electrical properties.

*Table IV: Summary of the parameters used to characterize paper microstructure.*

- Fibre morphology
  - fibre length, width and thickness
  - moment of inertia
  - fines fraction and quality - i.e. the specific surface area of the fines
  - curl, kinks
  - microcompressions
  - coarseness
- Fibre properties
  - fibre strength, distribution of strength
  - fibre modulus and stress-strain curve
  - shear and torsional properties
  - hygrothermal properties - transverse and longitudinal
- Fibre position
  - orientation distribution
  - z-direction distribution of orientation, lengths, fines, etc.
  - fines position
  - pore size distribution
- Fibre connectedness
  - relative bonded area
  - bond strength
  - bond modulus and the stress-strain curve of the bond
  - free fibre length between bonds
- Microstructural variables which represent useful combinations of the above
  - sheet density
  - fibre flexibility
  - fibre collapsibility
  - specific surface area

In most cases, both the mean and distribution of the variables listed above is required for detailed modelling. The variables in the last category of this list are redundant. For example, the specific surface area is known if the distributions of fibre length, width and thickness are known. These variables are included because they are used in the literature to capture the combined effect of a group of other variables and so are useful. Flexibility, which is a function of the elastic modulus and effective moment of inertia of the cell wall, is perhaps the most important of these.

Pavilaainen made a distinction between wood fibre morphology and pulp fibre morphology, identifying the critical wood fibre properties as cell wall thickness, fibre width, fibre length, chemical composition, S2 fibril angle, degree of crystallinity, and weak points in the fibre wall (61). The pulp fibre properties identified included coarseness, intrinsic fibre strength, conformability (flexibility, collapsibility), external fibrillation, and fines. Since, for example, pulping can alter the mean fibre length, these two lists are not treated separately in Table IV, but the effect of any process on these variables must be considered. It is the condition of the fibres as they are found in the sheet which determines the sheet properties.

The measurement of the parameters described above has become a field of research in itself. A review of some important measurement methods has been presented by Mark (62). Basic fibre length measurement is often done using a Kajaani fibre analyzer which registers length optically as individual pulp fibres pass down a capillary tube. The various methods of computing a useful average length from the distribution are reviewed by Mark (62), and Clark (26). Fibre cross-section can be taken from microtomed cross sections of sheets embedded in epoxy, (62) but it is now very convenient to use optical sectioning and scanning confocal laser microscopy for this purpose (63).

Curls, kinks and microcompressions are important pulp qualities reviewed by Page et al. (64). Mohlin et al. have very recently reaffirmed the need to consider "deformations" such as curls and kinks when examining the relationship between pulp and paper properties (65). Curl refers to gradual curvature and one method of quantifying it is the curl index (64):

$$curl\ index = \frac{real\ fibre\ length}{longest\ dimension} - 1$$

Kinks are sudden directional changes, typically characterized by a kink index which is a measure of the number of kinks per unit fibre length multiplied by a number between 1 and 4 depending on the severity of the kink (66). Curl and kinks are normally measured by image analysis, however a new imaging fibre analyzer has been developed by Olsen et al., and is capable of characterizing both the length and shape of fibres passing an CCD camera in a special flow cell (67).

In mechanical pulps, curl and kinks reduce the tensile properties, and pulps with "missing" properties are said to have latency.(68, 69). Note that the term latency describes the absence of properties, not the structural features themselves, and hence latency can only be characterized by the increase in properties associated with treatments which remove curls and kinks.

The measurement of tensile strength and modulus of single fibres has already been discussed. These are functions of internal structure. Fibre flexibility and conformability are listed with density and porosity as a "combination" variables, because they can, in principle be derived from the fibre morphology and the modulus of the cell wall. Flexibility and conformability measurement has attracted a great deal of attention because of the effect of these properties on fibre bonding. The dominant methods involve measuring the deflection of a fibre in a flow field, and the collapse of a fibre deposited over a wire on a glass slide. The best recent comparison of the available methods has been produced by Lawryshyn and Kuhn (70).

The mean fibre orientation distribution can be characterized in terms of sonic modulus measurements (71), or through some more direct measurement, such as those reviewed by Mark (62). A relatively new method involves measuring the far infrared dichroism and can be used to provide an areal map of local fibre orientation in zones as small as 1 mm (72). Information about the dependence of fibre orientation on position through the sheet thickness is usually obtained by sheet splitting.

The measurement of bonded area and strength have been reviewed by Uesaka (73). Relative bonded area is a term which describes the ratio of fibre surface area involved in bonds to the total surface area and is a critical parameter in many models. Bond characteristics are affected by fines, which can be imaged using back-scattered electrons in a scanning electron microscope if they have first been

halogenated (74). Sheet thickness and density measurements have been reviewed by Fellers et al. (75).

Of course, some of the structural variables in Table IV can be predicted from a knowledge of the fibre morphology and properties. The interactive multi-planar model (IMPM) is a model which describes the structure of the sheet, and in particular the frequency of bonds between layers, in terms of the fibre thickness, width, coarseness and wet flexibility (76). This model has been used to predict the density of paper (77). A simple calculation of the number of fibre to fibre contacts in a sheet was made by Komori and Makisima (78). Deng and Dodson have presented theoretical calculations of RBA (79).

Taken together, the measurement of all of the parameters in Table IV constitute a fairly complete description of the microstructure of paper. In practice, most theoretical and experimental studies of paper microstructure only consider a subset of these variables.

**Processing/Microstructure Relationships**

The microstructure of the sheet, as represented by the variables in Table IV, is affected by every part of the pulping and papermaking process. The basic aspects of fibre morphology are controlled by genetics and growth conditions.

The key "process parameters" include:

- species
- climate
- age of the tree at harvest
- part of the growing season when fibres were formed
- tension/compression during growth
- location of the fibre within the tree
- function or type of fibre

Experimental studies of species and growth conditions are numerous. A wide database of fibre morphology and properties for various species and pulping methodologies was provided by Lee (80). Hatton has discussed the papermaking properties of Douglas fir, Jack pine and Lodgepole pine as a function of the age of

the tree (81). Juvenile wood produced shorter fibres of lower coarseness when compared to the mature wood, resulting in denser, smoother, stronger sheets.

After the species and climate are determined, pulping is the next dominant process controlling fibre morphology and sheet microstructure. A discussion of chemical pulping is beyond the scope of this paper, but the structure of such a discussion would be identical to that presented here: the effect of the various process parameters (chemical type, temperature, mechanical energy, time, etc.) on the morphology and properties of the fibres must be determined and quantified. An example of this type of study was provided by Paavilainen, who discussed the effect of alkali charge and sulphidity on the fibre length, coarseness, strength, and flexibility and the RBA and zero-span bond index (82). She went on to measure the tear index and other properties of the resultant sheets and explained the dependence of these properties on cooking with reference to the morphological differences produced by cooking.

Paavilainen has also published a series of papers which typify the general methodology and approach described here (61). Using softwood kraft pulps, she measured the fibre length and fines distribution (83) cross-section and coarseness (84), wet fibre flexibility and collapsibility (85), bonding properties (86), and fibre strength (87). She determined the effect of pulping and beating on some of these parameters, and then related them to the final properties. A major component of this work was the fractionation of fibres into springwood and summerwood fractions using a hydrocyclone (88). For example she found that beating resulted in fibre length reduction and fines generation, and that both effects were more pronounced in thick walled summerwood fibres than in springwood fibres (83).

Beating leads to fibre cutting and the development of fines, but can produce other changes in fibre morphology such as curling (or straightening) and kinking (24). Fibre curl is introduced by mechanical treatment at consistencies in the range 15-30% (64). This may be done unintentionally, as with the introduction of mechanical pulp latency, or intentionally. Karnis reviewed the creation and removal of latency in mechanical pulps (89). The key to understanding the mechanism of curl creation and removal is an understanding the viscoelasticity and degradation of the interfibrillar matrix during processing (90). The effect of the refining of mechanical pulps on fibre morphology is discussed by Mohlin (91) and Karnis (37) and is illustrated in Figure 8.

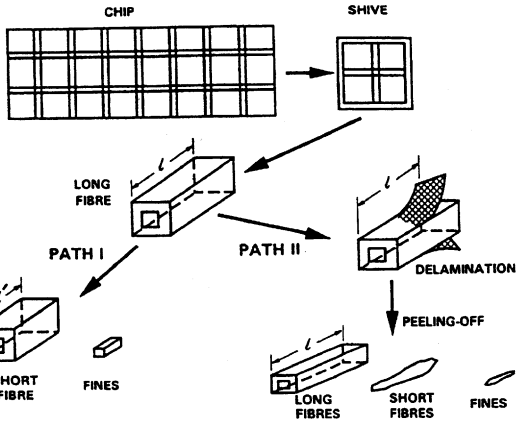


*Figure 8: Schematic showing the mechanisms of fibre development during refining. Reprinted from Karnis (37) with kind permission from the Journal of Pulp and Paper Science.*

Microcompressions at the bonds themselves can be caused by mismatch of transverse and longitudinal shrinkage during unrestrained drying (92). Nanko et al., (93) using in-situ drying experiments with scanning laser confocal microscopy and identified a critical solids content where most shrinkage occurred - the fiber collapse point. At the FCP, the fibres shrink rapidly in the transverse direction, introducing microcompressions in the crossing fibres. Microcompressions can also be induced deliberately to create high stretch papers by processes such as double roll compaction for creating high stretch papers (94).

Papermachine processes which influence microstructure include:

- the action of the slice, where the rush/drag ratio influences the orientation
- dewatering which influences the z-direction distribution of fillers and fines
- pressing, which affects the relative bonded area and density of the sheet
- drying, where restraint affects the formation of microcompressions.

A discussion of these effects is beyond the scope of this paper, and the interested reader is referred to the proceedings of the Third Fundamental Research Symposium.

**Microstructure/Property Relationships**

A primary goal of paper physics is the prediction of the mechanical properties of the sheet. A typical experimental study involves a series of experiments in which the effect of one or more structural parameters on the properties of interest is investigated. Because of the difficulties in quantifying the microstructure and the internal structure of the fibres, these experimental studies sometimes involve a series of controlled changes in process parameters - the level of beating or wet pressing for example - together with final property measurements. Studies which only relate process to properties with little consideration of structure will not be reviewed because it is difficult to use the information they provide in subsequent quantitative modelling.

Paavilainen's work (61, 83-88) involved extensive analysis of the relationships between the sheet microstructure and its properties. She found that tensile and tear index increased with increasing fibre strength and that fines had a more pronounced effect on the relatively thick walled summerwood fibres (83). The effect of fines on the mechanical properties of the sheets was also studied extensively by Retulainen, et al. (95). Paavilainen found a high correlation between coarseness and tensile index, with higher levels of beating leading to improved tensile index for all coarseness values (84). The tensile strength of unbeaten pulps was found to increase with increasing wet fibre flexibility (85). The tensile strength of thick walled fibres increased more rapidly than that of thin walled fibres in response to beating.

Page found that curl affected both pulp drainage and paper properties (64). Curl improved wet web stretch at low solids, while microcompressions improved wet web stretch at high solids when bonds are permanent. Curl also affected dry sheet properties leading to increased bulk, reduced strength and modulus, and improved tear at constant bulk (64). Karnis (89) reported an increase in tear for TMP with latency removal, however, the density of the sheets was allowed to change in his experiments. Mohlin, et al. studied the effect of fibre "deformations" on mechanical properties and also found a general degradation in tensile strength and modulus as the number of deformations in the fibres increased (65).

Quantitative studies involve an attempt to relate the main network parameters to important mechanical properties such as modulus and strength using mathematical models. In this case, the authors typically assemble a subset of "important" structural parameters from Table IV, and relate these to mechanical properties through mathematical equations. There are two principle methods by which this is done, physical models and regression or statistical approaches (96).

**Regression models**: Regression models are equations derived on purely empirical grounds using a statistical curve fitting approach. Examples include the work of Lee et al. (97) and Clark (98). Clark has suggested that only five pulp properties are required to make a complete set (26). His set includes the average fibre length, fibre coarseness, wet compactability, intrinsic fibre strength, and the cohesiveness (bonding strength) (26). Lee, et al. tested a wide variety of species and pulping methods in an attempt to cover the spectrum of potential pulp characteristics. The critical variables identified in their work were: zero span breaking length (a measure of fibre strength), average fibre length, fibre width, fibre coarseness, fibre saturation point, fines turbidity, fibre density, Canadian Standard Freeness, number of fibres per gram, fines fraction, and wet fibre flexibility (97). They derived models for breaking length, tear index, the elastic component of the J-integral, the average roughness, and porosity in terms of these 11 fibre characteristics.

**Physical Models**: While multiple regression models may be useful from a technological point of view, they do not really provide insight into the fundamental physics of paper performance. Physical models are based on an understanding and mathematical representation of the actual processes involved in deformation and failure. Unfortunately, intuition must often be substituted for real understanding, since unequivocal evidence of specific deformation and fracture mechanisms is difficult to obtain. There has, in the past, been vigorous debate about the origin of sheet plasticity, with one group of researchers claiming that bond failure in an otherwise elastic network was responsible, and others claiming that fibre plasticity was predominant. Another debate concerns the prevalence and importance of fibre fracture during paper failure. Van den Akker, et al., demonstrated that a substantial number of fibres do fail during the rupture of a variety of paper sheets by studying the rupture of a small fraction of dyed fibres which spanned the crack line (99). They found that the percentage of fibres failing increased as the level of beating, and wet pressing increased. Similar results were obtained by Helle (100).

Nevertheless, the relative effect of fibre fracture and fibre pull-out on the tear energy is not yet known with certainty (101, 102).

There have been many attempts to derive models for the elastic modulus, tensile strength and tear strength of paper. Baum's review of subfracture mechanical properties includes a table summarizing the of network theories for paper modulus (71), and Niskanen (103) and de Ruvo et al. (104) have reviewed the theories for tensile strength. Models of fracture toughness and tear strength are reviewed by Yan and Kortschot (102). Retulainen applied a modified Shallhorn-Karnis model to illustrate the effect of some basic microstructural variables on tear and tensile strength (4).

The physical models for tensile modulus are often based on the fundamental premises put forth by Cox (105). Cox derived the force in fibres as a function of the sheet strain, their length and orientation, and summed the load direction contribution from each fibre. This approach has been modified to account for such things as fibre plasticity, bond failure and so on. While we will not discus the derivation of the models, it is interesting to review some of the structural parameters built into these models in order to determine which are the dominant parameters in Table IV.

Page and Seth modelled the elastic modulus with the following equation: (106)

$$E_p = \frac{1}{3} E_f \left( 1 - \frac{w}{L\,RBA} \sqrt{\frac{E_f}{2G_f}} \tanh\left( \frac{LRBA}{w} \sqrt{\frac{2G_f}{E_f}} \right) \right)$$

where $E_p$ is the elastic modulus of paper
$E_f$ is the axial elastic modulus of a fibre
$G_f$ is the shear modulus of the fibres in the (L,w) plane
$w$ is the mean fibre width
$L$ is the arithmetic mean fibre length
$RBA$ is the relative bonded area

The important parameters for the elastic modulus of paper are thus identified: $E_f$, $G_f$, $w$, L, and $RBA$. Two of these are fibre properties, dependent on internal structure, two are fibre morphology parameters, and RBA describes the network structure. Their work also discussed the inelastic regime, and introduced an

additional parameter $E_f^*$, the effective fibre modulus in the plastic regime. In fact, the discussion suggests that the non-linear behaviour of fibres arises from the microcompressions within the fibre, and that $E_f^*$ incorporates these effects. Gross kinks and curls were treated differently, however, by imagining that they reduced the effective length of the fibre (107). Transverse fibre properties were introduced to the model some years later (108). Other authors have produced modulus models with additional parameters and varying degrees of complexity (12, 71,109, 110).

The modelling for tensile strength and tear energy absorption is based on similar principles, and contains the same sort of relationship between network structural descriptors (including fibre properties) and the property of interest. Important tensile strength equations include those by Page (10), and Kallmes et al. (111, 112). More recent work has been done by Karenlampi (113), and Feldman et al. (12). Tear models have been proposed by Kane (114), Shallhorn and Karnis (14), and Yan and Kortschot (102). A common characteristic of all of these tensile and tear models is that they involve a description of the physical mechanism of fracture, and attempt to capture the dominant parts of this mechanism in mathematical form. The goal of these studies is to be able to predict the sheet properties based on a few structural parameters. The most critical question in this field may be stated as follows: *Is it possible to represent the physics of deformation and failure in enough detail to provide truly universal predictive capability in terms of a finite number of measurable parameters?* The author's personal view is that this question has not yet been answered.

## PAPER MESOSTRUCTURE

### Characteristics

The term mesostructure has recently been coined for composite materials to describe those intermediate aspects of structure which exist between the microstructure, which is at the scale of the fibre diameter, and the macrostructure, which would describe the position and orientation of various plies in a laminated composite (115). In composite materials, mesostructure describes such things as fibre waviness, and local fibre packing density differences. This is an ideal term to describe the structure of paper at the millimetre scale. In paper, the structural features with this scale include the local grammage variations, local variations in

mean fibre orientation, local variations in density arising from calendaring, etc. The formation, or optical variability, is a property of the sheet, not a structural variable, for although it depends on the relative placement of fibrous elements, pores, and interfaces in the sheet, it really describes how the sheet interacts with incident light.

Note that it is not the density, grammage, and fibre orientation which are the mesostructural features - these terms have already been discussed as elements of the microstructure. Rather it is the way in which these features vary from point to point which is being considered now, and this variability, perhaps described by a coefficient of variation, that is of interest now.

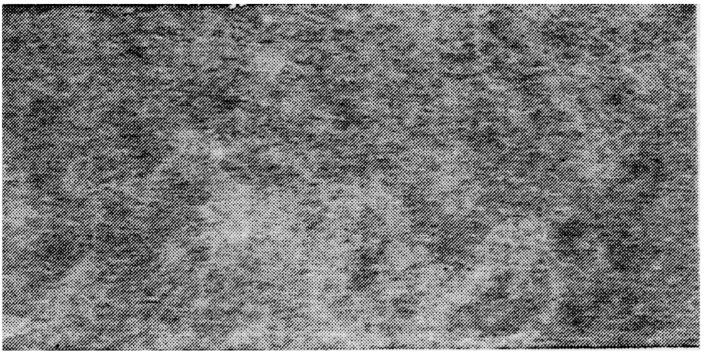

*Figure 9: Typical radiograph of a poorly formed handsheet indicating mass variations.*

Grammage variations in the sheet have received by far the most attention, both because they are extremely significant for optical and printing properties, and because they can be described by interesting and elegant mathematics. A good early reference is the work of Corte and Kallmes which used statistical geometry to describe the distribution of mass and interfibre pores resulting from a random deposition of fibres (116). Norman and Wahren described the relationship between the mass distribution and the properties of paper with an emphasis on the optical properties (117). More recently, Deng and Dodson have published a text on the subject of the paper structure and properties, with an emphasis on the structure at

the millimetre scale and above (79). This text is a good starting point for studies of formation and flocculation phenomena. Other reviews include those by Norman (118), and Corte (119). Norman also provides a brief review of measurement techniques (118).

Most of the studies in this area have focused on the description of the structure resulting from the deposition two dimensional rectangles of uniform density. The effect of fibre width, length and coarseness on the formation of randomly deposited sheets is readily derived (79). However, the statistical geometry becomes rather unwieldy if kinked, curled or non-uniform fibres are discussed. Recently, Chan et al. introduced an efficient method of simulating random deposition which was capable of creating simulated mass maps using fibres of arbitrary complexity (120). This study determined that random deposition of curled fibres or fibres with a density which varied across their width resulted in a mass density distribution which was effectively the same as that produced by the deposition of uniform rectangles. From a purely geometric point of view, then, there is little interaction between the fibre curl and resulting mesostructure in random deposition. Any such relationship observed in practice must arise from the interactions of fibres in the headbox and slice under the influence of hydrodynamics.

**Processing/Mesostructure**

One of the central issues in this field has been the comparison of real sheets with statistical geometric predictions of grammage variation in random sheets. Norman's studies indicated that a real handsheet had more uniform mass distribution than a random sheet and he speculated that this was due to preferential drainage (118). The role of hydrodynamic forces in smoothing out the mass distribution has been studied (121). On the other had, the role of flocculation in the higher consistency furnishes typical of paper machines has been extensively studied, and is known to lead to paper which is almost always less uniform than a random sheet (122). The effects of hydrodynamic smoothing and flocculation compete with each other, with flocculation dominating this competition.

Since it is well known that the hydrodynamics of flocculation and pulp drainage affect formation, there has been a great deal of effort to describe the effect of forming conditions on the resultant mass distribution in the sheet. Norman provided a good overview of the physics of forming in terms of the various processes which comprise papermaking (123). Kerekes, et al., concentrated on the

physics of flocculation at various consistencies (124). In recent years, Kerekes and Schell created the widely cited crowding factor, N, "...defined as the number of fibres in a spherical volume of diameter equal to the length of a fibre." (125). The crowding factor has been found to be a good parameter for characterizing the tendency of fibres to flocculate and withstand the hydrodynamic rupture forces in suspension.

Although it is difficult to produce quantitative theory relating flocculation in suspension directly to the formation of the dry sheet, Dodson (126) and Farnood and Dodson (127) have characterized sheets in terms of the deposition of groups of fibres which represent flocs and/or generic low grammage disks.

**Mesostructure/Property Relationships**

The mass distribution is known to affect optical and printing properties, of course (117, 128). The effect on mechanical properties is rather more subtle. An interesting study was conducted by Norman, who tested very small tensile specimens taken from random positions in the sheet to determine a property which he called the *specific tensile strength (*129). The specific tensile strength is the strength that a perfectly uniform sheet with no weak spots would possess. He found that the local specific tensile strength was independent of stock concentration, while the overall tensile strength of the sheet was reduced by increasing consistency during forming. Norman also conducted a clever set of experiments with sheets created by wet pressing discs of pulp on a uniform base sheet to investigate the effect of mass variability on burst and tear strength. More recently, Wong et.al used a combination of video image correlation and finite element analysis to examine the effect of grammage variation on strain variation and ultimate failure of poorly formed handsheets (130). They were unable to isolate a universal failure criterion based on the grammage variation alone, and concluded that there must be substantial local variations in microstructure in addition to grammage variations. The dependence of strain on local grammage has also been studied by Lyne and Hazell (131), Thorpe (132), and Korteoja et al. (133).

## MACROSTRUCTURE

In the context of the previous discussion, the macrostructure is the structure of something which is made from sheets of paper or board. Examples include corrugated boxboard, boxes, rolls, stacks of fanfold sheets, etc. At this level, the paper is typically treated as a homogeneous sheet with uniform properties. A discussion of structure and properties at this level is really outside of the domain of materials science, and is beyond the scope of this discussion.

## CONCLUSIONS

An understanding of structural hierarchy and the way in which materials science deals with it is critical for paper physicists. In the past, there have been many arguments about whether paper should be treated in terms of its bonds, its fibres, as a collection of fibre segments, or indeed as a homogeneous sheet. This type of argument is unnecessary and artificial. Every material model dealing with the atomic scale and above is based on the same fundamental principles. The structure at the lower level is ignored, and it is instead characterized by a set of properties. These are combined with structural variables at the scale of interest. This methodology partitions the task of studying the material into manageable pieces and is essential when dealing with a material with as much structural hierarchy as paper.

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# Transcription of Discussion

**Review Paper: The Role of the Fibre in the Structural Hierarchy of Paper**

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*Corrections/Addenda*

An additional reference describing the structure of paper at its various levels and the influence of this structure on the stress-strain behaviour is the dissertation of Kari Ebeling. This dissertation emphasizes the structural heterogeneity at each of the structural levels.

Ebeling, Kari, "Distribution of Energy Consumption During Straining of Paper", Ph.D. dissertation, Institute of Paper Chemistry (affiliated with Lawrence University), 1970.

*Errata:*

The perrnission line in the caption of Fig. 7 (pg. 372) should read: "Originally published in TAPPI JOURNAL, Vol.60, No.4, pp.114-117. Copyright TAPPI 1997."

Unfortunately, a version of the reference list which had not been properly proofed was printed with the rnanuscript. The following references should corrected.

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In addition, there are a number of other rninor typographical errors in the reference list The citations appearing in the text are correct. The author apologizes for the errors.

*Professor Douglas Wahren, The Paper Professor AB, Sweden*

Thank you very much. I think the definitions and distinctions you have made are important because they make it easier to be precise in our discussions. The floor is open.

*Dr Derek Page, Institute of Paper Science and Technology, USA*

This was a very nice presentation Mark. You and I have had a lot of correspondence over this by e-mail and I had a lot of things to say - I guess that's why you put a lot of references to my work in there. Seriously, this was a very useful contribution. Hierarchy is important and I have no problem with the way in which you have analysed it. However, I am concerned about talking about hierarchy when considering it from an engineering view point. For example you build a bridge or some other structure. You specify the steel and you take the steel and drill holes in it of a certain size. Now the size of the holes in the bridge is not dependent upon the steel. If you take a different steel and drill it with the same drill you get the same size holes. Unfortunately, in papermaking these hierarchies are not separate. They interact constantly. For example, if you take low yield sulphite pulp as a reinforcing pulp for newsprint and you raise the yield you get some remarkable results. As the hemicellulose content of the fibres increase they swell more, they are straighter. There is not so much curl in the fibres. This effects the stretch of the wet web, affecting the running of the machine. Fibre curl also affects flocculation and hence formation. So these hierarchies are not independent. I would not want anybody to deal with one level and think that they can ignore what is going on at all other levels. I think that many of the most interesting problems in papermaking are those that cross the hierarchical boundaries.

*Mark Kortschot*

I agree completely and I tried to fit that comment in towards the end. You need to be rather careful when you are dealing with a process. In particular processes in the paper industry are notorious because they always involve changing the structure at a variety of levels. Almost every process we can think of changes the structure at more than one level. Pressing perhaps is one that is confined to the microstructural level, but almost every other process I can think of changes the structure at all of these levels. I agree that we need to consider the structure at all levels. Now how would you go about this? You would have to integrate a knowledge of structure/property relationships at each of the levels. For example, it is not possible to tie degree of polymerisation of cellulose to the tensile strength of paper except in a empirical way unless you follow the chain all along. I think that when people logically think about paper and paper properties they are already

going through this process. All I have tried to do is to put it on the screen so that everybody can see the same picture.

*Douglas Wahren*

This is very good. You define 6 levels from nanometers to kilometres. There are quite distinct differences in the mechanisms over that range.

*Professor Jacques Silvy, Universidade da Beira Interior, Portugal*

This is a very nice piece of work indeed. My comment is about the difficulty to find the appropriate parameters that we need to characterise the structure. I am surprised that you do not speak so much about the conditions at the limit of the material we experiment with. For instance, if we speak about the tortuosity. We could look at this as a parameter of the structure. Indeed it is a parameter if you speak about transfer of fluid but not for tensile strength. I would point out that we need to look at the conditions in which we experiment the structure to choose the right parameters. Yesterday I read a book by Boyle in 1680 , entitled "Chemico-physical doubts and paradoxes touching the experiments". You could have a look at this book in the Newton library. You will see that he defines the structure of the bodies in terms of the arrangement of particles but he points out that we must look at this in a dynamic state . The conclusion is that we need to look at the motion of the bodies and in this case for paper for instance if we are interested in fluid transfer, we need necessarily to take account of the conditions of the fluid solicitation .

*Mark Kortschot*

I would say that tortuosity is a structural parameter and the permeation of fluid depends on this and the pore size distribution.

*Jacques Silvy*

No the tortuosity depends on the nature of the fluid flow and you will not find the tortuosity as a geometrical pass well defined if you do not make some assumption about the conditions of the flow. The tortuosity factor is a constant any matter of the nature of the porous media if it is a turbulent flow. But you will need to define the tortuosity as a directional parameter for the structure if it is a laminar flow.

*Dr Raj S Seth, Paprican, Canada*

Where does the history of the material come in your model. I am concerned that recycled materials are different, never dried and dried pulps are different. How would you bring these into your model?

*Mark Kortschot*

How do you know when you are making paper that the pulp is never dried or dried. How is that information conveyed into the papermaking process? This information is conveyed in the structure. If there was not a structural change from never dried to dried pulp there would not be any difference between the pulps. The fact that we can't measure the structural change - maybe we do not have the right instruments to see the structural change - does not mean that it is not there. Unless the structure is changed there can be no influence of a process on a property.