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SUBFRACTURE MECHANICAL PROPERTIES

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ABSTRACT

Virtually all paper and board grades have one or more mechanical property specifications. These are typically fracture properties, but the subfracture mechanical properties are also important. In many situations raw material and papermaking variables impact subfracture and fracture properties in similar and predictable ways.

In this review we discuss the impact of fiber and paper machine variables on the mechanical properties of paper and board up to the point of failure. As with any real material, the physical properties (mechanical, optical, electrical, etc.) are not independent but depend upon the constituents and structure of the material. We discuss these connections where appropriate.

From a historical perspective, those "turning points" that led us to greater understanding of the mechanical properties are pointed out, as are situations where work is needed.

INTRODUCTION

All paper grades have mechanical property specifications. Most often these are basis weight and/or caliper and some strength property such as tensile, tear, tensile energy absorption, or burst. Many grades, however, have mechanical property requirements other than strength properties. For example board grades have bending stiffness, the resistance to bending, as an important specified attribute that is relatable to end-use performance.

Material science tells us the physical properties of materials are dependent on the nature of the chemical bonding that exists in the material and the extent and type of defects present. Figure 1 attempts to illustrate this interdependence between physical properties. For example, in gemstones the mechanical properties [rigidity or ductility, hardness, toughness, directionality (crystalline structure)] and optical properties (index of refraction, color) are traceable to the nature of the chemical bonds. In gemstones these bonds are typically some combination of ionic and covalent bonds. On the other hand, defects in the structure also affect all of these properties. Defects include nonstoichiometry or imperfect crystalline growth or impurity atoms present in the structure at substitutional or interstitial sites.

Properties of noncrystalline materials can also be understood in terms of Figure 1. For example, wood is piezoelectric. Fibrous webs, as we typically make them for paper and board products, fit the illustration fairly well, but we must stretch our imagination to some extent. For one, the fiber web is very heterogeneous and, thus, we need to consider the properties of both the fibers (and modifications thereof) and the nature of the bonding that holds the fibers together in order to describe the properties of the overall structure. In addition, because of the nature of the fiber web, paper may be viewed as a collection of "defects" (voids). The optical properties of paper are strongly dependent on light scattering from the air/cellulose interfaces. Finally, we know that the hydrogen bonds holding the

fibers together are very sensitive to moisture (because the water molecule is very polar with a high dielectric constant) and water itself may be considered a "defect". Nevertheless, the fibrous network does still follow the scheme shown in Figure 1 fairly well and, as we discuss the prefracture mechanical properties of the fibrous network in this review, we should attempt to understand how changes we observe in these properties might impact or relate to the other physical properties.

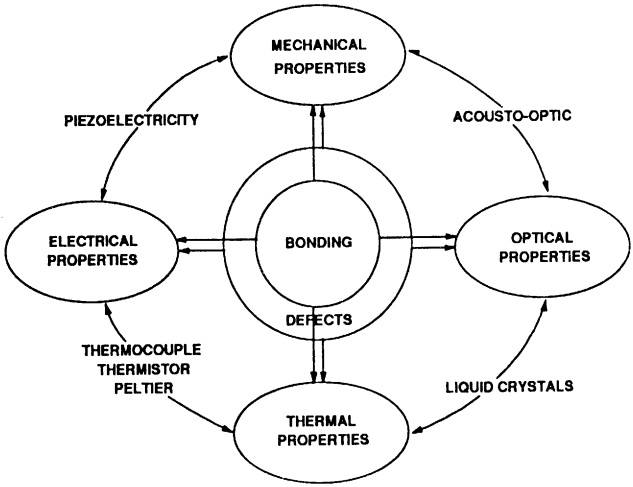

Figure 1. The physical properties of crystalline and most other materials depend on the nature of the chemical bonding and the types of defects present in the structure.

This review deals with those nonfracture (nonstrength) or prefracture mechanical properties that are important in understanding and characterizing the basic fiber structure and for defining end-use performance. In addition, we have an interest in understanding the mechanical behavior of the moving paper web, either during manufacture or in some subsequent converting process.

Steenberg (1) points out that what is needed is the ability to predict the behavior of paper or board from a small set of properties. This would provide the scientific basis for helping us select raw materials and manufacturing variables to enable the design of products with the desired attributes. Figure 2 (2) provides an illustration of the complexity of the situation for paper or board manufacture and, also, will help us to define some terms. In order to engineer a product with specific end use (or converting) attributes, we must specify many raw material and manufacturing variables. A problem with this is that, while we may know the response of some property to a given input, we seldom know the response of that property to the collection of all the inputs. Steenberg (1) also discusses this point, noting that such a disciplinary analysis of the influences on the mechanical properties of paper is unlikely to provide us an integrated knowledge of the behavior of the system as a whole. What is needed here is a structural model which explains existing results and allows us to make predictions, but thus far a definitive model does not exist.

Scientists often describe the fibrous structure in terms of network parameters that, in turn, are (hopefully) related to physical properties. Network parameters, as the name suggests, define the attributes of the network, for example, bond area, bond strength, relative bonded area, fiber lengths and widths, unbonded fiber segment lengths, etc., and the statistical distributions of these attributes. Such network parameters can be very useful in trying to understand the nature of the fibrous structure, but generally do not lend themselves to easy measurement. We will discuss some of these parameters in more detail later.

Finally, Figure 2 reminds us that the local environment, temperature and relative humidity, play an important role in paper and board properties and end-use performance (and convertibility). This sensitivity is described in a separate review paper from this Symposium and will not be considered in any depth here. Figure 2 implies that relationships exist between end-use performance (convertibility) and measurable physical properties, but this may not be the case. We

have fallen into the situation where we define "goodness" or "quality" using physical properties, but the quality so defined may not be relatable to the desired end-use performance. That is, we often do not know how to define end-use performance.

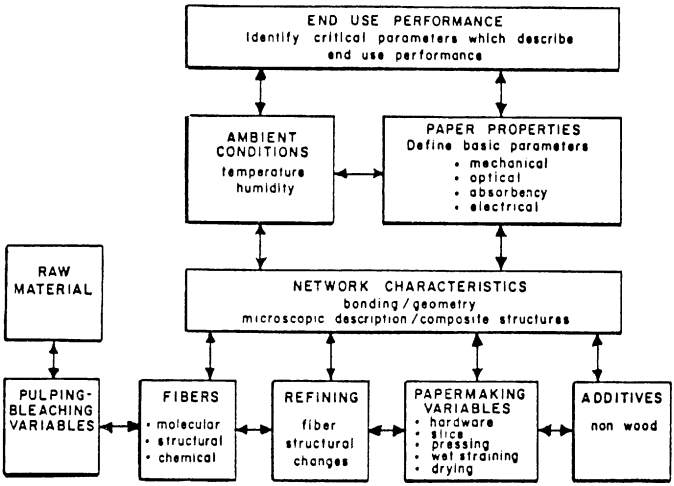

Figure 2. Schematic diagram showing the relationships between raw materials, manufacturing variables, network and paper properties, and end-use performance.

There are different "levels of organization" from which we can discuss the fibrous network (e.g., 2). We could start with the cellobiose unit that makes up the cellulose polymer chain. The cellulose chains arranged in a close packed (crystalline character) or in an amorphous (noncrystalline) array, make up "microfibrils" which, in turn, form "fibrils". Kolseth and de Ruvo provide a comprehensive description of the cell wall components (3). The fibrils are the structural elements from which the fiber cell wall is constructed. These are arranged in

an orderly fashion in distinct "secondary layers" that have a strong bearing on what happens during subsequent fiber treatments and the papermaking process. More on this later. Finally we can discuss the arrangement and bonding of fibers in the network. In this review, for completeness, we will start with an introductory treatment of the fiber cell wall and how it influences the papermaking process and mechanical properties. We will then move on to discuss the network itself.

Before proceeding, however, it is worth looking at the potential strength that might be realized for paper, based on fiber properties. Wood pulp fibers, when compared on a mass basis, are stronger than many common engineering materials as depicted in Figure 3.

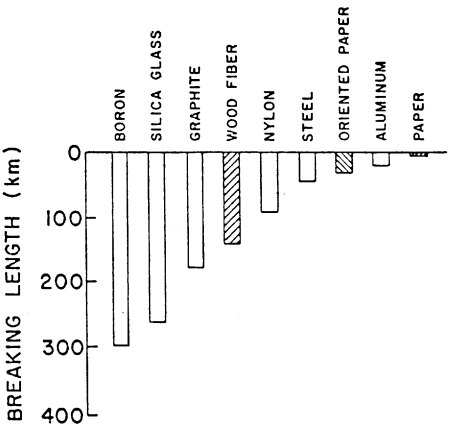

Figure 3. A comparison of breaking lengths or specific strengths for some common engineering materials. On a mass basis, wood pulp fibers can be stronger than some metals.

The breaking length (tensile strength/density • acceleration of gravity) or specific strength of the wood fiber is greater than that for steel or aluminum. While the 140 km breaking length for the wood fiber in the figure is one of the strongest reported in the literature (4), even if the average was one-third or one-half the reported value, we have a

remarkably strong material. Yet the paper we make from such fibers is typically much weaker (right side of Figure 3).

The literature on the mechanical properties of paper and board is vast and typically combined with discussions of strength properties. The mechanical properties of paper comprise a very active research area. Because of space limitations, this review cannot be comprehensive in the discussion of all of the aspects of prefailure mechanical properties, but will rely heavily on several books (5-9) and a number of excellent reviews in the literature for the finer points and details. The reviews by Herdman and Dodson (10) and Perkins (11), and the book edited by Bristow and Kolseth (9), are particularly good and recommended to the reader. In addition, much of the work done in this area is presented in the proceedings of these Fundamental Research Symposia (Cambridge-Oxford Symposia) and these volumes are also important sources of information (12A-12H). The 1989 Cambridge Symposium, "Fundamentals of Papermaking" (12H), includes a number of excellent state-of-the-art reviews on topics related to our theme. I recommend the study of these for in-depth discussions of the material presented in this review.

CONSOLIDATION OF THE WEB

As an introduction to paper and board mechanical properties, the following sections give a brief overview on how raw materials and manufacturing variables interact to produce a given set of sheet properties. Where possible, we will try to describe how these properties may relate to converting requirements or end-use situations.

Paper is somewhat unique among engineering materials in that the separated wood fibers can rebond to each other by naturally occurring forces. The "bonds" between fibers are generally accepted to be a multitude of hydrogen bonds within some bond "area". A hydrogen bond is one in which the proton in a hydrogen atom (in a

hydroxyl group, for example) is "shared" between two electronegative oxygens. Because the bond lengths for hydrogen bonds are of the order of several Angstroms, the two surfaces (fibers, fibrils, or molecular entities) must come very close together for the bond to occur. A major advance in our understanding of this phenomenon occurred when Campbell (13) demonstrated how surface tension forces are responsible for bringing the wet fibers together so that bonding can occur. Surface tension forces become quite large as water is removed from the wet web. According to Lyne and Gallay (14) surface tension forces become increasingly important in the range from 10 to 25% solids, at which point hydrogen bonds begin to form. Lyne and Gallay were able to show that at higher solids the wet web strength caused by surface tension forces would decrease while that caused by chemical bonds would increase. This explanation is consistent with experiments done on wet web strength vs. solids in which an inflection point is often seen around 25% solids.

As air begins to enter a low solids web, the discontinuous liquid (water) film gives rise to (attractive) surface tension forces that depend on the length of the air-fiber-water contact line. At roughly 25% solids, the surface tension forces gradually change to those that depend inversely on the thickness of the water film. The pressure difference between two surfaces, separated by a water film of thickness x, is given by $P = 2\sigma/x$, where σ is the surface tension of the water. Decreasing the water film thickness between fibers (or between fibrils) leads to very high differential pressures that force the surfaces close enough for hydrogen bonding to occur.

The extent of hydrogen bonding over some fiber to fiber "contact area" clearly depends on the ability of the two surfaces in question to conform to each other. For example, two crossed rigid circular fibers would have only a small contact area in which chemical bonds might occur, whereas for "conformable" fibers surface tension forces would create much larger contact areas, allowing bonding over a larger area.

The word "conformable" here is taken to mean flexibility both along and perpendicular to its axis. Claudio-da-Silva showed that a good indication of fiber flexibility can be obtained from the reciprocal of its (calculated) bending stiffness (15). It should be clear that the flexibility or conformability of a fiber, as well as its other physical properties, will depend on many factors, some of which are: wood species (hardwood vs. softwood); the time of year the fiber was grown (earlywood vs. latewood, thin cell wall vs. thick cell wall); growth location and conditions (northern vs. southern); the age of the tree (juvenile wood vs. mature wood); the location in the tree that the fiber came from (compression wood vs. tension wood, slab wood vs. core wood); pulping method (chemical vs. mechanical, pulping liquor, yield); and refining method and level.

Paavilainen (16) recently studied the impact of softwood kraft fiber morphological properties on fiber strength, flexibility, and collapsibility and the subsequent impact on network properties. She noted that fiber cell wall thickness was one of the most important attributes. Gurnagul et al. (17), studied the sheet properties of Canadian hardwood kraft pulps. They noted that many of the variations in sheet physical properties could be explained in terms of the differences in fiber morphology. Seth (18) recently reported on the importance of fiber coarseness (mass per length) on pulp properties. He noted that a change in fiber strength or length primarily affects sheet strength, while fiber coarseness affects practically all sheet properties.

Many of these variables tend to be interdependent. For example, the level of refining required to produce a particular "wet fiber flexibility" will depend on all of the other factors named above. For a single piece of wood, of course, one typically finds a broad distribution in many of the fiber properties of interest (length, diameter, cell wall thickness, etc.), not just flexibility. Abitz and Luner (19) recently reviewed this area and showed that wet fiber flexibility was sensitive to refiner type, load, and consistency. One difficulty is that wet fiber flexibility is difficult to measure. There have been several techniques developed in recent years, however, which are beginning to provide

useful information. Tam Doo and Kerekes (20, 21) position a single fiber across the ends of a capillary tube within a water bath and measure the flexibility by observing the fiber as the liquid in the capillary is pulsated. Steadman's method (22), which permits more rapid measurements, involves placement of a very thin fiber network over a parallel array of fine stainless steel wires placed on glass. Fibers crossing the wires will be out of contact with the glass for some distance. This distance, measured optically, is inversely related to the fiber flexibility. Luner (23) recently used this technique to show that cell wall delamination was more important than fiber collapse in increasing wet fiber flexibility.

The Fiber Cell Wall

Since our objective is to review mechanical properties prior to fracture, it is appropriate to pursue the nature of the cell wall further, as this will also impact those events that occur after consolidation of the web. The first part of this section is not a review of current literature, but is included to help the newcomer in understanding the complexity of the paper structure. References (6) and (24) provide a good review of the subject.

Wood fibers in their natural state are hollow filament wound composite structures, composed of cellulosic fibrils surrounded by a matrix of lignin and hemicellulose, as shown in Figure 4. Kolseth and de Ruvo (3) discuss the components of the cell wall. Hemicellulose is believed to be the interface between the cellulosic fibrils and the lignin. The lignin-hemicellulose matrix distributes loads over the length of the fibril and provides moisture resistance for the fiber. The arrangement of the fibrils in the secondary cell wall provides the necessary structural attributes required by the fibers. That is, the innermost S3 layer provides lateral resistance to internal pressures, the S2 layer, with the stiff cellulosic fibrils oriented at a low angle to the fiber axis, provides the high axial stiffness of the fiber, and the outermost S1 layer provides additional resistance to internal stresses, e.g., swelling, and keeps the entire assembly together.

The thickness of the secondary layers in the cell wall and the angular distribution of the fibrils in each layer relative to the fiber axis depend on those factors named above (species, climate, age of the tree, location in the tree, etc.). Pulping modifies the structure of the cell wall (see, for example, 25). Mechanical pulp fibers, in which much of the lignin remains in the cell wall, tend to be rather rigid and do not readily collapse during papermaking since the fibrils are held rigidly in position by the lignin-hemicellulose matrix material. During chemical pulping, however, the chemicals that remove lignin from the interlamella region between fibers also remove lignin from within the cell wall. This means that the fibrils (in the wet fiber) can more easily move relative to one another, especially when water is present between them acting as a lubricant and, also, acting as a plasticizer softening the hemicellulose component. Thus, chemical pulp fibers in the wet state tend to be much more flexible than mechanical pulp fibers and this leads to greater bond strength. In addition, the chemical pulp fiber is more likely to collapse, again because of the ability of the fibrils to readily move relative to each another.

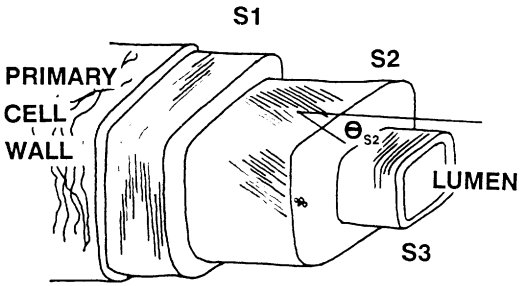

Figure 4. A schematic representation of the fiber cell wall showing the arrangement of the fibrils in the S1, S2, and S3 layers (Ref. 2).

Pulping opens up the cell wall creating more surface area up to a point. At very low yields, however, degradation of the cellulose may occur as evidenced by a reduction in the degree of polymerization (26). Beating or refining of a pulp fiber also opens up the cell wall. There are several good reviews on refining (27-29). Chemical pulps, because they have some lignin removed from the cell wall, are more easily "refined" than mechanical pulps. That is, it is easier to separate layers of fibrils or fibrils from each other. This "internal fibrillation" allows the fibrils to more easily move relative to one another, making the fibers "conformable". Surface tension forces during web consolidation can then draw fibers together more extensively than possible if the fibers were rigid.

Ostberg and Salmén (30) recently conducted mechanical fatigue experiments on a never-dried softwood pulp. They attempted to characterize the increase in internal fibrillation by specific surface analysis using water sorption isotherms. The results suggested that the cellulose-water interfacial region was not altered by the mechanical fatigue of the wood.

Prolonged or more extensive refining will cause fibrils or layers of fibrils on the fiber surface to unwrap and separate from the fiber. This "external fibrillation" also promotes fiber-to-fiber bonding because the surface area of the fiber is considerably enhanced, allowing more opportunities for surface tension forces to draw fibrils (hence fibers) together. It is also possible that fibrils from two or more fibers in proximity could become tangled which would provide some mechanical bonding. This form of flocculation may not be desirable if it occurs prior to web consolidation.

Fibrils hanging from the surface can be broken off by hydrodynamic shear stresses, interactions with other fibers, or subsequent refining, thus becoming "fines." Fines can enhance bonding in chemical pulps by bridging between fibers, or can just be redeposited on the fiber surface during consolidation and drying. On the other hand, fines

may be lost with the white water, representing a material loss. All these topics are discussed in the references given above.

In summary, from the perspective of the cell wall, chemical pulping and beating help to separate fibrils from each other, which leads to increased surface area and more flexible fibers. During consolidation, pressing, and drying, water removal from these regions results in high surface tension forces that act between fibers, fibers and fibrils, and fibrils in the cell wall. This leads to large areas of contact and the possibility of many hydrogen bonds and therefore to a well bonded (strong) network. We should not underestimate the importance of the cell wall structure on this overall scenario of formation of the fibrous structure and, therefore, on the mechanical properties of interest to us here.

Much of the information in the literature concerning the impact of fiber properties and fiber treatments on paper structural properties has not been related to changes in the cell wall. This is unfortunate, since cell wall mechanics seem to be the commen denominator that could help us form an integrated picture of the process.

Models of the Cell Wall

A model of the cell wall capable of describing the mechanical properties of the fiber in terms of the properties of the components and their arrangement in the structure would be desirable. Such a model would enable us to investigate the sensitivity of fiber properties to changes made in the components via pulping, bleaching, refining, etc. Salmén (24) has reviewed this area.

Mark (31) developed a two-dimensional elastic model of the cell wall that included the S1, S2, and S3 layers. Each layer was assumed to be orthotropic. Input parameters for each layer were the amount of material present in the layer, the proportion of framework (cellulosic fibril) to matrix (hemicellulose and lignin), the orientation of the fibrils in the layer, and the elastic properties of the framework and matrix

materials. Using realistic values for the above variables, he calculated the axial, transverse, and shear moduli for the fiber, and then studied how these varied as the elastic properties of the components changed or as the S1 or S2 fibril angle changed.

Page, et al. (32) developed a similar model based on a three-dimensional S2 layer (only). Their 3D model allowed them to set the shear strain to zero, rather than the shear stress as had been done in earlier models. Page and his co-workers tested their model predictions against elastic modulus data obtained on softwood fibers having a broad range of S2 fibril angles. They showed that the theoretical curve was an upper bound for the data.

More recently, Salmén extended these models (24, 33), using a micromechanics composite laminate approach in which the properties of the fiber are modeled in terms of the properties of the constituents of the cell wall, i.e., the cellulose and hemicelluloses. Salmén used the structure-property relationships for fiber-reinforced or filled composites (based on the rule of mixtures) suggested by Halpin and Tsai (e.g., 34), and showed they gave good predictions for single fiber elastic moduli (33).

Drying of the Network

Because refined chemical pulp fibers tend to be more swollen with water, they also have the greatest shrinkage during drying. As water is removed from the cell wall, the fiber begins to decrease in cross section as surface tension forces draw the fibrous components together. Stone and Scallan (35) used a nitrogen adsorption technique to study the effect of drying on the cell wall structure of bleached softwood fibers. Their data suggested that in the fully swollen state there are on the order of several hundred lamellae, each about 100Å thick, with a median separation of about 35Å. During drying the lamellae draw together into thicker and thicker aggregates, decreasing the pore volume. When the fiber was dry, the pore volume remaining in the cell wall was negligible.

Little shrinkage occurs along the fiber axis because the S2 fibrils, which comprise the bulk of the cell wall, are aligned more or less along this axis. Thus, the removal of water from between fibrils results primarily in a lateral collapse of the cell wall. The extent of the transverse shrinkage, which can be more than 20%, depends on the extent to which the cell wall was swollen. This, in turn, is a consequence of the pulping method, extent of refining, and fiber morphological factors.

Page and Tydeman (36) discovered that interfiber bonds form before the transverse shrinkage of the web. This creates a rather complex situation at the fiber-fiber interface. Figure 5 shows two swollen fibers bonded together. As the upper fiber shrinks in cross section, stresses are transmitted into the horizontal lower fiber, causing it to also shrink along its axis. If we now envision that there are many

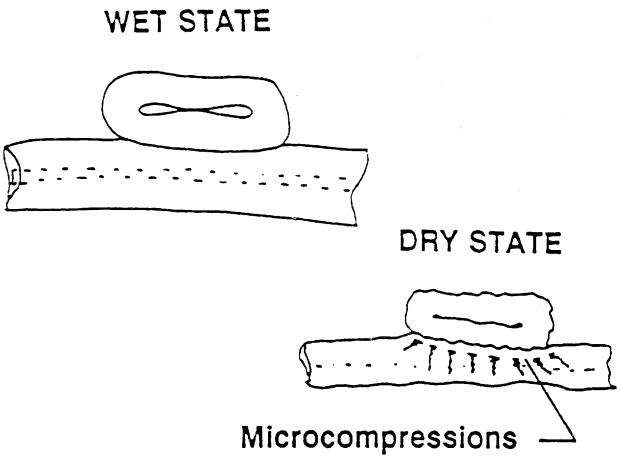

Figure 5. A schematic representation of two bonded fibers swollen with water (top) and after drying (bottom). The lateral shrinkage of the upper fiber causes microcompressions in the lower fiber (Ref. 2).

crossing fibers bonded to the horizontal fiber, we can conclude that its axial shrinkage will be a sum of all of the separate contributions of the fibers bonded to it. If the average lateral shrinkage was 15% and fiber-fiber bonds occurred all along its length, we could expect up to a 15% contraction of the horizontal fiber. The compressed regions along the horizontal fiber are referred to as "microcompressions".

Figure 5 may be misleading in that it depicts events occurring in one direction only. Since both fibers would shrink transversely at the same time, the overall effect would be web shrinkage in both directions. If more fibers were aligned in one direction than the other, the shrinkage would be less in this direction since the S2 layer resists shrinkage along the fiber axes. The z-direction shrinkage in paper during drying is a direct consequence of the fiber cell wall shrinking as water is removed as well as collapse of the lumen.

Fiber shrinkage also impacts the bonding in the web. One consequence is that the bonded area between fibers is not planar, but most likely has a three-dimensional character (2). Ebeling (37) proposed a three-dimensional character for the bond, suggesting that fibrils from the two fibers could become intertwined. Recent work by Nanko (38, 39) suggests, however, that external fibrils are not deeply entangled throughout the bonding zone. Nanko's photomicrographs do show irregularities at the bond interface, including regions where one fiber has wrinkled and moved away from the other. This wrinkling effect increases as beating increases. At the higher beating levels the interface between the two fibers also contains some of the fines present in the system.

A three-dimensional character for the bonds means that a simple geometric bond area may not be an appropriate measure of fiber-fiber bond area. We can also argue that the strength of a fiber-fiber bond will depend on circumstances during shrinkage (drying) of the web. For example, an S1 layer bonded to an S1 layer would likely result in a different situation than an S1 to S2 or an S2 to S2 bond. In the first case, the transverse shrinkage of the first fiber in compressing the S1

layer of the second fiber, may result in an interlaminar cell wall failure at the S1-S2 interface in the second fiber since the S2 layer would be much more resistant to axial compressive loads than the S1 layer. Figure 6 illustrates this situation (2). Such separation at the S1-S2 interface has been reported in the literature (39, 40). Nanko's work (39), in fact, suggests that S1-S2 delamination also occurs opposite the bond site.

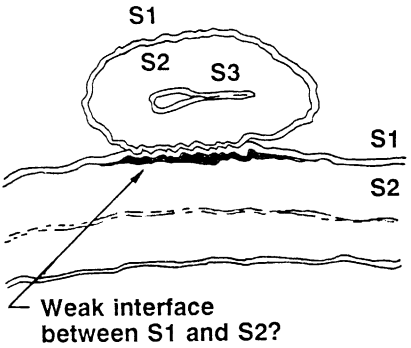

Figure 6. A schematic diagram illustrating how the axial compression of a bonded fiber could lead to a weak S1-S2 interface. Along the fiber axis the S1 layer is much more easily compressed than the S2 layer (Ref. 2).

Since fiber-fiber bonds in paper occur naturally as water is removed from the network, a negative aspect of this is that if water is added back into the structure, it softens and swells, and bonds are broken. The continuous dimensional changes that occur in going from the swollen state to the dry state are reversed, although not completely. This lack of dimensional stability is a problem in many paper grades. If the moisture enters the network from one side only, that side will begin to expand while the opposite side will not, resulting in curl, another undesirable characteristic. These subjects are discussed completely in another of the review papers presented at this conference.

Giertz (41) has summarized the consolidation and drying of a fibrous network as depicted in Figure 7. The top of the figure represents the wet swollen state as surface tension forces begin to act. Next the bonds form and fibers collapse as water is removed from the network. Upon drying the transverse shrinkage causes microcompressions that result in overall shrinkage of the "network". Finally, if a uniaxial load is applied to the ends of the network, the microcompressions are first "pulled out" and then the fibrous material itself is stressed to failure. From a strength point of view, Giertz refers to the shrinkage as "activating" the fibers.

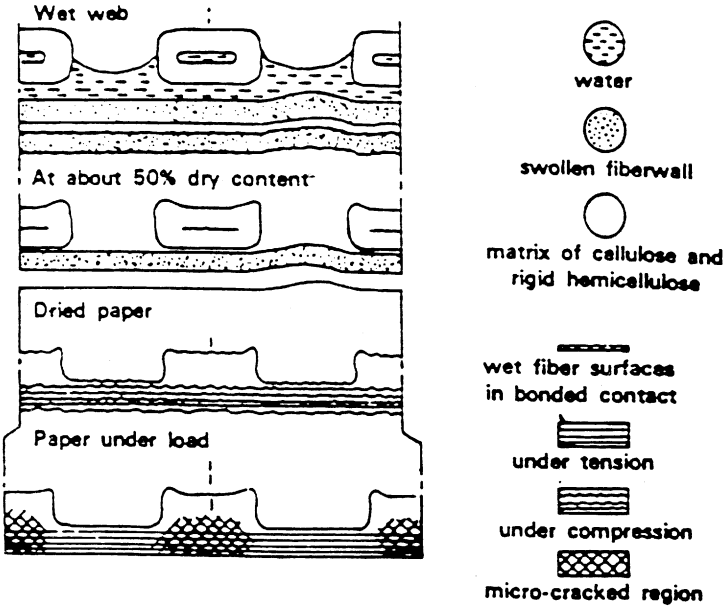

Figure 7. A schematic drawing of the consolidation of the wet paper web and the phenomena caused by fiber shrinkage taking place during drying (Ref. 41).

CHARACTERIZATION OF THE SHEET STRUCTURE

Our discussion thus far assumes paper is made from discrete fibers that have different dimensions and properties and which are arranged in a random fashion. There are some notable exceptions: (1) fibers typically lie in the plane of the paper with little z-direction (ZD) orientation (e.g., 42); (2) conditions on the paper machine give rise to more fibers aligned in the direction of manufacture (machine direction, MD) than in the perpendicular or cross machine direction (CD); (3) the fibers themselves may exhibit kinks, crimps, curl, and microcompressions (43, 44); and (4) as fibers are refined at higher levels, resulting in destruction of the cell wall, the notion of "discrete" fibers may lose meaning.

We normally think of paper as a heterogeneous, anisotropic, composite material. It is heterogeneous because of the discrete nature of the fibers and also because papers may contain a mixture of hardwood and softwood fibers, chemical and mechanical pulps, inorganic fillers, or other nonwood constituents. As we refine to higher levels, however, and the individual fibers (chemical pulp, in particular) begin to "unravel" and fines are generated, the structure tends toward a more homogeneous structure. This will be important as we begin to examine mathematical models that attempt to describe the structure. Some models presume the structure to have discrete fibers with specific characteristics and orientations and bonded in certain ways, while other models will treat the structure as a homogeneous composite or as a continuum.

Formation

Above we described paper as heterogeneous because discrete fibers are arranged in a more-or-less random array such that there are many voids in the structure. Paper is nonuniform on a larger scale as well. This is a consequence of the fibers not being deposited uniformly throughout the structure as it is formed and because fibers may tend to flocculate prior to deposition on the wire. Cutshall (45)

has recently discussed the nature of paper variations from small to large dimensions. The variation of local basis weight in paper is stochastic. A sheet with better basis weight uniformity will typically be stronger, smoother, have better optical properties, and better retention of additives and fines than a sheet with poorer uniformity, see e.g., (12B, 46, 47).

We refer to the property that characterizes the degree of uniformity of distribution of the solid components (and in particular fibers) as the formation. While this definition of formation clearly relates to the distribution of mass in the sheet, the most common measures of formation typically involve viewing light transmitted through the sheet. In this way, a papermaker could rate the formation as "good" or "wild".

Kallmes and Corte (48) constructed a model for low density paper in which straight lines of uniform length were positioned at random. Comparing this model to a very low basis weight paper, they found regions of high and low density in both that displayed irregular arrangements. Corte (46) discusses this and related topics in his excellent review of the structure of paper.

A measure of the intensity of the local basis weight variations in paper is the standard deviation, $\sigma(w)$. Norman and Wahren (47) use the normalized standard deviation, or coefficient of variation, V(w), as the intensity of the mass distribution, F. Thus

$$F = V(w) = \sigma(w)/\bar{w}$$

where $\bar{w}$ is the mean basis weight. F is progressively built up from flocs of increasing size. The coefficient of variation is the number probably most commonly used today to describe formation. Dodson (49) has proposed a universal law of formation for random paper. The coefficient of variation of local basis weight for a random paper decreases with the reciprocal square root of the mean basis weight. Based on this observation, Dodson has proposed a model for

flocculated paper that may be useful over narrow basis weight ranges. Treating paper as a three-dimensional stochastic fibrous network, Dodson (50) has recently extended our thinking by considering the coefficient of variation of the local volume density. He derives this analytically and thus offers a three-dimensional formation index.

Norman and Wahren sought correlations between mass distribution and paper properties and felt that F, as a single number, was not well suited for this. They used the spectral distribution of mass density as a function of wavelength (or frequency). Figure 8 is an example of the wavelength spectra of mass distribution in calendered and uncalendered bleached sulfite handsheets as measured by beta radiography techniques and compared to a calculated random sheet. In this case the handsheets are superior to the random sheet. Norman and Wahren studied a wide array of variables and the interested reader is referred to their work (47).

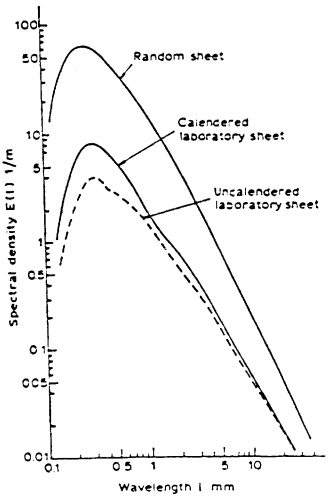

Figure 8. Wavelength spectra for bleached sulfite handsheets and calculated random sheet (Ref. 47).

Light transmission results can be taken as a measure of basis weight variations only for thin sheets and if the light absorption characteristics of the fibers are uniform. The latter would not be the case for a blended or filled pulp. At heavier basis weights, light transmission is a complicated function of basis weight (e.g., 51). Komppa and Ebeling (52) specifically sought to determine the correlation between mass density and optical densities. An instrument was developed (53) that permitted measurement of the two factors at the same spot in the paper. They found that optical density and mass density were not correlated in all cases, especially in the case of extensive refining or heavy calendering.

Wahren (54) found that the detrimental effects of uneven mass distribution on the optical properties of paper can be quite large assuming the Kubelka-Munk equations are valid. Hasuike, et al. (55) studied the relationships between mass density variations and structural anisotropy. They found for machine-made papers that the degree of anisotropy was higher in the lower grammage regions. They also noted that variations in the structural anisotropy were characteristic of the sheet forming process used.

Waterhouse (56, 57) has recently evaluated a number of off-line and on-line formation measuring instruments using paper and board samples and has correlated formation measurements with other physical properties.

Loewen et al. (58) have recently summarized the interrelationships between flow, floc, and formation size scales during papermaking from both theoretical and experimental viewpoints. A number of recent experimental investigations have been concerned with the impact of table activity (59, 60), suspension parameters (61), and flow conditions (62-65) on flocculation and formation. Steen (66, 67) has been modeling fiber flocculation in turbulent flow. The work of Jokinen and Ebeling (62) and Kaji et al. (63) suggests that increased fiber flexibility due to beating, at constant fiber length, reduces flocculation and increases the fractal dimension of the suspension.

Kaji et al. also studied the impact of the molecular weight of a retention aid on flocculation. He observed that increasing molecular weight (by two orders of magnitude) increased the population of larger flocs and decreased the fractal dimension. Zhao and Kerekes (68) have recently shown that the uniformity of fibers suspended in a water-sucrose solution is a strong function of viscosity, reaching near-perfect uniformity at high viscosities.

Tomimasu et al. (69) compared methods for imaging paper including ß-radiography, electrography, light transmission, and soft x-radiography. Electrography gave high spatial resolution and short exposure times compared to ß-radiography, while soft x-radiography gave the highest spatial resolution but poorest spatial variation and contrast. Light transmission gave the poorest spatial resolution and correlation with mass. Cresson et al. (70) developed a two-stage technique for sensing paper formation using video-beta radiography, which combines video-image processing with beta radiography. Based on those measurements, Cresson and Luner (71) introduced a co-occurrence method, from the field of texture analysis, showing how formation could be characterized in terms of textural properties.

Network Parameters

The varied composition, lack of homogeneity, and the fact that there are always distributions for the fiber properties make the paper structure difficult to characterize. We attempt to do this, however, in terms of network parameters or the macroscopic physical properties (see Figure 2).

Network parameters attempt to define the structure in terms of the dimensions, physical properties, and geometrical orientations of the fibers and the nature and extent of the bonding between fibers. Such characterizations are difficult not only because of the broad distributions in fiber properties, but also because papermaking variables can significantly alter the properties (and distributions).

Network parameters that have been studied extensively include formation (as discussed above), bond area, fiber-fiber bond strength per unit area, relative bonded area, interbond distance, the number of bonds per length of fiber, and fiber orientation. These are not necessarily independent. For example, a simple idea like the geometric bond area between two fibers goes from a minimum when the two fibers are at right angles to a maximum when the fibers are aligned on top of one another. Thus, fiber-fiber bond area and fiber orientation are interrelated.

Fiber-fiber bond strength

The strength of a fiber-to-fiber bond is a straightforward concept, but it is a property difficult to measure. Much of the difficulty arises because wood fibers are tiny, but also because it is difficult to reproduce, in the laboratory, the stresses experienced by the fiber in the paper. A single fiber-to-fiber bond tested in the laboratory may not be representative of the state of stress seen by the fibers in the paper. Since chemical pulp wood fibers can shrink 15 to 20% perpendicular to their axes if allowed to do so, a fiber in the paper that makes many bonds with other fibers will likely have properties markedly different from one dried outside the network. Therefore, we cannot be sure that laboratory measurements are representative of conditions in the real structure.

Robinson (72) has prepared a comprehensive review of fiber bonding and Retulainen and Ebeling (73) have reviewed the literature through 1985. Early investigators focussed on sheet measurements. Nordman (74, 75) defined a "bond strength value" as the energy dissipated in breaking bonds divided by the change in scattering coefficient when bonds were broken. The former, obtained from the area between the stress-strain curves for loading and unloading, is assumed to be the energy expended in breaking bonds, while the latter was determined by measuring scattering coefficients before and after straining. Subsequent work by Nordman (76, 77) revealed that the bond strength value appears to be a characteristic of a pulp.

Smith and Graminski (78) characterized the interfiber bonding of networks by preparing very low basis weight sheets that were tested to breaking in a tensile tester. The resultant curves were jagged when bond breakage began to occur and each jagged peak was taken as the breaking of a bond between fibers. They computed a characteristic energy interpreted as the average energy lost per interfiber bond breakage by fibers in the vicinity of the break. This parameter increased with beating but was independent of pressing pressure.

Skowronski (79, 80) has used a technique in which interfiber bonding strength is obtained by measuring the force necessary to delaminate a paper sheet by pulling on plastic tape fastened to opposite surfaces. The bond breaking energy is obtained from the product of (constant) breaking force times the length of the (monolayer) delamination over which the force was constant. To obtain specific bond strength the bond energy is divided by the increase in light scattering coefficient (assumed to be representative of bonded area). Skowronski observed that the method seemed to be applicable in a basis weight range between 30 g/m2 and 60 g/m2. At lower weights he observed adhesive tape interference and at higher basis weights he found the sheet delaminated in multilayer modes.

A number of researchers have investigated fiber-fiber bonding between two fibers (81-85). In each case the fibers are stressed in the plane of the bond, thus the measured values are bond shear strengths. Page (81) measured the areas of fiber crossing in optical contact. Mayhood et al. (82) made low basis weight sheets, cut single bonded pairs from them, and measured the force to pull the fibers apart. McIntosh (83) prepared bonded pairs from individual never dried fibers, as did Stratton and Colson (84). Mohlin (85) used a technique where individual fibers were bonded to cellophane film to determine shear bond strength. Her technique gave greater rupture loads than single fiber crossings because larger contact areas were possible with cellophane.

Stratton (86) compared fiber-fiber bond strengths measured on fiber pairs with values computed from paper mechanical properties. Z-direction tensile strength and z-toughness were shown to be indicators of enhanced bonding resulting from a strength additive, whereas z-direction elastic stiffness was not. Hieta et al. (87) recently reported a specific bond strength that may be considered a normal or z-direction fiber bond strength.

When we discuss fiber-to-fiber bond strength, we usually assume that the fibers themselves are uniform and stronger than the bonds between them. This is probably not always true. Since wood fibers are excellent examples of "fiber reinforced composites", and since the two outermost layers (S1 and S2) have fibrils oriented in quite different directions, we can anticipate that these layers will respond differently to bonding stresses. This type of analysis suggests that the S1-S2 interface may be a weak zone. If the failure between two bonded fibers originates within one of the cell walls, rather than between the fibers, as indicated in Figure 6, the meaning of bond area or bond strength becomes obscure. Nanko's work (38, 39), mentioned earlier, suggests that such events are not rare. Stratton and Colson (88) also have recently reported similar fiber wall damage during bond failure.

In mechanical pulps, where the lignin reinforcing material in the cell wall is still present, the concept of bond area would appear to be more straightforward. For such pulps, the fibers are less flexible and so the resultant contact area (not necessarily bonded area) will be less than for the case with chemical pulps. The stiffer mechanical pulp fibers also likely result in fewer actual bonds per length of fiber. In addition to the above, the bond strength per area will likely be different (less) for the lignin rich surface of mechanical pulps, compared to those of chemical pulps.

Bond area

Page et al. (89) in a piece of classic research studied the impact of refining and drying restraints on fiber-to-fiber bonding by directly observing the fiber to fiber bonds in 60 g/m^2 papers. They determined the bonded area by measuring the cross polarized light scattered from the fiber-air interfaces. Bonded regions do not scatter light, so these regions were dark compared to the surrounding non-bonded areas. [Actually, two surfaces in optical contact will not scatter light. The separation distances for optical contact are apt to be two or more orders of magnitude greater than the distance necessary for hydrogen bonding. Nevertheless, we normally assume that fiber surfaces in optical contact are also bonded. Experimental evidence suggests this is not a bad assumption (72).]

Page et al. found that the area of a single bond increased with level of refining treatment as shown in Table 1. Longer refining times (and one would assume higher wet pressing pressures as well) led to larger bonded area. Drying restraints, on the other hand, had little impact on bonded area. The degree of bonding is the ratio of the observed bonded area to the geometric crossing area of the two (or more) bonded fibers. A "simple" bond was defined as one involving only two fibers whereas frequently three or more fibers were observed to participate. Table 1 shows that the degree of bonding or the mean bond area increases as beating time increases while both are insensitive to drying tensions.

Page and coworkers also studied the distance between bonds. They defined an "intercrossing distance", the distance between the centers of bonded crossings, and a "projected interbond distance", the distance measured along the fiber axis between bonded areas projected onto the fiber axis. The projected interbond distance could assume negative values. They found that as refining increased the interbond distance (by either measure) decreased. In fact, there was very little length of fiber that was not bonded on one side or the

Table 1. Effect of refining and drying tension on degree of bonding and mean bond area (Ref. 89).

Beating Time, min	Drying Tension, g/cm	Degree of Bonding, %	Mean Bond Area*	
			Simple	All Bonds
	0	46.6	772	643
0	35	38.0	656	483
	55	40.3	708	572
	0	71.6	1102	956
20	35	75.1	1199	989
	75	69.0	1003	856
0	All	41.7	712	567
20	All	71.8	1099	932

* Mean bond area has units of (μm^2). Simple bonds involve only two fibers. All bonds includes simple bonds plus those involving three or more fibers.

other. Photomicrographs of most papers confirm there is very little distance between bonds.

Relative bonded area

One network parameter based on bonded area that appears to be particularly useful is the relative bonded area, defined as the ratio of the total bonded area to the total (surface) area available for bonding. Expressed as a percent, the relative bonded area (RBA) increases as the number of bonds or bond area increases (say by increased refining or wet pressing) but says nothing about the quality (or

strength) of the bonds. The RBA can never be 100% because the outermost fibers cannot be bonded on their outside.

Kallmes (90) considered paper to consist of two dimensional fibers (of negligible thickness) lying in the plane of the sheet. For a random sheet the fiber distribution was assumed to be described by a Poisson distribution. He argued that if n fibers are piled on top of one another, there are n-1 interfaces between pairs of fibers, or n-1 potential bonded areas. If there are two or more fibers in the pile the outermost fibers cannot be bonded on one side, and if there is only one fiber in the pile it cannot be bonded on either side. Thus Kallmes notes that all of the fibers in paper can be characterized by one of three conditions or "states", those bonded on both faces, B(2), on one face, B(1), and on neither face, B(0). In terms of these bonding states, RBA = [B(1) + 2B(2)]/2, where the two in the denominator accounts for the two faces of a fiber. Figure 9 shows the bonding state diagram constructed from these results. The actual RBA of the sheet will be some fraction of the maximum RBA, or RBAmax.

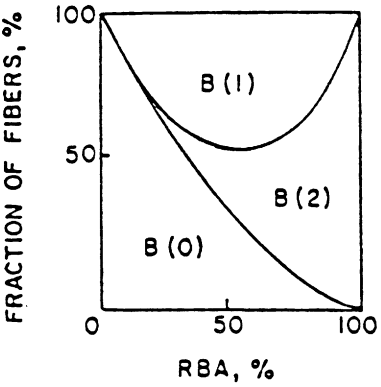

Figure 9. Bonding state diagram (Ref. 90).

To obtain the maximum bonded area of the sheet then, one needs the proportion of fibers in the sheet that are unbonded (n = 1), bonded on one face only (outermost fibers when n ≥ 2), and the internal fibers bonded on both sides when n ≥ 2. The Poisson distribution gives:

$$RBAmax = [1 - (1/H)(1 - e^{-H})] \cdot 100\%,$$

where H is the average number of fibers lying over a point in the plane of the sheet given by $(L \cdot w/A) \cdot N$, with L and w the fiber length and width, respectively, and N the total number of fibers dropped randomly into area A. If ß is the fiber mass per unit length, then the basis weight, BW, is $N \cdot L \cdot ß/A$. Thus H (= $BW \cdot w/ß$) is a measurable quantity and RBAmax can be computed.

The experimental determination of RBA is difficult. Some techniques include direct observation (89, 91), measurements of electrical conductivity (92), shrinkage energy (93), the addition of nonbonding fibers (94), gas adsorption (e.g., 95), and measurement of light scattering coefficients (e.g., 96). The latter two methods have been used most frequently and correlate quite well with each other (96, 97), but both require measurements on an unbonded reference sheet. Kallmes (98) has discussed several of these techniques and the role RBA and other network variables play on sheet strength. We will examine the light scattering technique more closely.

The light scattering coefficient, determined optically, is related to the fiber surface area that can scatter (reflect) light per gram of fiber. Light scattered in the visible part of the spectrum is due to the difference in the index of refraction between fiber and air. As described earlier, no light will be scattered from the region where two fibers are bonded (or, more correctly, in optical contact) (e.g., see 72, 89). The greater the bonded area, the smaller the light scattering coefficient. Rennel (99) gives a good overview of the impacts of refining and wet pressing on scattering coefficients and breaking lengths of chemical and groundwood pulps.

To compute RBA from measurements of light scattering coefficient, one needs to know the light scattering coefficient, s, for the bonded sheet as well as the completely unbonded sheet. Since the latter is difficult to accomplish, usually the scattering coefficient for the unbonded network, s_u, is usually obtained by extrapolation to zero tensile strength in a plot of scattering coefficient vs. tensile strength. Then RBA = $(s_u - s)/s_u$.

Sheet density

Another basic network parameter is sheet density, the mass per unit volume, or basis weight divided by caliper. Bulk is the reciprocal of density. In general, as one increases relative bonded area by increasing refining or wet pressing pressure, density increases also since more material (mass) is being compressed into the same volume. This rule of thumb doesn't work in the case of dry pressing (calendering), however, where sheet density can increase but relative bonded area may not. Calendering can cause crushing of fibers which decreases bonding while still compacting the material to higher densities (e.g., 100). Wet straining of a web can decrease both density and RBA (101). Shrinkage during drying will have the opposite effect, increasing both density and RBA.

One major problem with using density as a measure of network structure or as an indicator of sheet performance is that the calculation of density relies on the measurement of a somewhat nebulous property, the caliper. Caliper, or thickness, is defined as the thickness of the sheet under standard conditions of platen size and pressure (e.g., see Ref. 102). This is an acceptable definition for monitoring production but is not acceptable if we wish to use density as a fundamental network property. There are several reasons for this. First, paper is a compressible material and the caliper, and thus density, depends on the load applied during the measurement. Second, the surface roughness of paper contributes to the caliper measurement, which introduces an error in the density. This is unacceptable if we wish to use the density to predict other properties.

To complicate matters further, the "density" and compressibility of the surface regions are apt to be quite different from those in the bulk. Taylor (103) studied the impact of surface properties on sheet density. Using a complex statistical analysis of a simple model of paper, Uesaka et al. (104) developed theoretical results similar to those found by Taylor.

A good review of the problem of surface roughness on caliper is given in Ref. 105. Several groups have studied this problem (106-109). Setterholm (106) proposed an "effective thickness" related to the ratio of bending stiffness to extensional stiffness. Since bending stiffness depends on thickness cubed and extensional stiffness on the first power of thickness, the square root of the ratio gives a calculated value of the effective thickness, assuming that elastic modulus and mass distribution are uniform through the thickness of the sheet. The effective thickness values compare favorably to values obtained using pycnometric (mercury intrusion) methods. The pycnometric method itself is not unambiguous in that the depth to which mercury will penetrate the surface roughness depends on the applied pressure.

In practice, Setterholm measured the displacement of a spherical stylus moved across the paper, calibrated by adjusting the platen pressure, so that the mean value was equal to the calculated value. Kimura et al. (107) refined the spherical platen method. Wink and Baum (108) described a "soft platen" caliper technique in which soft rubber platens contact the sheet and conform to the gross roughness features of the surface, thereby eliminating the surface roughness contribution to caliper and, hence, to density. In use the device is calibrated against precision metal shims of known thickness.

While both the spherical platen and soft platen techniques have drawbacks, they give similar results and compare favorably with pycnometric measurements (105, 108). The measured calipers are less than those obtained using standard hard platen measurements, and the computed sheet densities are therefore larger. The smoother the surface of the paper, the more closely the hard platen

measurements will agree with the new techniques. The soft platen method may be simpler to use, but the spherical platen method also allows measurement of point to point variation in thickness (110).

There are numerous cases in the literature where sheet physical properties are measured and correlated against sheet density. Many of the density measurements are based on hard platen caliper measurements, making some of the conclusions questionable. This is one area where additional work is necessary.

Sheet densification by pressing

Fiber bonded area and density are strongly influenced by wet pressing. We will review briefly here what happens to the fiber network during the wet pressing operation and discuss the impact on sheet properties. A review of wet pressing was presented at the last Cambridge Symposium by MacGregor (111), and numerous studies of the wet pressing phenomena have been reported (e.g., see Ref. 12).

In a sense wet pressing helps to bring the fibers into more intimate contact and thus promotes bonding. The compression of the network during wet pressing can cause fiber lumen collapse leading to more flexible fibers as well as greater local compressive stresses at fiber crossing points. Together these can lead to greater bonded area and a denser network and, in turn, typically result in higher values of elastic stiffness and strength values. Szikla and Paulapuro (112) found that the z-direction distribution of filler and fines did not change during wet pressing, but that wet pressing could create a significant density gradient, even in thin sheets. They showed that the density increase primarily resulted from increased fiber bonding.

Since refining leads to more flexible fibers and greater relative bonded area, one might suppose that wet pressing and refining are very similar or even "interchangeable" processes as far as densification is concerned. This is not the case, however, as can be seen in Figure

10 which shows a strength property plotted against density for a number of pressing and drying conditions (113). The curve for refining rises faster than that for hard press nips. At a given density, refining results in a greater value for the strength property. The explanation is that refining enhances bonding by its action on the fibrils comprising the cell wall, making a more conformable structure and increasing the surface area as well. In contrast, wet pressing physically forces the fibers together but without altering the fiber cell wall structure, except perhaps at the fiber crossing points. Wet pressing may also cause the lumens to collapse.

The longer residence time in an extended nip press (ENP) leads to more effective dewatering but, also, promotes bond development to

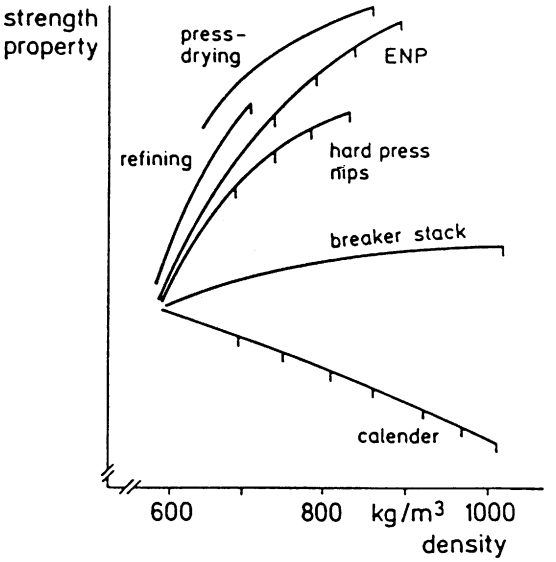

Figure 10. A schematic diagram showing how strength properties vary with density for different methods of densifying the sheet (Ref. 113).

a greater degree than pressing in a short residence time hard nip press.

The applicability of the above descriptions will depend on whether we are discussing chemical pulps or high yield mechanical pulps, since the action of refining or wet pressing on these will be different. While the general explanation above may apply, the relative magnitudes of the refining and wet pressing effects for different pulps will vary. Szikla and Paulapuro (112, 114) have recently studied the compression behavior of wet pressed fiber mats and Bither and Waterhouse (115) have examined the impact of refining and wet pressing on sheet properties.

The enhanced density and property development brought about by wet pressing requires that water be present so the fibers are still compliable and so that surface tension forces can lead to good bonding. Pressing on a web at high solids content can still provide intimate contact and lead to a greater network density, but does not necessarily lead to enhanced bonding and development of strength properties. This is evidenced by the line in Figure 10 for the breaker stack where the significant increase in density is not associated with a concomitant increase in strength. One can envision that the densification comes about because fiber segments are physically forced into void areas without chemical bonding occurring. In the extreme case, where the fibers are "dry", such as in calendering, this action may actually degrade the bonding in the network such that an increase in density is associated with a decrease in strength properties (Figure 10). As it is not possible to discuss calendering in any depth here, the interested reader is referred to the review by Peel (116).

STRESS-STRAIN BEHAVIOR

Figure 11 (117) shows a typical uniaxial stress-strain curve for paper. Paper is a viscoelastic material. At low strains, however, the response of strain to an applied stress is assumed to be linear and

the paper is normally viewed as obeying Hooke's law. The material is said to be elastic and the elastic constant is defined as the ratio of stress to strain as strain tends toward zero. At larger strains, the linear relationship with stress may disappear, but the material will still be considered recoverable as long as the stress-strain behavior is reversible, i.e., if the stress is reduced to zero, the strain will also return to zero. At some level of strain, however, a yield point is reached in which a deformation remains upon removal of the stress. This deformation typically has a reversible time dependent part, i.e., some strain will recover in time, and an irreversible permanent part. Beyond the yield point the material is said to be plastic until the point of failure.

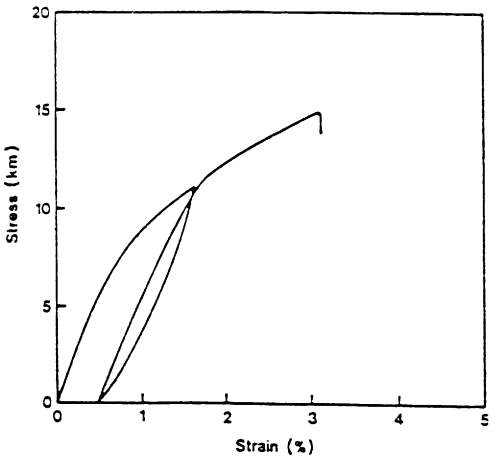

Figure 11. Typical stress-strain curve for paper (Ref. 117).

Viscoelastic Character

Paper is a viscoelastic material by virtue of its constituents being viscoelastic. When a polymer is stressed, there can be a redistribution of molecular states and significant time can elapse before the reconfiguration is complete. If a single thermal relaxation process is

operative, a step change in the stress can initiate a redistribution that proceeds exponentially. The temperature and the presence of a plasticizer, such as water, can greatly influence the reconfiguration of molecular states.

Paper displays all of the usual phenomena associated with viscoelasticity, including stress relaxation, creep, and molecular relaxation processes. We will touch briefly on the latter below, but will not consider the viscoelasticity of paper in any detail. Kolseth and de Ruvo (118) have discussed the measurement of viscoelastic behavior for the characterization of time, temperature, and humidity dependent properties of paper. Shapery (119) has prepared a comprehensive review of the time dependent deformation behavior of polymeric composite materials. Another review presented at this conference will discuss the response of paper properties to changes in the local environment.

The linear viscoelastic response of cellulose has been attributed to three different thermally activated transitions (120-130). These are molecular level motions that contribute to macroscopic compliance. Each transition requires a finite relaxation time. Only those experiments with time bases greater than the relaxation time will be sensitive to the transition. The relaxation times and magnitudes of the transitions are temperature and moisture dependent.

The Γ transition is the lowest temperature transition. It is considered to be the result of the rotation of the methylol side group on the cellulose chain. The Γ transition in dry cellulose occurs at about -95° C at 1 Hz and has an activation energy of about 10 kcal/mol. Moisture antiplasticizes the Γ transition, in that its intensity decreases with water content. Water combined with cellulose produces a different relaxation that is not present in dry cellulose. This is the β transition. Its molecular origin is tentatively identified as motion of a water-methylol complex. The transition temperature is about -70° C at 7% moisture and 1 Hz, and its activation energy is about 15 kcal/mol. Water efficiently plasticizes the β transition: its intensity increases with

increasing moisture content while the transition temperature decreases. The third transition is the α relaxation. This is the glass transition in the amorphous regions of the cellulose. The activation energy is large (over 100 kcal/mol), and the peak of the relaxation would be at about 200°C. It very easily plasticized by water. In fact, the low temperature limb of the α transition is responsible for much of the room temperature moisture sensitivity of the physical properties of paper.

Salmén and Back (131-134) studied the combined influence of temperature and moisture on the stress-strain behavior of paper. Figure 12, taken from their work (134), shows failure envelopes for a kraft sack paper over ranges of temperature and moisture that might be found in end use situations. It is clear that elastic modulus, stretch, TEA, and tensile strength are strong functions of moisture and temperature. Salmén and Back demonstrated that the temperature or moisture derivatives of elastic modulus showed transition regions, interpreted as the glass transition temperature for the cellulose-hemicellulose water system. Rigdahl and Salmén (135) studied the effects of density and drying restraints on the dynamical mechanical properties of paper. They observed that the dynamic modulus increased strongly with increasing sheet density and was always higher for sheets that had been restrained during drying. They concluded that paper was a nonlinear viscoelastic material. Munoz et al. (136) recently measured the dynamic viscoelastic properties of handsheets and interpreted their results in the framework of percolation theory.

In general, if the paper is dry, stresses are low, and the duration of the applied stress is short, we often assume that paper behaves as a linear elastic solid. If the duration of the load is long, the applied stress is low, and the humidity and temperature are constant, paper should be described as a linear viscoelastic material. If the stresses are high the behavior is inelastic, and this behavior is greatly influenced by environmental conditions.

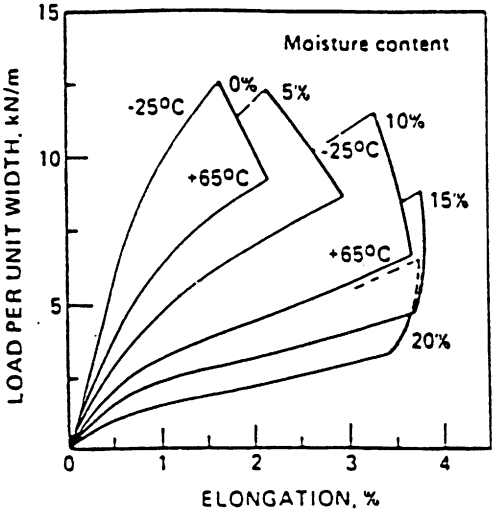

Figure 12. Failure envelopes for a kraft sack paper in the MD at temperatures from -25° to 65°C and moisture contents from 0 to 20% based on moist paper (Ref. 134).

Nature of the Stress-Strain Curve

Stress-strain curves for paper (actually measured as load-elongation curves) are routinely obtained for many paper grades, providing tensile strength (stress at failure), stretch (strain at failure), toughness or tensile energy absorption (area under the stress-strain curve), and elastic modulus (the initial slope of the stress-strain curve). The details of the measurements are described in the literature (102, 137-139).

The stress-strain behavior of paper as it relates to fiber and network properties has been fairly extensively studied from both the experimental and theoretical viewpoints. The latter are discussed in some

detail in the section on Modeling, but we will discuss briefly both viewpoints here.

Seth and Page have worked extensively in this area (140-142) and have shown that the observed linear elastic response of paper can be explained in terms of fiber and network properties (117). Based on the work of Cox (143) they developed a micromechanics model that predicts the sheet modulus, E_S:

$$E_S = (1/3)E_F[1-(w/L \cdot RBA)(E_F/2G_F)^{1/2}\tanh\{(L \cdot RBA/w) \cdot (2G_F/E_F)^{1/2}\}],$$

where E_F and G_F are the fiber elastic modulus and shear modulus, respectively, w and L are the mean fiber width and "effective" length, respectively, and RBA is the relative bonded area as defined earlier.

The factor 1/3 comes from the Cox theory which assumes a two-dimensional homogeneous isotropic sheet with infinitely long, randomly arranged fibers. The term in the [ ] parentheses results from considering fiber ends or other points along the fiber (e.g., a kink) where the stress is zero. Thus, L represents the effective fiber length. The term in parenthesis then is a measure of stress transfer in the fibers in a sheet. Seth and Page call this the efficiency factor.

Seth and Page tested the above equation by independently varying RBA and L, and found excellent agreement between experiment and theory. If one has a well-bonded random sheet composed of long fibers, so that both RBA and L are large and $L \cdot RBA >> w(E_F/2G_F)^{1/2}$, then the efficiency factor approaches one and $E_S = (1/3)E_F$. Seth and Page found this relationship to be valid for such sheets.

Plastic Regime

Seth and Page (117) also discuss the plastic region of the stress-strain curve for paper. They review the two different points of view concerning the origin of the plastic regime as presented in the literature. The first is that the plastic regime is a consequence of fiber-to-

fiber bond failure. During straining of the sheet, the fibers are viewed as straining elastically with progressive disruption of fiber bonds (e.g., 78, 144, 145). Early measurements of the stress-strain response of individual fibers supported this idea, since fiber stress-strain curves tended to be generally linear with very little plastic behavior (e.g., 146). The other viewpoint is that the plastic regime is largely connected with irreversible intrafiber deformation of the fiber cell wall structure (e.g., 147, 148). While there will be bond breakage and changes in bond area during straining, these effects are considered to be only a small part of the overall effect.

Seth and Page support this latter view for several reasons. First, stress-strain curves for fibers that are more representative of those actually found in paper, that is, having defects and microcompressions, do tend to display a plastic response that is similar to that observed for paper (149). Thus one might anticipate that the plastic regime of the stress-strain for paper results entirely from the response of the fibers to the applied stress. Second, they demonstrated experimentally that the plastic behavior for paper could be adequately described by an expression similar to that presented above for the elastic behavior. In this case,

$$E_S^* = \alpha \, \delta^* \, E_F^*,$$

where α is taken as 1/3, E_S^* and E_F^* now represent stress divided by strain for both the elastic and inelastic, time dependent, regimes, and δ^* is the strain dependent efficiency factor. They noted that this latter factor may vary during straining if bond breakage does occur.

Habeger (150) refined the Seth and Page model for the nonlinear stress-strain behavior of paper. He showed that α is not 1/3 in the nonlinear regime, but is a function of strain and fiber properties. This does not alter Seth and Page's comparisons made at constant strain and pulp properties, but leads to the following corrections. First, the stress-strain curve of the sheet is, in general, not proportional to the fiber stress-strain curve. Second, if the fibers yield, the apparent

Poisson ratio in a random network is less than 1/3 and the sheet modulus is greater than 1/3 the fiber modulus. This occurs because fibers aligned to the stress direction yield at lower sheet strains than those normal to the direction of stress.

Perkins et al. (151) confirmed that the post elastic region of paper deformation is characterized by extensive interfiber deformation that is largely irrecoverable. We will consider this topic in more detail when we discuss modeling.

ANISOTROPY IN PAPER

The above discussions have focussed on the uniaxial stress-strain curve for paper and have not considered the fact that paper is anisotropic. Figure 13 (Ref. 152) depicts typical stress-strain behavior

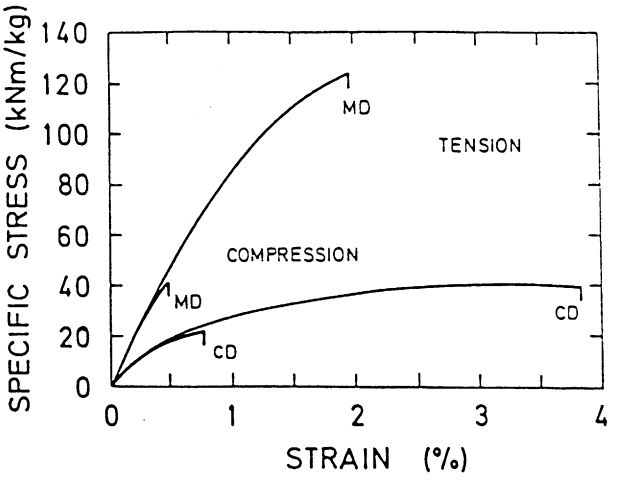

Figure 13. Typical stress-strain curves in tension and compression for paper, showing the anisotropy between the MD and CD (Ref. 152).

for the machine direction (MD) and cross-machine direction (CD) in anisotropic paper. We observe that elastic modulus and tensile strength are greater in the MD than in the CD, but that stretch is greater for the CD. The failure stress and failure strain in compression are roughly one-third the values found in tension. The differences in MD and CD properties are traceable to the manufacturing conditions on the paper machine. We will discuss these further, but first we must address the nature of stress-strain behavior in three dimensions and the symmetry conditions that will help us characterize the material in three dimensions.

Three Dimensional Linear Elasticity

Paper is a three-dimensional material. Unfortunately, we often neglect the thickness direction properties and the important role these play in converting[1] and end-use performance. The "traditional" paper physical properties that we typically measure, even collectively, are not always effective in describing the response of the paper to the complex mechanical stresses that it may experience during converting operations or in end use. This is not necessarily a shortcoming in the tests, but rather a consequence of the need to describe the stress-strain response of the material in three dimensions.

In general, there are nine stresses that can act on a three-dimensional solid as shown in Figure 14. Equilibrium conditions, however, result in only six independent stresses. Likewise, there are only six independent strains. In linear elasticity theory the stresses and strains are related through generalized Hooke's law expressions:

$$\sigma_{ij} = \sum_{k,l} C_{ijkl}\, e_{kl} \qquad i, j, k, l = 1, 2, \text{ or } 3.$$

[1] "Converting", as used here, means any process which alters the properties of the web after it has been dried once. Thus, sizing, coating, calendering, etc., would all be converting processes.

where σ_{ij} are the stresses (force/area), e_{kl} are the strains (dimensionless), and C_{ijkl} are the elastic stiffnesses (force/area). Written in this form we have nine stresses, nine strains, and 81 stiffnesses.

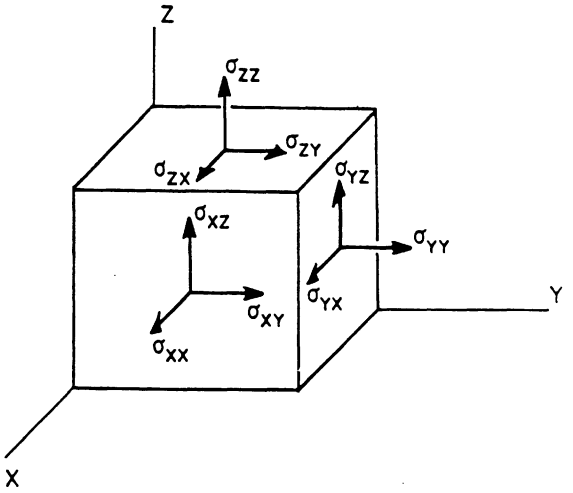

Figure 14. Nine stresses acting on a small element. Equilibrium conditions will reduce the number of independent stresses to six.

In Figure 14 when we apply equilibrium conditions we find $\sigma_{ij} = \sigma_{ji}$. It is customary to redefine the six independent stresses or strains such that xx = 1, yy = 2, zz = 3, yz = 4, xz = 5, and xy = 6. The generalized Hooke's law then is written:

$$\sigma_i = \sum_j C_{ij} e_j \qquad i, j = 1 \text{ to } 6.$$

Thus we have six stresses, six strains, and 36 elastic stiffnesses. For a completely anisotropic material we would need to define 36 elastic stiffnesses ($\mathbf{C}$) to completely characterize its stress-strain behavior.

We can also characterize the strains in terms of the stresses and, in this case, the coefficients of the stresses are called the elastic compliances, S_{ij} (= **S**), and have inverse stress units. The matrix product **SC** equals **E**, the identity matrix. Thus if either **S** or **C** is known, the other can be computed.

Most materials have some structural symmetry that, together with energy considerations, makes some of the 36 elements of the elastic stiffness or compliance matrices equal to zero and elements $C_{ij} = C_{ji}$. In the simplest crystalline case, that of a cubic material with equal properties along any orthogonal axis, there are only 12 nonzero elements in the stiffness matrix and of these only three are independent. These are C_{11}, C_{12}, and C_{66}, related to elastic modulus, Poisson ratio, and shear modulus, respectively.

For an isotropic material, one that has no directionality at all (the same properties in any arbitrary direction), we still define three elastic properties: an elastic (Young's) modulus, E, relating axial stress and strain; a shear modulus, G, relating shear stress and shear strain; and a Poisson ratio, ν, the ratio of the lateral contraction to the axial extension during uniaxial stressing. However, for the isotropic material, only two of the three elastic properties are independent. If any two are known, it is easy to show that the third can be computed from $G = E/2(1 + \nu)$.

In the case of paper we normally define three orthogonal axes: the MD or direction of manufacture, the CD or cross machine direction, and the thickness direction, ZD, as depicted in Figure 15. We often use x, y, z or 1, 2, 3 in place of MD, CD, ZD. The plane defined by any two axes in Figure 15 is taken as a mirror symmetry plane. Three mutually perpendicular symmetry planes define an orthorhombic crystalline structure, but in the case of noncrystalline materials we use the word "orthotropic" to define the symmetry. Thus we often treat paper as a linear orthotropic material, even though we know that the symmetry conditions may not always be met. Wood and prestressed concrete are other examples of orthotropic materials.

Applying the orthotropic symmetry conditions, we find that the elastic stiffness matrix reduces to nine independent elastic properties. The generalized Hooke's law thus takes the form:

$$\sigma_1 = C_{11}\, e_1 + C_{12}\, e_2 + C_{13}\, e_3$$
$$\sigma_2 = C_{12}\, e_1 + C_{22}\, e_2 + C_{23}\, e_3$$
$$\sigma_3 = C_{13}\, e_1 + C_{23}\, e_2 + C_{33}\, e_3$$
$$\sigma_4 = 2C_{44}\, e_4$$
$$\sigma_5 = 2C_{55}\, e_5$$
$$\sigma_6 = 2C_{66}\, e_6.$$

A comprehensive review of orthotropic elasticity, including the relationships between the engineering constants (E's, G's, and ν's) and the elastic stiffnesses and compliances can be found in Ref. 153.

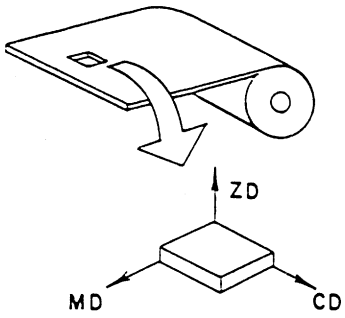

Figure 15. Principle directions assigned to paper.

Cráver and Taylor (154, 155), using elastic stiffnesses measured ultrasonically, and Jones (156) first demonstrated that in the MD-CD plane of the paper experimental results could be described in terms of two-dimensional orthotropic elasticity. Habeger (157) has described a technique for testing the orthotropic symmetry of polymeric sheets by measuring their elastic shear coupling coefficients. He

found that paper could adequately be described as an orthotropic material (158). Mann et al. (159, 160) assumed three-dimensional orthotropic elasticity theory could characterize paper and devised means to measure the nine elastic stiffnesses. If the nine elastic properties of paper are known, the three-dimensional elastic response of the paper to applied stresses can be computed. Such information is necessary for characterizing the end use behavior of paper and for use in modeling containers or other structures.

In terms of engineering constants, the nine elastic stiffnesses above are related to three Young's moduli (one in each principal direction), three shear moduli (one in each plane), and three independent Poisson ratios (one in each plane) (e.g., 153). In principle, all of these can be determined from stress-strain measurements. A uniaxial stress-strain measurement along the x (or MD) direction, for example, would give Young's modulus in this direction (See Figure 9). The two Poisson ratios could be determined by taking the ratio of the lateral contraction in the y (or CD) or z (or ZD) to the axial extension in the x-direction. Thus we could measure three elastic constants from a single uniaxial measurement. Likewise, we could repeat the experiment in the y and z directions, to obtain all three Young's moduli and six Poisson ratios. Only three of the Poisson ratios will be independent, however. To obtain the shear moduli we would need to apply shear stresses in the x-y, x-z, or y-z planes and measure the corresponding shear strains.

A number of researchers have measured some of the orthotropic elastic properties for paper using stress-strain measurements. Early work focussed on the MD-CD plane (161-165). In an effort to determine if paper fit a two-dimensional orthotropic model, Jones (156), measured the MD and CD elastic moduli, the MD-CD shear modulus, and the Poisson ration in the plane, $\nu_{MD\text{-}CD}$. He measured the resonant frequency of a paper cylinder in torsion to obtain shear modulus and used a photographic technique to determine the strains necessary to compute the Poisson ratio. Because the lateral contractions in a uniaxial stress-strain experiment are very small and,

thus, difficult to measure and since paper tends to warp out of the plane during straining, there were questions concerning the validity of the calculated Poisson ratios. Nevertheless, Jones concluded that the orthotropic model did apply to paper for stresses in the plane of the sheet.

Other measurements of Poisson ratios using mechanical methods have been reported (163, 166-171). Uesaka et al. (170) described some of the difficulties in measuring Poisson ratios using mechanical methods. Brezinski and Hardacker (171) measured the Poisson ratios for a series of southern pine kraft handsheets using a sophisticated biaxial testing device (172). They reported values of approximately 0.3, which are consistent with the value of 1/3 predicted for well bonded isotropic handsheets.

Suhling et al. (168) carried out uniaxial experiments where both axial and transverse strains were monitored using the lateral vacuum restraint apparatus designed by Gunderson (173). They plotted lateral strain against axial strain and took the slope of the best straight line representation for all of the data as Poisson's ratio. They noted that the data was reasonably linear suggesting that Poisson ratios in paperboard were independent of strain. The Poisson ratios determined in this way are taken as large strain Poisson ratios. They also determined the slopes of the individual data curves at zero strains and averaged these to obtain small strain Poisson ratios. For the large scale strains $\nu_{12} = 0.403$ and $\nu_{21} = 0.135$, whereas for the small scale strains $\nu_{12} = 0.367$ and $\nu_{21} = 0.168$.

In addition to Jones, others have measured in-plane shear moduli (174-177) using mechanical techniques, or have calculated shear modulus from the other elastic moduli measured in the plane (167). Erykhov et al. (177) used high- and low-frequency torsional oscillations to measure shear moduli of unbleached kraft softwood handsheets. Van Liew (178) seems to be the only one to have measured Z-direction elastic stiffness using stress-strain measurements.

Acoustic Measurements of Specific Elastic Stiffnesses

As noted above, the specific elastic stiffnesses for any material describe its stress-strain response. Acoustic methods are routinely used to measure elastic stiffnesses of three-dimensional materials nondestructively, and these techniques have been extended to sheet-like materials (154, 155, 159, 160). Procedures have been developed for measuring the nine elastic properties necessary to describe paper, or other sheet materials, in three dimensions (179-184). Seven of these can be measured routinely in the laboratory. Measurements have been made on essentially all grades of paper and board, non-wovens, wood, and some plastics. There are limitations on the method, however, relative to sample thickness and area and the measuring frequency (181).

The elastic properties are determined by measuring the velocity of ultrasound in the paper. The theory has been described in detail elsewhere (182). The following discussion briefly presents the theory behind the measurements.

With reference to the generalized Hooke's Law for a three-dimensional orthotropic material presented above, the elastic stiffnesses are measured by propagating certain types of acoustic waves in specific directions in the paper. Once these are known, the elastic compliances, S_{ij}, or engineering constants (Young's moduli, shear moduli, and Poisson ratios) can be computed (153).

Three of the stiffnesses are determined by measuring z-direction bulk wave velocities:

$$C_{33} = \rho V^2_{Lz}; \qquad C_{44} = \rho V^2_{Sy\text{-}z}; \qquad C_{55} = \rho V^2_{Sx\text{-}z}$$

where

V_{Lz} = velocity of a longitudinal wave in the z-direction
$V_{Sy\text{-}z}$ = velocity of a shear wave polarized in the y-direction

$V_{Sx\text{-}z}$ = velocity of a shear wave polarized in the x-direction
ρ = apparent density.

It is worth noting here that the sound velocity is the square root of the elastic stiffness divided by sheet density. That is, the square of the measured quantity (e.g., V_{Lx}) gives us a specific elastic stiffness, having units of $[(N/m^2)/(kg/m^3)]$ or $N \cdot m/kg$. It is not necessary to measure the sheet density separately. (If we divide this by the acceleration due to gravity, we obtain a length unit similar to the breaking length discussed earlier.)

The elastic stiffnesses C_{11} and C_{22} can be determined by propagating longitudinal waves in the machine and cross directions, respectively. The velocities of V_{Lx} and V_{Ly} may then be used to compute C_{11} and C_{22} from:

$$C_{11} = \rho V^2_{Lx}; \qquad C_{22} = \rho V^2_{Ly}.$$

The stiffness C_{66} is easily determined by measuring the velocity of a shear wave propagated in either the x or y direction with polarization in the y or x direction, respectively, where:

$$C_{66} = \rho V^2_{Sx\text{-}y}$$

This shear velocity can be measured on either plate or bulk materials.[2]

The stiffness C_{12} is obtained by propagating a shear wave, polarized in the x-y plane, at a direction 45° to both the x and y axes. The expression for C_{12} in this case is:

[2] A bulk material is one in which the boundaries may be considered to be at infinity and thus do not affect the wave propagation. A plate material, of which paper would be an example, has one dimension which is finite (paper thickness) and can affect the nature of the wave propagation.

$$C_{12} = \{[2\,V_s^2(45°) - 1/2(C_{11} + C_{22}) - C_{66}]^2 - [(C_{11} - C_{22})/2]^2\}^{1/2} - C_{66}$$

where V_s (45°) = velocity of the in-plane shear wave propagated in a direction 45° to the x and y directions. The stiffnesses C_{13} and C_{23} are more difficult to obtain, and at present are not measured routinely.

Table 2 (185) presents results for the orthotropic elastic stiffnesses for several paper and board samples as determined ultrasonically. The engineering elastic constants[3] in the table are values computed from the measured elastic stiffnesses. These will be 20 to 30% larger than values measured using regular tensile tests. The reason for this is the difference in the time bases of the two measurements (124, 129, 130). Since paper is a viscoelastic material, its deformation depends on the time frame of the experiment. Ultrasonic measurements are conducted at frequencies between 20 kHz and 2 Mhz. On the other hand, while it requires only about 0.1 second of straining time to establish a secant modulus from a load-elongation curve, this time scale is much larger than that for the ultrasonic case. There is much less time available for viscoelastic relaxation in the ultrasonic test. Thus the ultrasonic stiffnesses will be higher than those measured from load-elongation measurements.

We return now to the question of the origin of the anisotropy in paper and how it arises. We will do this by discussing manufacturing or machine variables and their impact on the collection of elastic stiffnesses. In the remaining sections we will discuss results in terms of elastic stiffnesses whenever possible, since they permit us to examine the three-dimensional response of the paper.

[3] The use of the "constant" is quite a misnomer since these elastic properties are functions of measuring frequency, sheet temperature and moisture content and, as we shall see, also very sensitive to fiber properties and manufacturing variables.

Table 2. Elastic stiffnesses (measured ultrasonically) and computed engineering "constants" for several grades of paper.

Paper type	Apparent density ρ ($kg\,m^{-3}$)	Stiffness[a] (GPa)									Engineering constants[b] (GPa)								
		C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	E_x	E_y	E_z	ν_{xy}	ν_{xz}	ν_{yz}	G_{yz}	G_{xz}	G_{xy}
Carton stock	780	8.01	3.84	0.042	1.36	0.092	0.91	0.099	0.137	2.04	7.44	3.47	0.040	0.15	0.008	0.021	0.099	0.137	2.04
Linerboard 90 lb	691	8.12	3.32	0.32	1.19	0.113	0.082	0.104	0.129	1.80	7.46	3.01	0.029	0.117	0.0109	0.0208	0.104	0.129	1.80
Laboratory BKSW[c] handsheet I	721	10.9	6.40	0.172				0.290	0.343	3.09	10.3	6.04		0.182			0.290	0.343	2.97
handsheet II	673	16.6	2.78	0.073				0.151	0.260	2.28	16.5	2.76		0.036			0.151	0.260	2.40
Corrugating medium	538									1.24	5.28	1.97		0.167					1.24
Linerboard 42 lb	721										8.72	4.14		0.138					2.43
Linerboard 42 lb (mechanical measurements)											6.83	3.17		0.125					1.22

a Three-dimensional bulk stiffness b The Poisson ratios ν_{yx}, ν_{xz} and ν_{yz} are dimensionless c BKSW, bleached kraft softwood

Effects of Machine Variable on Elastic Stiffnesses and Anisotropy

As we have noted above, paper is typically very directional in its plane. This is commonly expressed as the ratio of MD to CD tensile strengths (MD/CD ratio), or less often as the MD to CD ratio of some other property. Htun and Fellers (186) have presented a review of the in-plane anisotropy of paper.

Figure 16 is a polar plot of specific elastic stiffness (determined ultrasonically) in the MD-CD plane, showing the MD-CD values and values at angles in between (187). Orthotropic elasticity enables us to compute the off-axis values from the measured values and when we do this we find theory and experiment agree very well. The area of the polar diagram is related to machine variables and in particular refining and wet pressing pressure. Increased pressing pressure or increased density leads to increased elastic stiffness values and thus increased area for the polar diagram. The difference between the MD and CD values is related to other manufacturing variables, viz., fiber orientation, wet straining, and drying restraints.

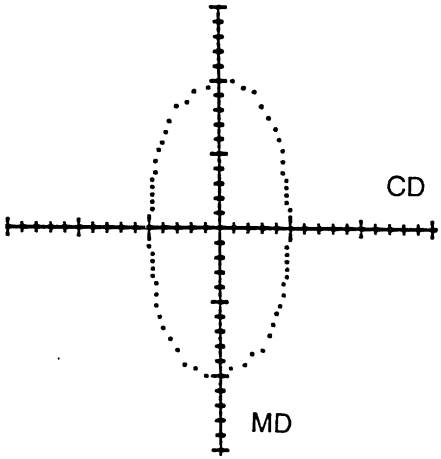

Figure 16. Polar diagram showing anisotropic specific elastic stiffness in the MD-CD plane (Ref. 187).

The terms "MD/CD ratio" and "fiber orientation" should not be used interchangeably. Actually, fiber orientation is only a part of the directionality normally found in most machine-made papers. Directionality also results from wet stretching of the web (in an open draw) and/or the drying restraints imposed on the web in the dryer section (see e.g., 186).

Ideally, one would like to have the fibers in the stock suspension delivered to the wire uniformly separated from each other and, sometimes, with completely random orientations in (three-dimensional) space. This is never really the case, however, since hydrodynamic forces and the chemical interactions cause entanglement and flocculation of the fibers as discussed earlier. But even if we had perfect "formation" at the wire, in most situations we would still find some level of fiber alignment in the final (dried) sheet.

Fiber orientation

As the stock suspension is accelerated toward the slice, the shear stresses tend to cause fiber orientation in the machine direction. In addition, some fibers will tend to align with the papermaking wire when they are deposited onto it.[4] If the velocity of the fibers in the stock flow and the velocity of the wire are different, shear stresses can cause fibers to partially align with the wire. This effect is at a minimum when the two velocities are the same, and increases as the velocity difference increases in either direction. Figure 17 (188) shows MD/CD ratio versus speed difference. The contribution of fiber orientation to anisotropy can be large, depending on the furnish, type of equipment, and operating conditions. MD/CD ratios can range from a value near one (random fiber orientation in the plane) to values of five or more for a cylinder former.

Niskanen (189) analyzed the nature of the resultant fiber orientation distribution relative to paper machine flows and fiber properties. He found that fiber-fiber interactions seemed to determine the extent of rotation of an individual fiber in an oriented shear field. The shape of the fiber orientation distribution depended on fiber properties, and in particular, the wet fiber flexibility. Hasuike et al. (190) used image analysis techniques to determine fiber orientation relative to paper formation. They found that the degree of anisotropy tended to be higher in the low grammage regions for machine made papers. Variations in structural anisotropy were found to be dependent on the nature of the sheet forming process.

[4] A fiber randomly oriented in three dimensions in the stock suspension, upon encountering the forming fabric during drainage, to first approximation, may be thought of only losing its z-direction orientation while retaining its angular orientation in the x-y (MD-CD) plane. The latter is altered, however, if there are speed differences between the fibers and the fabric. This tends to orient more fibers parallel to the MD.

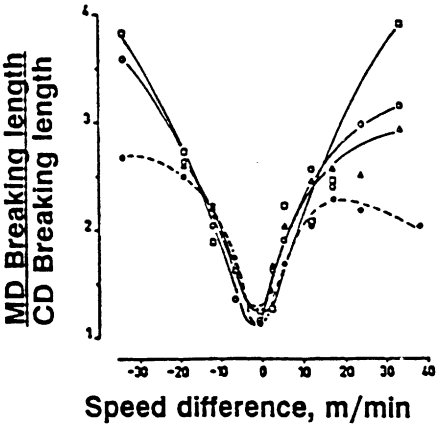

Figure 17. A graph showing how the MD/CD ratio of breaking lengths varies with the jet to wire speed differential (Ref. 188). The speed differential affects the fiber orientation in the sheet. Stretching the web in an open draw or shrinkage during drying can also affect the MD/CD ratio.

The alignment phenomena can occur most readily with those fibers that are in the stock flow nearest the wire during forming. As the mat thickens while moving down the machine, the effect will be smaller, leading to a gradient in the fiber orientation from the wire side to the top side (see e.g., 191). For a twin wire machine, with dewatering in both directions, the fiber orientation through the sheet would be more symmetrical and uniform. In like manner, the fiber orientation may not be uniform from point to point across the width of the machine. This seems to have received little attention, most likely because of the difficulty in measuring fiber orientation. An MD/CD ratio determined mechanically is easily obtained across the machine, but measurements at the end of the machine also contain contributions due to wet stretching or shrinkage effects.

The measurement of fiber orientation is complicated by the sheer number of fibers present in the sheet and the fact that fibers are not straight, but are kinked and curled (43). The most direct approach is to measure fiber segment orientations of dyed fibers (192). Other techniques include zero span tensile strength (193), x-ray diffraction (194), light scattering (195), light diffusion (196), and microwave measurements (197-199). The latter depend on the anisotropy of the microwave dielectric constants which arises because of moisture present in the fiber cell walls (200). Recently Bernard et al. (201-202) have described ellipsometric measurements made in the far infrared, at wavelengths from 50 μm to 1.5 mm, that depend on the birefringence of cellulose. Olofsson et al. (203) used holographic interferometry to examine sheet anisotropy. Rodriques et al. (204) developed a method for measuring the randomness of the fiber distribution based on measuring the entropy of the image of the paper. They found a good correlation between this and the degree of randomness of the spatial distribution of the fibers as measured by a laser diffraction technique.

Several authors have compared some of the fiber orientation techniques (197, 205, 206). Of the various techniques, light diffusion, x-ray diffraction, and microwave measurements are judged to be reliable methods (206). Ultrasonic velocity measurements should not, in general, be used to predict fiber orientation because these measurements are also sensitive to wet straining and drying effects.

Another phenomenon related to fiber orientation can occur at the slice. If the stock flow is not exactly parallel to the wire, it is possible to have the fiber distribution maximum lying at some angle to the MD. Figure 18 is a polar diagram of elastic stiffness that illustrates this (187). In the figure the ellipse is seen to be tipped or leaning to the right of the MD. It was shown that this behavior was a consequence of fiber orientation by measuring "lean angles" for papers before and after rewetting and drying. While the area of the polar diagrams decreased as stresses were relieved by wetting, the lean angle did not change.

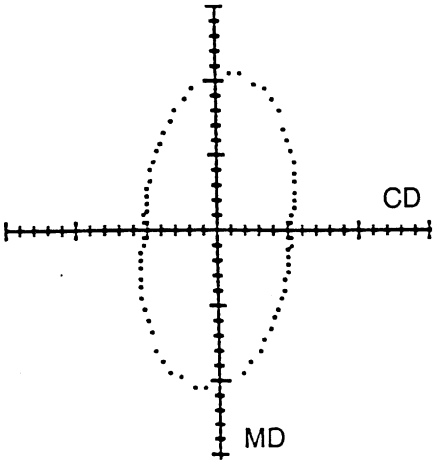

Figure 18. Polar diagram of specific elastic stiffness in the MD-CD plane. The "lean" of the ellipse away from the MD results from the maximum in the fiber orientation distribution not lying along the MD (Ref. 187).

The transverse (CD) component of stock flow does not have to be very large to create a fairly large angle in the fiber orientation distribution. Wahren (207) noted that what is important is the magnitude of the difference between the MD jet velocity and the wire velocity relative to the transverse component of the jet velocity. Figure 19 illustrates this effect, where ΔV is the difference between the MD jet velocity and wire velocity (V_{jet}(MD) - V_{wire}). For example, a 1 fpm transverse flow [V_{jet}(CD)] with V_{jet}(MD) = 2000 fpm and V_{wire} = 2010 fpm, will produce an angle from the MD, ϕ, of about 5.7 degrees [arctan (1/10)], compared to an angle of 0.029 degrees between the resultant of the jet velocity and the wire. Such transverse flows are apt to vary from point to point across the paper machine as slice screw settings change, as a consequence of nonuniform manifold flows, or as a result of in-plane shear stresses during consolidation of the web. If the mean fiber orientation angle is too large (angles in excess of 15 degrees have been observed) there may be problems

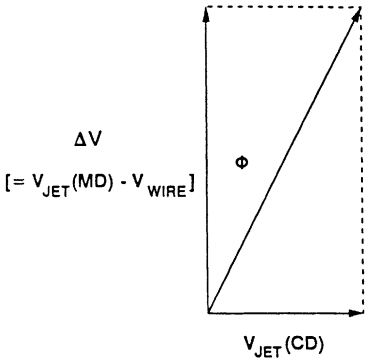

Figure 19. Vector diagram illustrating how a small transverse component of jet flow, $V_{JET}(CD)$, can translate into a fairly large lean angle away from the MD. ΔV is the difference between the MD component of jet velocity and the wire velocity, i.e., $\Delta V = V_{JET}(MD)-V_{WIRE}$.

in subsequent converting or end uses of the paper (depending on the product) (187, 208, 209). Diagonal curl and pile lean are examples of this.

Figure 19 suggests that if the jet and wire speeds are nominally the same, ΔV becomes very small compared to $V_{jet}(CD)$, and ϕ approaches 90°. This observation merits further study.

Straining the wet web

Excessive draws (wet straining) on the paper machine tend to pull the sheet apart, causing deterioration of the properties. From this standpoint, open draws are to be avoided, if possible. In newsprint or coating rawstock, minimizing draws is recognized as a key factor in improving the runnability of these grades. On the other hand, draws also can lead to improved paper properties in the direction of stressing, the MD, similar to the effects of drying under tension. For

example, MD tensile or MD bending stiffness can be enhanced by tightening an open draw at low solids, say coming off the couch or out of the press section, as long as the draw is not so tight as to pull the wet web apart.

Thus in addition to fiber orientation effects, anisotropy also arises because of restraints on the paper during drying and the extent to which the wet sheet was stretched in an open draw. These latter two variables are related. Setterholm and Kuenzi (165) showed that what is important is the extent of the dimensional change in going from wet paper to dry paper. As discussed earlier, paper dried with no restraint can shrink up to 15%, depending on the nature of the furnish. If the paper is stretched while wet, the dimensional change can be even greater. MD shrinkage on the paper machine is largely prohibited because the web is under tension in this direction. In the CD, however, some shrinkage is likely to occur, especially near the edges since there is nothing to restrain the sheet other than contact with the felts and dryer cans. The shrinkage lessens as one moves toward the center of the web. These can lead to a normal or "bell-shaped" distribution across the web of MD and CD mechanical properties such as elastic stiffness or tensile strength, or a concave distribution in properties like stretch.

Wet straining, with all other factors constant, tends to increase the extent of dimensional change as the sheet dries. Intuition suggests that stretching of the wet web would cause an increase in the fiber alignment in the MD (in the MD-CD plane), but this seems not to be the case (e.g., 210, 211). There may be a decrease in the out-of-plane fiber orientation, however (101). Wet straining elongates the paper, which is thought to give rise to a better distribution of stresses in the MD. This leads to improved MD properties when the paper is dried.

Increases in MD properties, e.g., elastic stiffness, resulting from wet straining are offset by decreases in these properties in the cross machine direction if CD shrinkage during drying is prevented (211).

For example, near the center of the paper web (where CD shrinkage may be expected to be minimal) an increase in MD elastic stiffness by wet straining also produces a decrease in CD elastic stiffness. Thus the anisotropy, or directionality, increases. If the product being manufactured calls for maximizing a CD property, such as CD ring crush in linerboard or corrugating medium, it would be desirable to make the sheet as square (nondirectional) as possible. Clearly the way to do this is to minimize wet straining by slackening the draws and to run the jet and wire at the same speeds to minimize fiber orientation effects.

The above behavior leads to the empirical observation that the geometric mean of an in-plane mechanical property, $(MD \cdot CD)^{1/2}$, is approximately invariant. Htun and Fellers (212) studied this behavior and concluded that $(MD \cdot CD)^{1/2}$ is an invariant quantity only if the sheet is dried symmetrically. In a review of this topic, Htun and Fellers (186) suggest that failure in paper is controlled in the sense that the mobility of the microfibrils governs the strain allowed in the structure. If paper is considered an orthotropic laminate, the Tsai-Pagano invariant expression for laminate properties is also applicable to paper (186).

Perhaps a less well known fact is that wet stretching also affects ZD properties, including caliper and, hence, density and probably internal bond strength. Baum et al. (101) showed that wet straining a long fiber furnish by a few percent can cause an increase in the wet caliper that will persist even when the sheet is dried. A 2% wet strain, for example, can produce an 8 to 10 percent increase in caliper. A caliper increase, of course, produces a decrease in density. Figure 20 shows how density can decrease with wet straining. Since most mechanical properties depend on density, the decreased density would be expected to cause a decrease the mechanical properties in all three directions as well.

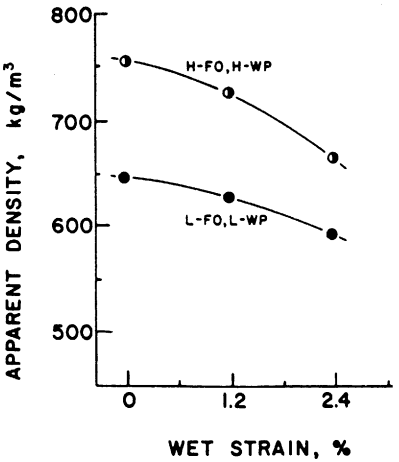

Figure 20. Change in sheet density with wet straining for samples with a high fiber orientation and high wet pressing pressure (H-FO, H-WP) and a low fiber orientation and low wet pressing pressure (L-FO, L-WP). The density decreases with wet straining because the caliper (of the dried sheet) is increased (Ref. 101).

Normally, a material strained elastically in tension becomes thinner due to Poisson contraction effects. This was observed in the experiments at very low strains, but as wet straining continued the trend reversed and the thickness increased beyond the initial value. Similar effects were reported by Öhrn (213). All of the observed effects seem to be explained by a fiber straightening model (101, 213), which assumes a flattening of the ZD undulations of the wet fibers when they are in tension. The model further assumes that the straightening of a fiber under tensile loading causes crossing fibers bonded to it to be pushed apart, thereby increasing the "sheet" caliper and decreasing the extent of bonding or "connectedness" in the thickness direction. A decrease in bonding in the ZD ought to be apparent by a decrease in ZD elastic stiffness and internal bond strength of the

paper and this is observed. In Figure 20, at constant density, the 2% wet strain produces about a two-fold decrease in the ZD tensile strength (internal bond strength) (211) compared to the unstrained sheet.

The impact of wet straining a long fiber furnish on some paper mechanical properties is presented in Table 3. It is possible that in a shorter fiber furnish the effects due to wet straining described above are not as large or not observed. The fiber straightening model suggests that this would be the case.

Table 3. Effect of increasing the indicated variable on strength properties and elastic stiffnesses.

	Yield	Refining	MD Fiber Orientation	Wet Pressing	Wet Straining	Super-calendering
MD Tensile Strength	–	+	+	+	+	–
CD Tensile Strength	–	+	–	+	–	–
ZD Tensile Strength	–	+	o	+	– –	– –
MD Compr. Strength	–,o	+	+	+	+	–
CD Compr. Strength	–,o	+	–	+	–	–
MD Bending Stiffness	?	?(E+,I–)*	+	?	+	
CD Bending Stiffness	?	?(E+,I–)*	–	?		
Brightness	–	–	o	–	+	–
Opacity		–	o	–	+	–
MD Elastic Stiffness	–	+	+	+	+	–
CD Elastic Stiffness	–	+	–	+	–	–
ZD Elastic Stiffness	–	+	o,(+)	+	– –	– –
MD-CD Shear Stiffness		+	–	+	o	–
CD-ZD Shear Stiffness	–	+	–	+	–	– –
MD-ZD Shear Stiffness	–	+	+	+	–	– –

*Young's modulus, E, increases, but moment of inertia of cross-section, I, decreases.

Drying the web

As already mentioned, the nature of the drying of the network has significant impact on the physical properties. In this section we expand on the earlier discussions and attempt to bring together those factors which strongly interact during the drying process to affect web properties.

We earlier noted that the extent of lateral fiber shrinkage will depend on the wood species and related morphological variables, the type of pulping method and yield, and on the type and extent of refining. The more the fiber cell wall was swollen with water, the greater the transverse shrinkage of that fiber during drying. If this fiber is capable of strongly bonding to many other fibers, the total shrinkage of the web results from the collective effects of the individual fibers shrinking. Such a "freely dried" paper tends to be very rough with both short range (fiber scale) and longer range variations (e.g., cockle) in roughness. The elastic stiffness or tensile strength of such a sheet will be lower than if it had some restraint during drying, whereas the strain at failure and moisture expansivity will be higher (214).

The extent of shrinkage will also depend on the anisotropy due to fiber orientation. Paper will shrink less in the direction of orientation (MD) than in the cross direction; a consequence of the fact that there are fewer fiber cross sections that can undergo shrinkage in the MD. Wet pressing, because it enhances bonding, will partly determine the effectiveness of the stress transfer from the laterally shrinking fibers to the fiber to which they are bonded. Wet straining impacts properties as noted earlier and may be thought of as a negative shrinkage. A graph of a physical property against shrinkage will form a continuous line (214, 215).

On the paper machine, of course, the web structure never really has an opportunity to freely dry. In conventional can drying, the sheet is pressed against the dryer can prohibiting shrinkage in the CD (as long as the shrinkage stresses do not exceed the frictional stresses). In an open draw, however, the web experiences wet straining and undergoes Poisson contraction, and shrinkage is allowed as well. These effects, acting together at any given point in the web, produce a local drying "restraint", which together with the local moisture content and those variables mentioned above, determine the physical properties of the dried network at that point including any graininess or cockle. If the MD or CD restraints vary with position or time, the sheet physical properties will vary as well. Arlov and Ivarsson (216)

studied the stress-strain behavior of paper at various positions along the dryer. As they moved through the dryer the elastic modulus progressively increased while strain to failure progressively decreased. MacGregor and Conners (217) reported MD microstriations in paper that they attributed to an interaction between pressing and drying. They concluded that the interaction leads to a different rate of shrinkage on each side of the paper during drying, causing a microscopic buckling.

The shrinkage effects on mechanical properties are well documented (165, 210, 214, 215, 218-219). Htun (220-222) has extensively studied the impact of drying restraints on mechanical properties. He showed that drying stresses of paper measured during restrained drying were identical to the internal stresses measured using stress relaxation techniques (220), independent of the level of heating, wet pressing, or furnish. The latter suggests that the mechanism for building up internal stress during restrained drying is related to the viscoelastic nature of the fibers rather than changes in the structure. Waterhouse et al. (223) investigated the variation in elastic properties relative to drying stress variations in the thickness direction of paper. Using stress relaxation and curvature measurements, they reported a significant variation in internal stresses in the ZD.

Nanri and Uesaka (224) recently studied the effects of drying shrinkage, wet expansion, and hygroexpansivity on the dimensional stability of four mechanical pulps. The model developed by Uesaka (225) was used to explain differences in hygroexpansivity and drying shrinkage between mechanical and chemical pulps in terms of drying stress, and fiber stiffness and dimensions. Salmén et al. (226) found that hygroexpansivity was highly sensitive to drying restraint at solids contents in the range 30 to 100%, whereas elastic modulus was most sensitive to drying restraints below 75%. Htun et al. (227) measured the mechanical behavior of paper during drying. They found that paper behaved as a linear viscoelastic body during restrained drying. The maximum loss coefficient and change in the elastic modulus during drying were interpreted in terms of a transitional change in the

amorphous regions of the polymers plasticized by water. Htun (228) has recently reviewed the subject of drying restraints on mechanical properties.

Wadhams et al. (229) demonstrated that the wavelength of the wire mark in paper can be used to determine the local dimensional changes of the web from wire to reel. Viitaharju and Niskanen (230) used this method to measure the shrinkage of commercial papers in the cross machine direction and compared the shrinkage measurements with other physical properties. They found that the inverse of the CD elastic modulus agreed most closely with the overall variation in shrinkage across the width of the web, but even then the two profiles did not correlate exactly. Shands and Genco (231) studied the CD variation of paper curl on a twin-wire paper machine. They found a good correlation between curl and the reciprocal of the CD specific elastic stiffness, concluding both were caused by a variation in restraint in the cross machine direction.

Figure 21 shows a polar diagram in which CD shrinkage has occurred (187). Note that in this case, the diagram is "necked down" along the CD axis, a consequence of some shrinkage in this direction. It is also possible to get this behavior via a combination of fiber orientation and wet straining effects. As a summary, this figure also depicts an anisotropic paper that has a fiber orientation distribution maximum (lean) that is about 15 degrees off the MD. The anisotropy is caused by fiber orientation and wet straining.

In the laboratory, sheets are typically dried against a plate to prohibit shrinkage and thus eliminate the complicated effects of nonuniform drying on properties. A Yankee dryer can provide the same benefit in a commercial setting for the lighter weight grades. Hansson et al. (232, 233) have described a lateral restraint technique for use on the paper machine that should allow more uniform cross directional properties in the paper. In practice, the choice of drying systems (besides economic considerations) will depend on the particular physical property requirements for the grade of paper. A through-air

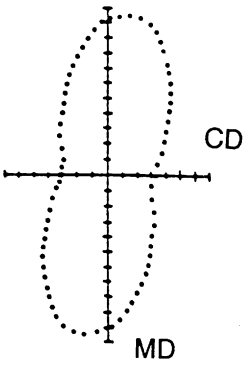

Figure 21. A polar diagram of specific elastic stiffness in the MD-CD plane showing how the ellipse can be "necked down" as a result of nonuniform drying restraints (Ref. 187).

dryer, for example, may be desirable if one wishes to have high stretch in the sheet.

A number of novel pressing and drying developments have been under way in recent years (e.g., 234), including press drying (e.g., 113) and impulse drying (e.g., 235). Press drying is a technique that has received much attention because the sheet is restrained (in all three directions) during drying and unusual physical properties can result. For example, the uppermost curve of Figure 10 depicts the high strength values that can be achieved with this technique.

INFLUENCE OF PROCESS VARIABLES ON SHEET PROPERTIES

Elastic Properties

Figures 22-24 provide a summary of the collective effects of fiber orientation, wet pressing, and wet straining on the three elastic moduli

in the MD, CD, and ZD for a chemical pulp (211). These experimental sheets with different fiber orientations were prepared on a laboratory dynamic sheet former and either not wet strained (called low) or wet strained to 2% (called high). The sheet density was varied by wet pressing. After wet straining, the sheets were dried under full restraint. Measurements of the specific elastic stiffnesses were made using ultrasonic techniques.

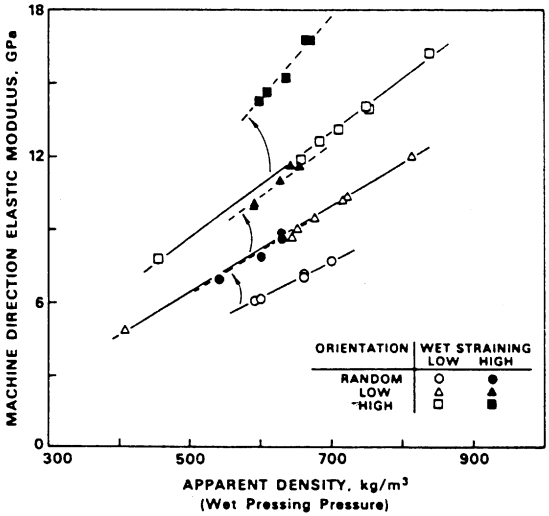

Figure 22. The MD elastic stiffness vs. density (by wet pressing) with changing fiber orientation and wet straining. Compare with Fig. 23 and 24 (same samples) (Ref. 211).

Figure 22 plots MD elastic modulus (calculated from the specific elastic stiffness, C_{11}/ρ) against density. The random sheet with no wet straining is the lowermost curve and the high fiber orientation with wet straining is the uppermost curve. For the six papers shown, there is a greater sensitivity of elastic modulus to wet pressing

(greater slope) as the degree of anisotropy increases (higher fiber orientation and wet straining). At a density around 650 kg/m^3 the elastic modulus increases from near 6 GPa to about 15 GPa, an increase by a factor of 2.5. If MD elastic stiffness is an important converting or end use property, Figure 22 suggests there is a fairly large window in which to operate.

Figure 23 shows CD elastic modulus plotted against density. Here we see the trends are reversed. The random sheet with no wet straining is on the top and the oriented sheet with wet straining is on the bottom. Increasing the fiber orientation and wet straining in the MD decreases the CD elastic stiffness. These results are expected from the invariance of the geometric mean of a property, $(MD \cdot CD)^{1/2}$, as discussed earlier (212).

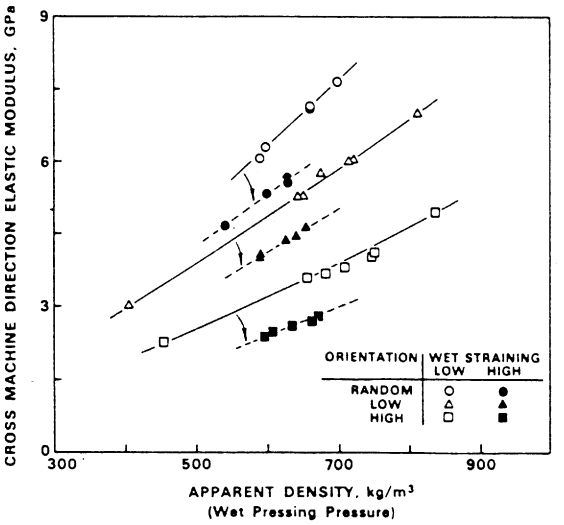

Figure 23. The CD elastic stiffness vs. density (by wet pressing) with changing fiber orientation and wet straining. Compare with Fig. 22 and 24 (same samples) (Ref. 211).

Fleischman et al. (211) observed that at a given wet pressing pressure the density of the sheets increased with increasing fiber orientation. This effect was attributed to the dynamic sheet former since the drum velocity was increased to obtain higher levels of fiber orientation. Recently Amiri et al. (236) developed a model for paper that predicts that the apparent density of paper increases with increased fiber orientation. They experimentally verified this prediction, but they also used a dynamic sheet former.

Figure 24 shows ZD elastic modulus plotted against density. (In this case the elastic stiffness, C_{33}, is actually plotted, since the conversion to elastic modulus involves Poisson ratios in the MD-ZD and CD-ZD planes that are not known.) The figure shows that the out-of-plane stiffness is several orders of magnitude smaller than the stiffness values in the plane. Fiber orientation in the MD-CD plane has little effect on C_{33} and the data points for each fiber orientation condition are grouped together at each wet straining level. The medium wet straining curve in Figure 24 were samples that received a 1% wet strain. The figure clearly shows that the out-of-plane elastic modulus is very sensitive to wet pressing pressure and to wet straining. The magnitude of C_{33} increases by a factor of ten over the range of pressing pressures used, while the 2% wet straining decreases C_{33} by a factor of two or more at a given density.

C_{33} is also sensitive to calendering or supercalendering. Figure 25 shows the sensitivity of specific elastic stiffness, C_{33}/ρ, to wet pressing and supercalendering (100). As above, this out-of-plane property increases with increasing wet pressing pressure, but decreases sharply with increasing levels of supercalendering. The loss in C_{33}/ρ is greatest for the lower starting densities. The loss at 0.5 g/cm^3 is about 70%, compared to a 30% loss at the higher density (0.9 g/cm^3).

Measurements of shear modulus, G_{66} (or $G_{MD\text{-}CD}$), as functions of wet pressing, wet straining, and fiber orientation for the papers discussed in Figs. 22-24 have also been reported (182). G_{66} is a strong, linear

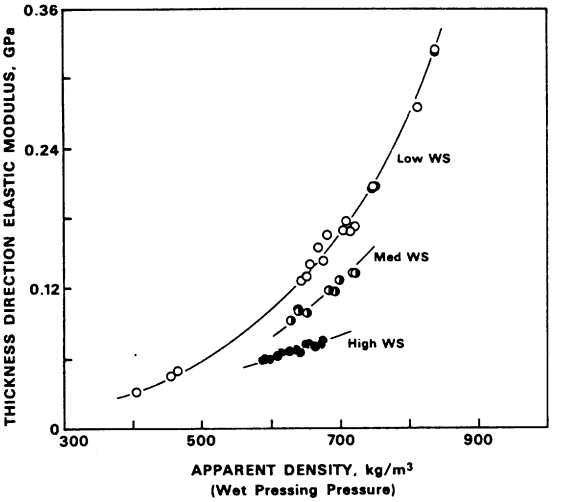

Figure 24. The ZD elastic stiffness (actually C33) vs. density (by wet pressing) at different wet straining levels. Fiber orientation in the MD-CD plane does not affect the ZD elastic stiffness (Ref. 211).

function of wet pressing (density) over the range studied. Except at the highest levels of fiber orientation and wet straining, all of the data grouped reasonably closely together. The highly anisotropic sheets had much lower values of G_{66} at a given density, with the high wet strained sheet lying the lowest.

Baum et al. (181) studied the in-plane elastic properties for a variety of sheets and found that the empirical relationship between elastic properties for orthotropic materials, as proposed by Szilard (237):

$$G_{MD\text{-}CD} = [(E_{MD} \cdot E_{CD})^{1/2}]/2[1 + (\nu_{MD\text{-}CD} \cdot \nu_{CD\text{-}MD})^{1/2}],$$

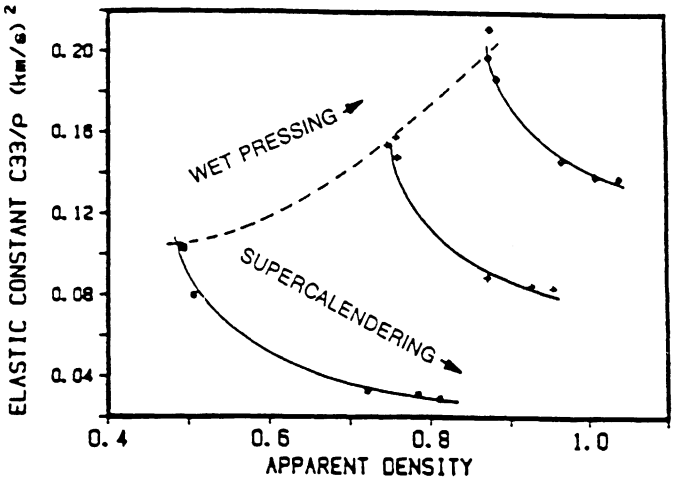

Figure 25. A plot of specific elastic stiffness vs. density showing how densification by wet pressing or supercalendering impacts the former (Ref. 113).

was valid for paper. The Poisson ratios for the (twenty-nine) papers studied were insensitive to density, furnish, forming method, and moisture content. In addition, while $\nu_{MD\text{-}CD}$ and $\nu_{CD\text{-}MD}$ would be expected to be functions of wet straining and fiber orientation, their product would not be expected to be very sensitive to these variables because of the invariance relationship discussed earlier. (The quantity $[\nu_{MD\text{-}CD} \cdot \nu_{CD\text{-}MD}]^{1/2}$ is a measure of how interrelated the tensions in the MD are to those in the CD.) Therefore, the term in the denominator of the above expression is essentially constant and the expression reduces to:

$$G_{MD\text{-}CD} = a\,(E_{MD} \cdot E_{CD})^{1/2},$$

where a, determined experimentally from the Poisson ratio data, was 0.387 ± 0.007. This empirical expression has been validated many

times for both ultrasonic and mechanical measurements of the in-plane elastic properties.

Berger and Baum (238) used ultrasonic methods to study the effects of wet pressing, refining, and yield on the out-of-plane elastic properties [C_{33}, C_{44} ($G_{CD\text{-}ZD}$), and C_{55} ($G_{MD\text{-}ZD}$)] of an unbleached kraft oak pulp. They found all these properties were very sensitive to wet pressing pressure. Increasing refining level or decreasing pulp yield increased the out-of-plane elastic properties by an amount greater than wet pressing alone to the same density. They attributed these changes to changes in the ZD stiffness and shear stiffness of the fiber cell wall. They also verified the relationship above for the in-plane elastic properties and demonstrated that similar relationships exist in the MD-ZD and CD-ZD planes.

In many instances, the elastic properties measured ultrasonically have been shown to correlate with strength properties measured on the same sheets (e.g., 2, 239). In addition, Pan et al. (240) showed that tissue softness could be correlated with out-of-plane ultrasonic measurements. Since the elastic stiffnesses can be measured non-destructively using ultrasonic techniques, such measurements may be used to quickly assess product quality in the mill (even on the paper machine), as well as permit a more complete characterization in three dimensions of a single paper sample.

Three Dimensional Anisotropy

Figure 26 shows the behavior of the three anisotropy ratios R_{xy}, R_{xz}, and R_{yz} for the MD-CD, MD-ZD, and CD-ZD planes, respectively, as a function of wet straining at two levels of wet pressing (101, 239). The anisotropy ratios are defined as R_{xz} (or $R_{MD\text{-}ZD}$) = C_{11}/C_{33}, R_{yz} (or $R_{CD\text{-}ZD}$) = C_{22}/C_{33}, and R_{xy} (or $R_{MD\text{-}CD}$) = C_{11}/C_{22}. The in-plane anisotropy R_{xy} increases steadily with wet strain, as expected, since C_{11} is increasing (in the direction of wet straining) while C_{22} is decreasing. The sheet ruptured just above 3.5% wet strain. The small differences between the two levels of wet pressing for R_{xy} (solid

and dashed lines) probably arises from differences in the two sets of handsheets used, although densification by wet pressing could alter the response of the network to wet straining.

In the case of R_{xz} or R_{yz} at zero wet strain, the wet pressing pressure has a large effect on the out-of-plane anisotropy. Increasing the pressing pressure from 175 kPa (solid line) to 690 kPa (dashed line) decreases R_{xz} (which is approximately the same as R_{yz} at zero wet

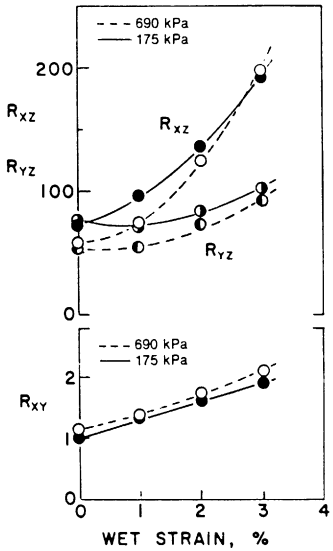

Figure 26. The three anisotropy ratios in the MD-CD, MD-ZD, and CD-ZD planes as functions of wet straining and wet pressing (Ref. 101, 239).

strain), from about 75 to 55. Higher pressing pressures would likely decrease this ratio more. It is unlikely, however, that the ratio would ever approach one, even with 100% bonding, because of the inherent anisotropy of the collapsed ribbon-like fibers.

Wet straining causes both R_{xz} and R_{yz} to increase. This happens even though C11 is increasing and C22 is decreasing (invariance relationship), because C33 is decreasing faster than C22. It should be apparent that a given level of R_{xz} (or R_{yz}) could be reached by different combinations of wet pressing and wet straining. The additional effects of changes in refining and fiber orientation (in the plane) also need to be included in the analysis. The implications of the out-of-plane anisotropy ratios on convertibility and end-use performance still need to be established.

BENDING STIFFNESS

An important property in many grades, and particularly board grades, is the bending stiffness, or the resistance to bending. Bending stiffness is often defined as the product of elastic modulus, E, and the moment of inertia of the cross section, I. EI is usually called the flexural stiffness. For a simple rectangular beam, if the mass is distributed uniformly, $I = wT^3/12$, where w is the width of the beam and T is its thickness. Therefore if S_b is the bending stiffness per unit width, $S_b = ET^3/12$, assuming that E (in the plane) is constant through the thickness direction (this may not always be a good assumption). This expression is sometimes written in terms of basis weight, BW, since $\rho = BW/T$:

$$S_b = (1/12) \cdot (E/\rho) \cdot (BW^3/\rho^2),$$

where (E/ρ) is the specific elastic stiffness. Either expression shows that bending stiffness is a strong function of thickness (or basis weight).

The bending stiffness could be calculated from the above expression if E and ρ are measured, assuming that the values of E and ρ did not differ through the thickness of the sheet. If E as a function of thickness was known, it would be possible to compute the bending stiffness by integration over the cross section.

Usual measurements of bending stiffness involve pure bending (no shear) of a strip of board by applying a bending moment to it. Two-point bending is a simple cantilever where the board is clamped at one end and a line load applied to the other end. Three-point bending involves supporting the strip at both ends and applying the load in the center. This may be thought of as two mirror image two-point bending experiments. In either case, the bending stiffness can be computed from the applied force and the deflection of the beam. Most routine test procedures used in the industry employ the two point bending method.

Fellers and Carlsson (241) have compared the various methods of measuring bending stiffness and discuss the problems associated with them. In the case of two- or three-point bending, one problem is that the applied force causes shear stresses in the strip, thus the required condition of pure bending is not met. The clamp also introduces error. In the four-point method (242) the strip is subjected to a pure bending moment between two symmetrically placed inner supports, and no shear stresses are present. Hohmann (243) compared the various methods and generally found reasonable agreement if recommended procedures were followed.

Other methods include the resonance method (241) and, more recently, Naito and Abe (244) reported a new method in which the sheet is bent in a circular arc at all levels of deformation. They studied the effect of papermaking variables on the bending properties. Koran and Kamdem (245) compared a number of the standard tests for measuring the bending stiffness of paperboard.

Because bending stiffness is sensitive to the position of mass relative to the neutral plane, where the material is unstressed, multi-ply structures can offer opportunities to maximize performance at lower raw material costs. Carlsson (246) studied the bending properties of paper and their relation to the layered structure of multilayer papers. He has recently reviewed the topic (247).

Luey (248) developed an expression for multi-ply boxboard that requires the elastic properties and thickness of each ply and the location of the neutral layer. Carlsson and Fellers (249) developed an expression for the bending stiffness of multi-ply boards using classical lamination theory. Figure 27 shows the ply coordinates z_K used by Carlsson and Fellers in the computation of bending stiffness. The bending stiffness is given by:

$$S_b = D - (B^2/A),$$

where $$A = \sum_K (E_x)_K (z_K - z_{K-1})$$

$$B = (1/2)\sum_K (E_x)_K (z_K^2 - z_{K-1}^2)$$

$$C = (1/2)\sum_K (E_x)_K (z_K^3 - z_{K-1}^3)$$

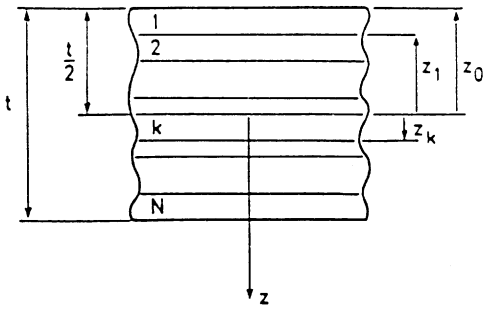

Figure 27. The ply coordinates z_K of a multi-ply sheet (Ref. 249).

and $(E_x)_K$ is the elastic modulus of ply k in the x-direction. The sum in each case is over the number of plies, from 1 to N. With respect to the figure, the ply coordinates are calculated from:

$$z_K = z_{K-1} + t_K \qquad k = 1,2,....N$$

where $z_0 = -(t/2)$, t is the total thickness, and t_K is the thickness of ply k.

The advantage of this approach is that it does not require knowledge of the neutral plane, making it simple to use. Carlsson and Fellers tested the applicability of the expression on homogeneous and multi-layer boards and found good agreement between calculated and measured values of flexural stiffness. It was necessary to have good values for the elastic modulus and density of the individual plies. They used the expression, as have probably many others since then, to determine the optimal flexural stiffness for multi-ply construction using different combinations of pulps.

Table 3 presents a general summary of the major effects on sheet properties (for a chemical pulp) of a change in certain process variables. In some cases the direction of change in a property cannot be determined and these are denoted with a question mark. An example of this might be the effect of wet pressing on flexural stiffness, EI. Whereas increased wet pressing would increase E, the moment of inertia, I, which depends on the cube of the caliper, would decrease because caliper is reduced. The table does not show the collective effect of changes in multiple variables on the property, nor can it give the relative magnitude of the change in the property. The latter would be furnish dependent.

EFFECTS OF ADDITIVES

Paper is held together by chemical bonds; specifically hydrogen bonds between the cellulosic constituents: fibers, fibrils, and fines. The nature of these interactions depends on the fiber characteristics, as discussed earlier, as well as the chemistry of the fibers, water, and any other materials present in the system. Not surprisingly, the addition of chemicals to the wet end of the paper machine can greatly

influence the efficacy of the consolidation process and thereby alter sheet mechanical properties. Chemical additives can enhance wet or dry strength (and simultaneously stretch and TEA), improve ash or fines retention, size the fibers, or even act as debonders to weaken or "soften" the sheet. This topic is simply too large to be considered in any depth here. The following is a very brief overview.

Inorganic fillers such as clay, titanium dioxide, or calcium carbonate, added to the furnish can interfere with bonding, leading to a weak sheet or one with poor bending stiffness. Chemical additives can be used to counteract this effect. Another approach is to load the filler material in the fiber lumens (e.g., 250) or by precipitating inorganic fillers within the micropores of the cell wall (251, 252) where the material cannot interfere with fiber bonding. Allen et al. (252) showed that at equal optical properties the papers made from cell-wall-filled pulps are stronger than those where the filler is positioned on the outside of the fibers. Just as in the case of the fibrous material, pigments and fillers may not be distributed uniformly through the thickness direction and this can also impact mechanical properties. Techniques are being developed to determine the distribution of these materials in the ZD (e.g., 253).

Lindström (254) has provided an excellent review of the fundamental physico-chemical aspects of retention chemistry. He discusses the surface chemistry of cellulosic materials, the nature of the interactions between them, and the implications of surface porosity on polymer adsorption. Scott (255) recently reviewed papermaking chemistry from a practical perspective, discussing retention, drainage, fiber flocculation, sizing retention and sizing development, wet and dry strength additive retention, dye retention, deposit formation and control, and defoamers. Neither Lindström nor Scott discuss in any depth the impact on sheet mechanical properties.

While chemical additives can influence mechanical properties, the elastic modulus is often much more insensitive to them than strength properties. Figure 28, for example, shows the stress-strain curves for

three papers (slightly offset along the strain axis to more clearly show the initial response). The lower curve is a sheet containing no dry strength additive, while the other two curves are sheets containing different dry strength additives. While the tensile strength, stretch, and TEA (area under the curve) are all increased for those papers containing the dry strength (or stretch or TEA) additive, all three sheets display the same elastic modulus (initial slope of stress-strain curve). This behavior in elastic modulus is not completely unexpected. In our earlier discussions of the work of Page and Seth (117), we observed that, for a well bonded sheet, the modulus of the sheet was related to the modulus of the fibers only. In like manner, Page and Seth (117) also showed that the addition of a debonding agent also did not impact the elastic modulus.

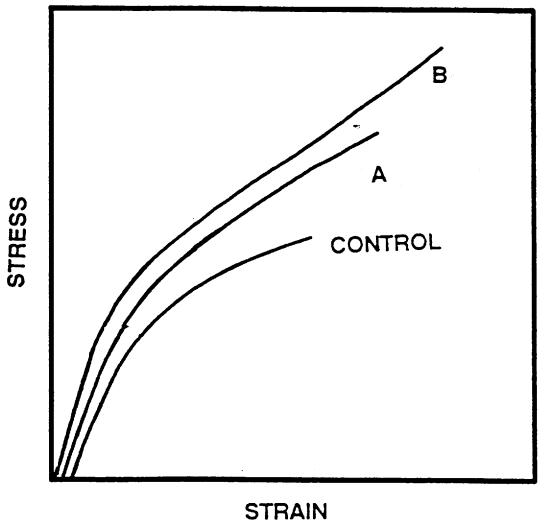

Figure 28. Stress-strain curves for sheets having different dry strength additives, A and B, compared to the control.

Internal sizing is used to control the rate and amount of moisture pickup by the fibers or sheet. Several papers describing mechanisms of internal sizing were presented at the last Fundamental Research Symposium (256, 257). Marton (256) reviewed sizing mechanisms and the effect of fillers. Aspler et al. (257) investigated the self sizing of a pure cellulose paper. They found that surfactants prevented self sizing by interfering with chemical bond formation between cellulose and fatty acid molecules. Alum accelerated self sizing.

Surface sizing of paper is said to be as old as papermaking itself (258) and is widely practiced. Because surface sizes form a more-or-less continuous film and penetrate into the sheet, they can effectively stiffen the outer layers of fibers, thereby increasing the bending stiffness. This behavior is understandable and explained in terms of the multilayer model of bending stiffness presented earlier. Coatings can have similar effects on bending stiffness.

Bown (259) investigated the relationships between strength properties and light scattering coefficients for filled papers. Robertson (260) incorporated polymers into paper by either solution impregnation, latex impregnation, or latex beater addition, and evaluated the impact on sheet mechanical properties, including elastic modulus. In this case the elastic modulus varied with the type and amount of polymer added.

SHEET PROPERTY MODIFICATION/DEGRADATION

While discussing the subfracture properties of paper we should spend some time discussing the modification of sheet properties to meet desired converting or end use criteria. The focus here is not on sizing, coating, or property modifications due to moisture, temperature, or time effects (these are discussed in separate reviews). The following discussion considers some situations that typically involve degradation of the sheet properties delivered off the paper machine, but do not result in "fracture".

We can define two general classes of operations that can degrade web properties. Localized processes, such as bending, folding, scoring, or embossing are those where the degradation occurs along well-defined lines or regions (these are usually intentional). The second group involves nonlocalized processes, such as creping, calendering, decurling, or any nip passage, where the degradation may be over the entire web (these can be intentional, as in creping, or unintentional). Some operations, such as fluting where the corrugating medium is degraded alternately at flute tips or roots would fall somewhere between the two definitions.

Paperboard has a unique property of being able to be delaminated in certain regions (scored) while retaining most of its tensile strength. Carlsson et al. (261), for example, and others have studied this behavior and these studies have led to improvements in board design. Fellers et al. (262) have summarized much of the knowledge related to carton board. Calvin (263) recently discussed the unique convertibility of paperboard. In like manner, Whitsitt (e.g., 264) and others have established relationships between corrugator runnability and medium and linerboard properties. Similar studies are needed in other converting operations.

Creping and the CLUPAK® process are examples of processes that intentionally alter the paper web in a nonlocalized fashion. Other converting operations can unintentionally degrade the structure in a nonlocalized way. For example, we earlier observed that the z-direction properties of paper were particularly sensitive to wet pressing pressure (increasing with greater pressures) and to draws and drying (decreasing with greater wet straining levels). Figures 10 and 25 demonstrate that calendering and supercalendering, respectively, have a large negative impact on out-of-plane properties. This suggests that for any paper grades where high ZDT or edge compressive strength is important, we should work to minimize open draws and avoid calendering or supercalendering, if possible.

Sheet properties may be mechanically degraded over long periods of time due to normal handling. For example, currency papers are subject to a loss of stiffness and folding endurance over time due to normal handling.

Perhaps the least understood area of paper science is that dealing with paper requirements for converting and end-use applications. We cannot always answer questions such as, 'What sheet properties are important in a given converting operation or end-use application?' or 'How are web properties impacted by converting operations?' In many cases the relationships between web properties and successful converting or end-use may not be known at all. Many converting operations have not been studied in detail, especially in fundamental terms, and we often do not understand the stresses that act on the paper. At the same time, the array of traditional paper tests used to characterize the web do not always provide a proper or complete description of the structure and, thus, may not be able to define the impact of converting process. A major advantage of measuring elastic stiffnesses ultrasonically is the ability to nondestructively characterize the material in three-dimensions.

It would be desirable to establish the properties of the structure that are important to performance in a given converting operation and to establish relationships between those properties and the converting operation. The latter knowledge would be expected to lead to superior structures or perhaps adaptation of the converting process to better utilize existing web structures.

MODELING

We briefly discussed the modeling of the paper structure earlier when we discussed the stress-strain behavior of paper. Here we will review some of that material and delve a little deeper into the models.

From the discussions thus far concerning the complexity of the material, clearly modeling paper will not be a simple task. The initial assumptions made concerning the models will determine how amenable the model is to mathematical calculations, the quality of the model predictions, and the closeness to physical reality. Paper is a viscoelastic material, as noted earlier, whereas most models treat it as a linear orthotropic material. The behavior of paper, however, is quite nonlinear even at relatively small strains, suggesting that a linear elastic model will not be sufficient.

The work to date, and there has been quite a bit, covers a broad range of models, including those at the atomic and molecular level, the cell wall level, the fiber level, up to macromechanics or continuum models (see e.g., 265). The low strain properties of paper have received the most attention. Models to predict low strain properties have primarily been either network or lamination models. Each offers some insight into the nature of paper, but, at the same time, each suffers from shortcomings. An advantage of network models is that the properties of the structural elements and the nature of their interactions are, in principle, obtainable. On the other hand such network models can be cumbersome to apply because of the large number of parameters required. Continuum approaches are simpler to use, but provide less insight as to physical or chemical changes taking place during the straining of paper. Thus far a single, comprehensive, model does not exist, but each new model brings new insights and computational methods that may eventually get us closer to the definitive and predictive model we desire.

Micromechanics Models

The early models began at the fiber level and can be considered micromechanics models (266). These two dimensional models sought to answer the question "What are the mechanical properties of the network, expressed in terms of the properties of the fibers, their geometric arrangement in the structure, and the nature of the bonds?" The original theory for a random fiber network of long

straight fibers attached at the ends is that of Cox (143). Cox assumed a uniform strain theory (where the strain in the fibers is equal to the strain in the sheet), rigid fiber bonds, and negligible fiber flexural stiffness so the fibers could transmit tensile loads only. Cox showed that for the random case (he also looked at nonrandom distributions) that sheet modulus of elasticity, E_s, was one-third the fiber axial modulus, E_F, or $E_s = (1/3)E_F$. Le Chacheux (267) developed a similar theory. Page, et al. (268) verified Cox's results for well-bonded paper.

Subsequent models (269-272) sought to improve upon the initial assumptions of Cox. The model of Van den Akker (271) is noteworthy because it first considered bending and shear of the interconnected fiber segments and also included distribution functions for fiber cross-sectional area, moment of inertia of the fibers, and fiber segment length. Van den Akker's results provided a better understanding of the nature of changes in paper properties as a result of nonuniform shrinkage restraints. His model predicted that for MD-direction tension, a fiber making an angle with the CD-axis whose tangent equaled the square root of Poisson ratio would not experience any net tensile or compressive axial force. For example, if the network Poisson ration was 1/3, fibers oriented between 0 to 30 (or 150 to 180) degrees would be subject to axial compressive forces, while fibers oriented at any other angle would experience axial tension.

Algar (273) reviewed the status of network theories up to 1965 and a part of his summary is presented in Table 4, along with several more recent additions (taken from 274). Van den Akker (275) reviewed the literature concerning the tensile characteristics and structure of paper in 1970.

Perkins and Mark (276) developed a micromechanics model similar to Van den Akker's but allowed the bonds to have some rotational stiffness. The model gave predictions for fiber modulus that were close to observed values. Hollmark (277) studied the discrepancy

Table 4. Comparison of some network theories (273).

AUTHOR	SHEET MODULUS	REFERENCE
Cox (1952)	$\frac{1}{3} \cdot \frac{D}{d} \cdot E$	(143)
Cnogi-Sasaguri (1961)	$\frac{8}{\pi^2} \cdot \left[\frac{1}{g^2/3r^2+1}\right] \cdot \frac{D}{d} \cdot E$	(269)
Campbell (1963)	$\frac{1}{3} \cdot \frac{D}{d} \cdot E$	(270)
Van den Akker (1962)	$\frac{1}{3} \cdot \left[1 + \frac{4 \cdot I \cdot G}{aGb^2+12EI+2GI}\right] \cdot \frac{D}{d} \cdot E$	(271)
Kallmes (1963)	$\frac{1}{3} \cdot \left[1+\frac{16 \cdot I \cdot G}{3aGb^2+36EI+8GI}\right] \cdot \frac{D}{d\tau} \cdot E$	(272)
Perkins-Mark (1976)	$\frac{1+2\beta}{3+2\beta} \cdot \frac{1}{1+(3/2)\cdot(2a_o/t_f)^2} \cdot \frac{D}{d} \cdot E$	(276)
Page-Seth (1979)	$\frac{1}{3} \cdot \left[1 - \frac{w}{gRBA}(E/2G)^{1/2}\right] \cdot \frac{D}{d} \cdot E$	(278)

a = cross-sectional area of fiber wall
a_o = measure of slackness in unstrained network
b = unbonded fiber segment length
d = density of fiber wall
D = sheet density
G = fiber shear modulus
I = moment of inertia of fiber cross section
r = fiber radius for circular
RBA = relative bonded area
t_f = fiber thickness for rectangular fibers
τ = fiber curl
E = fiber modulus
f_i = initial fraction of inactive fibers
g = fiber width for rectangular fibers
β = dimensionless parameter

between experimental and theoretical values for sheet modulus and noted an increase at lower basis weights. Taking into account basis weight effects on network density and fiber length and strains, he was able to predict the behavior of low basis weight sheets.

As discussed earlier, Page and Seth (117, 278) studied the falloff of elastic modulus with decreased bonding and showed it was caused by the transfer of stress from each fiber to its neighbors in the regions of its ends. Using essentially Cox's approach, but taking into account the impact of fiber ends, they obtained the expression presented earlier for sheet elastic modulus in terms of fiber properties. In that expression, the argument of the hyperbolic tangent function will always tend to be much greater than one, so that the hyperbolic tangent will essentially always be one. This leads to:

$$E_S = (1/3)[1-(w/L \cdot RBA)(E_F/2G_F)^{1/2}]$$

where the symbols are given in the caption to Table 4. For long fibers (large L) or high values of RBA, this equation reverts to the Cox result, $E_S = (1/3)E_F$, but otherwise E_S normally falls below this upper bound.

Perkins (279) prepared a rigorous summary "On the mechanical response of materials with cellular and finely layered internal structure" in 1972. In 1980 he developed a self-consistent micromechanics model based on straight segments of the fibers (280, 281). That is, he defined a typical curved fiber in terms of a number of straight lengths. He has used this model to describe relationships between fiber orientation, fiber geometry, and sheet mechanical properties (282). Perkins and Ramasubramanian (283-285) have carried out computer simulations for comparison with experimental data and have extended the model to include nonlinear or elastic-plastic behavior in the fibers and bond areas. Experimental investigations have dealt with relating inelastic behavior to structural changes, including fiber cell wall changes, partial bond breakage, and fiber rupture (151, 286). More recently, work has focussed on extending the micromechanics model to predicting elastic and strength behavior (287) and the elastic and plastic response of moderate to high density paper materials (288). Perkins (289) recently reviewed micromechanical models for predicting the elastic and strength behavior of paper materials.

Laminate Models

Laminate models assume the paper structure can be modeled as a laminate built up of plies consisting of cell wall material. The cell wall material in each ply is considered to be a unidirectional fiber reinforced composite where the cellulose microfibrils are the reinforcing material and the hemicelluloses are the matrix material. In this approach, the macroscopic properties of the paper are thus related to the properties of the constituent cellulose and hemicelluloses.

Salmén et al. (290) investigated the elastic and hygroexpansional properties of paper using a composite laminate approach. As in Salmén's laminate model for the fiber cell wall (33) the Halpin-Tsai equations were used to relate sheet properties to the reinforcing and matrix materials. The effects of fiber orientation and the influence of moisture on these properties was examined and the results compared to experimental data. They concluded that the laminate model predicted the effects of moisture on elastic properties and hygroexpansion quite well for isotropic sheets. The laminate model correctly predicted differences for the effect of water in the two principal directions in anisotropic paper, but the relative magnitudes were quantitatively off. They concluded that the elastic properties of paper must depend on both the longitudinal and transverse properties of the fiber cell wall. The model was used to study the impact of water on elastic modulus. The softening of hemicellulose with increasing moisture content was judged to be the cause of decreased elastic modulus for both fibers and paper (291).

Schulgasser and Page (292) used a laminate model to investigate the influence of transverse fiber properties on the in-plane elastic behavior of paper. The model assumes uniform strain in the sheet and the fibers are strained in all directions corresponding to the macroscopic stains in the sheet. The model successfully explained previous discrepancies between experiment and previous network models for the in-plane shear modulus and Poisson ratios. Schulgasser and Page deduced anisotropy ratios for the cell wall material:

$$E_1/E_2 = 9 \pm 1, \quad \nu_{12} = 0.15 \pm 0.05, \quad \text{and } G_{12}/E_2 = 0.65 \pm 0.02,$$

where 1 is the fibril direction and 2 is the transverse direction. These values were similar to results reported from measurements on single fibers (293).

Page and Schulgasser (294) also used the laminate model to predict the influence of moisture content and strain rate on the in-plane anisotropy ratio and Poisson ratios. Their laminate theory predicts that zero span strength is a measure of the strength of the cell wall material, not the fiber itself.

Continuum Models

Continuum or macromechanics approaches deal with physical properties such that their dependence on the discrete nature of the structure is unimportant. They are considered continuous functions of position. Such models, in general, do not offer mechanistic insights as to fundamental phenomena underlying observed behavior. They can, however, provide useful and valuable information concerning relationships for material response to a given set of stimuli.

The earliest models of paper were rheological models, involving spring and dashpots to characterize the response of paper to an applied load (e.g., 295). Nissan (e.g., 296, 297) modeled the elastic response of paper as a hydrogen-bonded continuum based on potential functions to give the energy density as a function of strain. He was able to show that the computed elastic modulus, expressed in terms of the atomic parameters from the potential function, agreed with experimental values at small strains. Nissan and Batten (298-300) have combined the hydrogen-bond theory with percolation theory in order to describe the structure or paper. Dodson et al. (10, 301) have provided an overview of some of Nissan's contributions.

Suhling (302) developed a general elastic plate theory for anisotropic media that included geometric and material nonlinearities that he

applied to paperboard. More recently, Suhling et al. (168) presented a two dimensional total strain hyperelastic constitutive model for nonlinear orthotropic materials and applied it to paperboard. A hyperelastic material is one for which a strain energy density function can be defined. Suhling et al. used the strain energy density function suggested by Johnson and Urbanik (303), who assumed that the strain energy density for a nonlinear orthotropic material could be expressed as a nonlinear function of the single effective strain measure that results from the linear orthotropic strain energy. One interesting outcome of Suhling's analysis is that the new nonlinear constitutive theory predicts constant Poisson ratios even though one has nonlinear uniaxial stress-strain curves. This prediction is in general agreement with experiment. The Poisson ratios presented earlier were taken from this work.

As mentioned earlier, Perkins (288) developed micromechanical models for predicting the elastic and plastic response of medium to high density paper. He also described a two dimensional elasto-plasticity continuum model which appears capable of representing a linear response at low strains and a strain-hardening plastic behavior above a certain level, as long as the moisture content is relatively constant. The model will require experimental verification. Perkins intends to extend this treatment to three dimensions.

Several researchers have used finite element analyses to characterize the paper structure (e.g., 304, 305). Lin and Suhling (305) performed a supercomputer analysis of paperboard structures in which they used a nonlinear iterative finite element approach to obtain numerical solutions to their analytical models. They investigated a uniaxially loaded sheet with a circular hole and uniformly loaded circular or square plates with clamped edges. They were successful in demonstrating that the stresses, strains, and displacements could be determined using models incorporating nonlinear material behavior.

Åström and Niskanen (306) simulated the fracture of paper on a supercomputer using a two dimensional random fiber network that

was linear elastic except for a reduction in network modulus that resulted from bond failure or fiber failure. One prediction was that the specific elastic modulus at low network densities is a linear function of density, in agreement with experiment. Ritala and Huiku (307) described scaling, percolation, and network theories, and discussed the applications of these methods to papermaking and related topics, and presented a number of examples.

CONCLUSIONS

This review has attempted to describe how the structure of the sheet develops during the manufacturing process, and how this is related to mechanical properties and particularly subfracture properties. We continue to advance in our understanding of paper on all fronts. As new measurement equipment and techniques become available and new methods are developed, we seem both to reconfirm and to advance our understanding of paper and its uses. While this review has not been rigorous, I believe it has presented some trends and observations that warrant consideration.

Observations

1. We still do not have a complete understanding of the collective effect of raw material and process variables on paper and board physical properties. We have many separate pieces of information, but, for the most part, the studies relating furnish, machine, or process variables to properties lack direct quantitative correlation with each other. For example, in addition to the kind of information given in Table 3, we need to understand the collective impact of the important process variables on the properties of interest before we can really begin to model the structure or control the process to give the desired web structure.

2. Our understanding of the requirements that converting places on the paper or board are still imperfect. We still are not sure what the appropriate or optimum paper or board structure should be for some converting operations. Furthermore, we probably do not often appreciate the abuse received by the paper during converting that can lead to a degradation of properties. Finally, we seldom consider how such degradation may impact subsequent converting operations or the ultimate end-use performance.

3. It is well established that paper is a viscoelastic material. We should be careful in our use of elastic "constants" to describe converting and use requirements that may occur in a time domain different from that in which the elastic properties were determined.

4. We need to take advantage of the opportunity to characterize paper in three dimensions. Paper is not a two-dimensional material and the ZD mechanical properties are not unimportant.

5. In terms of our understanding and modeling of the structure, much of the work discussed here (148, 186, 220, 238, 290, 294) points toward the cell wall, rather than fibers, as the basic building blocks that control many, if not most, sheet properties. Paper appears to behave as if it is far more homogeneous than we have believed.

6. In light of our current understanding, and the new measurement techniques available, some earlier work bears repeating. For example, much of the early work relating sheet physical properties and density is suspect, since the densities used typically included a hard platen caliper measurement.

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Transcription of Discussion

SUBFRACTURE MECHANICAL PROPERTIES OF PAPER AND BOARD

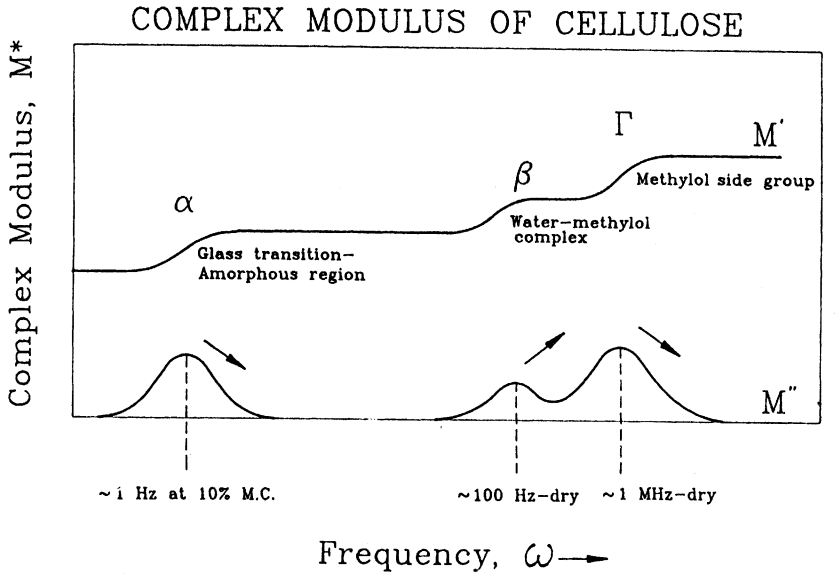
G Baum, James River Corp, USA (Review Paper)

ADDENDUM TO ABOVE PAPER

The linear viscoelastic response of cellulose has been attributed to three different thermally activated transitions (120-130). These are molecular level motions that contribute to macroscopic compliance. Each transition requires a finite relaxation time. Only those experiments with time bases greater than the relaxation time will be sensitive to the transition. The relaxation times and magnitudes of the transitions are temperature and moisture dependent.

The Γ transition is the lowest temperature transition. It is considered to be the result of the rotation of the methylol side group on the cellulose chain. The Γ transition in dry cellulose occurs at about -95°C at 1 MHz and has an activation energy of about 10 kcal/mol. Moisture antiplasticizes the Γ transition, in that its intensity decreases with water content. Water combined with cellulose produces a different relaxation that is not present in dry cellulose. This is the B transition. Its molecular origin is tentatively identified as motion of a water-methylol complex. The transition temperature is about -70°C at 7% moisture and 100Hz, and its activation energy is about 15 kcal/mol. Water efficiently plasticizes the B transition: its intensity increases with increasing moisture content while the transition is the α relaxation. This is the glass transition in the amorphous regions of the cellulose. The activation energy is large (over 100 kcal/mol), and the peak of the relaxation would be at about 200°C at 1Hz. It is very easily plasticized by water. In fact, the low temperature limb of the α transition is

responsible for much of the room temperature moisture sensitivity of the physical properties of paper.



Dr K Good, Oklahoma State University, USA

With reference to Z direction properties, you make the point that paper is a three dimensional structure, but in my observations and in my experimentation I often find that your constants C13 and C23 are very small because of the Poissons ratios which couple in plane to the out-of-plane deformation and if those are so tiny maybe it is a three dimensional structure in terms of geometry but I have a hard time saying constitutively that it is 3 dimensional. My experience is based on determining C_{13} and C_{23} for stacks of paper and film whereas your comment pertains to a single sheet I believe. Would you like to comment on this?

G Baum

Yes, my comments refer to a single sheet. In paper C_{13} and C_{23} are not small, but are typically larger than C_{33}. For a stack of sheets, in which the individual layers were not bonded or under high pressure, I suspect these stiffnesses might be small.

Dr J Brander, Arjo Wiggins R& D Limited, UK

If you look at paper structure from the point of a the physicist you have defects. What do you think are the defects?

G Baum

As regards defects in paper?

J Brander

Yes.

G Baum

When I refer to defects in other materials, I am thinking of point dislocations, interstitial atoms, vacancies etc. Because of the unhomogeneous structure, paper has been described as a collection of defects. I believe you could also consider moisture as a defect in paper.

Dr K Ebeling, Kymmene Corp, Finland

This is more of a comment than a question. Thanks for pointing out the important role of the cell wall structure and material - I think we are seeing its importance again in analysing why some totally chlorine free bleached long fibre pulps behave the way they do when we place them in the paper structure. As individual fibres they are all right, but when you put them into a structure sometimes you see some funny things which probably follow from different mature

of TCF cell wall material in comparison to the cell wall material of conventionally bleached pulps.

D Gunderson, FPL, US Dept of Agriculture, USA
I wondered if in listing your observations you considered adding to the list, 'Paper is a hygroscopic material?'

G Baum
Perhaps my thinking was too narrow since I wasn't charged with reviewing paper - moisutre interactions. Possibly this will be covered later in the paper by Salmen. You are right in suggesting that the hygroscopic nature of paper is very important.