ABSTRACT

In Part 1, the theory of hydrogen-band-dominated solids is extended to explain phenomena concerning the elastic behavior of paper, based on the postulate that the number density of effective hydrogen bands normalized to an average band stiffness, is higher for ultrasonic modulus measurements than for quasi-static measurements. This leads to the predictions: (1) The measured elastic modulus of a sheet of paper will depend upon whether the modulus is measured quasi-statically using load-elongation methods or ultrasonically using the time of flight method, and that the ultrasonic modulus, E_u, will exceed the quasi-static modulus, E_s, ($E_u > E_s$). (2) The rate of change of modulus with increasing moisture content, w, follows the rule: ln [E] = A - (C.I.) w, where the negative slope of the curve ln [E] vs. w is constant over a wide range of moisture contents. But again this slope will also differ whether measuted quasi-statically or ultrasonically, with $(C.I.)_s > (C.I.)_u$. (3) Moreover, the extended theory predicts that the ratio of moduli at zero moisture content is related to the ratio of slopes by the expression: $\{[E_0]_u / [E_0]_s\}^3 = [(C.I.)_s + 1] / [(C.I.)_u + 1]$.

The influence of water on the elastic modulus of paper

Part I: Extension of the H-bond theory

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SEVERAL RESEARCHERS (I-3) HAVE noticed a difference in the effect of water content of paper on its elastic modulus, *E*, when determined by two different methods. If the elastic modulus, *E*, is obtained from quasi-static measurements using a load-elongation method then a relatively simple rule describes how increasing the water content (mass of water/unit mass of paper), *w*, lowers its modulus. In the following discussion subscripts *s* and *u* refer to observations pertaining to quasi-static measurements and ultrasonic measurements respectively. Above a critical water content, w_c, the value $\partial \ln[E]_s / \partial w$ usually is a constant, which, in the terminology of the hydrogen bond theory, is called Cooperative Index $(C.I.)_s$ *(2)*. Similarly, if the modulus is measured by the speed of stress propagation on the same piece of paper using the ultrasonic time-of-flight method, one obtains a similar constant for $-\partial \ln[E]_u / \partial w = (C.I.)_u$ over a very wide range of values of *w*, up to the fiber-saturation value. It is found *(3, 4)* that $(C.I.)_u$ is of the order of $0.5 \cdot (C.I.)_s$ to $0.8 \cdot (C.I.)_s$.

Weatherwax and Caulfield *(1)* first tried to explain the discrepancy as a combination of a duration of load effect and flickering hydrogen bonding that exists in cellulose-water systems. They argue that under the longer stress durations found in quasi-static tension tests, H-bonds can reform with some H-bonds in stress relaxed configurations. This explanation is compatible with the observed viscoelastic deformation in paper but does not account for complete elastic recovery after removal of a load. This explanation also links paper elastic modulus to hydrogen bonds, the predominant type of the intermolecular forces found in wood polymers while they are in their glassy state. This is consistent with the view that it is the strength of intermolecular forces which determines the elastic modulus of most polymers in the glassy state *(4, 5)*. Later, the same researchers extended their explanation to account for the different types and numbers of H-bonds effectively responding in quasi-static and ultrasonic modulus measurements *(6)*. Compared with sonic methods, where the measured modulus corresponds to the fastest route that a compressional wave can travel through the material, modulus measured in a quasi-static test corresponds to an average modulus of the material between the test machine's jaws *(7)*. This means that in ultrasonic measurements only the stiffest H-bonds will contribute effectively to paper modulus. The way in which these different types of bonds are affected by water will then be reflected by a difference in slope of ln [*E*] vs. *w*. Nissan *(8)* points out that the transit time for a compressional wave will be a function of water content in the amorphous regions and that transit time will increase with increasing water content. This means that increasing water content in the amorphous regions will decrease the ultrasonically measured modulus.

Batten *(9)* discussed several causes for the discrepancies between ultrasonically and mechanically determined moduli and argues that accounting for them may reduce the observed discrepancy to the order of experimental error of the two measurement methods. The causes ,are (a) differences in the stiffness coefficients caused by measurements in two different thermodynamic regimes, (b) the low frequency approximation in ultrasonic measurements, and (c) relaxation phenomena in paper which are more prominent in mechanical measurements. Batten *(9)* argues that the

elastic stiffness coefficients are thermodynamic properties of a material and postulates that ultrasonic methods measure adiabatic stiffness coefficients, whereas quasi-static methods measure stiffness coefficients which are non-adiabatic and related to isothermal stiffness coefficients. Using the continuum approach of classical elasticity theory, Batten *(9)* shows that the adiabatic stiffness coefficients of a paper are slightly greater than the isothermal stiffness coefficients of the same paper. However, this difference cannot account for the differences observed between ultrasonic and quasi-static moduli.

Considering the stiffness matrix of an orthotropic material it is clear that non-principal stiffness coefficients contribute to the principal moduli of paper. However, the low frequency approximation in the ultrasonic measurement of moduli assumes that, for sufficiently low frequencies (<100 kHz), longitudinal waves in the plane of the paper do not induce out-of plane motion, i.e., plane stress analysis is sufficient to account for in-plane elastic properties *(10)*. Batten *(9)* showed that the low frequency assumption in ultrasonic measurements can lead to a consistent overestimate (2-7%, depending on paper orientation) of the in-plane elastic modulus of paper. Paper is a viscoelastic material and any measurement of modulus should account for the viscous component of strain. The modulus obtained in a mechanical test underestimates the "true" elastic modulus because the measurements are not conducted in infinitely short time periods and with infinitely small strains. Only in an infinitely short experiment (allowing no relaxation to occur), or an experiment in which the strain is infinitesimal, the measured modulus approaches the purely elastic value. By accounting for the causes mentioned above the discrepancy between moduli measured by ultrasonic methods and by quasi-static methods can be reduced *(9)*.

An alternate explanation *(11,12)* attributes the difference between ultrasonically and quasistatically measured modulus to moisture dependent relaxation phenomena in cellulosics. For dry cellophane, for example, the difference between the moduli is attributed, largely, to the B-relaxation process. In moist cellophane, however, the difference is due, in part, to the onset of the α–relaxation *(11-13)* which influences modulus measurement at low frequencies; i.e., an increase in moisture content (plasticization) causes a shift of the isothermal modulus-frequency response toward higher frequencies (shorter times). This behavior is consistent with the effects usually observed when plasticizers are added to polymers. This phenomenological explanation accounts also for the increase in the ratio of ultrasonic to quasistatic modulus with increasing moisture content. However, this alternate explanation does not provide for a quantitative prediction. We have chosen the H-bond approach because it more directly relates mechanical properties to the cohesive intermolecular forces that ultimately govern a materials elastic modulus.

The objective of Part 1 of this paper is to explain, using predictions of the theory of hydrogen-bond dominated solids, why moisture has a greater effect in lowering the elastic modulus of paper when measured statically than it does when measured ultrasonically. The hydrogen-bond explanation seems most appropriate of possible alternate explanations because cellulose remains in the glassy state at low and moderate moisture contents and ambient temperatures; the conditions usually encountered in modulus measurements. The elastic moduli of glassy polymers relate directly to intermolecular interactions as measured by cohesive energy density, or, for hydrogen-bond-dominated solids, to the number density of hydrogen bonds *(4,5)*. Testing of the predictions of the H-bond theory and considerations that take paper anisotropy into account are left to Part 2 of this paper *(14)*.

THE H-BOND THEORY

The theory of H-bond dominated solids (hereafter called the H-bond theory) *(2,15-17)* takes a molecular approach to describe the macroscopic deformation behavior of paper. Elasticity is assumed to arise from interatomic potentials and the straining of molecular bonds. In its most simple form, this theory disregards the network structure of paper and postulates that only the number density and bond stiffness of hydrogen bonds contributes to the elastic modulus. The H-bond theory provides a reasonable qualitative and quantitative description of the effects of moisture, temperature, and time on the elastic modulus of paper based on thermodynamical principles. A principal weakness of this theory is that, when compared with structural theories of paper elasticity, it completely ignores the contribution of fiber morphology and fiber distribution to the elastic modulus *(18)*. Recently Nissan and Batten set out to develop the link between molecular and structural theories of paper elasticity, using percolation concepts *(18, 19)*, employing the concept of an invariant modulus *(20)* and considering single-fiber elasticity *(21)*.

The hydrogen-bond theory makes the following assumptions relevant to the present study:

- Paper is a hydrogen-bond dominated solid. This means that the mechanical property, elastic modulus, is primarily governed by the characteristics of the hydrogen bond and only to a minor degree by other types of bonds or by entropy *(17)*.
- Although H-bonds having different bond lengths and different bond energies exist in paper, an average H-bond of an average

potential energy, U, and hence possessed of an average force constant $k_{(R)}$ for stretching the OH-O distance R may be assumed to control the modulus E. This assumption will be examined and modified in the present study.

The H-bond theory for E asserts as its initial assumption, that the elastic modulus of an ideally isotropic paper of a density equal to that of cellulosic crystals is proportional to the cube root of the total number, n_e, of effective bonds per unit volume:

$$E = \langle k_{(R)} \rangle \cdot [1/3 \cdot n_e]^{1/3} \quad (1)$$

$$= \lim R \rightarrow R_0 \{\partial^2 U_{(R)}/\partial R^2\} \cdot [1/3 \cdot n_e]^{1/3} \quad (2)$$

The factor 1/3, multiplying n_e, arises from the fact that an isotropic, randomly oriented network of H-bonds is mathematically equivalent to one with a third of the bonds oriented along each of the three, orthogonal, principal axes. Taking Lipincott and Schroeder's potential function for the H-bond, $U_{(R)}$, and assuming $U_{(R)}$ for H-bonds in paper to average 19.9 kJ/mole, then with an equilibrium H-bond length, R_0 = 0.274 nm, one finds $k_{(R)} = \lim (R - R_0)\, \partial^2 U/\partial R^2$ = 18.4 N/m (17).

The H-bond theory postulates two regimes of bond breaking by water adsorption. In Regime I, from zero moisture content to a critical water content, w_c, one water molecule may break only one H-bond. However, in Regime II, above w_c, one water molecule may break several H-bonds cooperatively. The influence of water on the elastic modulus is accounted for by Eqs. 3 and 4-6. For $O \leq w \leq w_c$ (Regime I), Eq.3 is derived *(2):*

$$\ln[E_{(w)}/E_0]^{I} = -w \quad (3)$$

where E_0 is the modulus in the dry state; w = 0).

$$\ln[E_{(w)}/E_0]^{II} = D - (C.I.) \cdot w \quad (4)$$

In Regime II, for a water content above w_c up to the water content at fiber saturation (FS) $(w_c \leq w < w_{FS})$ the following equations hold *(2):*

$$(C.I.) = (1/3w_c) - 1 \quad (5)$$

$$D = (1/3) - 2w_c \quad (6)$$

Where Cl., the Cooperative Index, is a measure for the cooperative bond breaking effect of water. The cooperative index is a direct measure for the influence of water on elastic modulus. If this value is small, the loss in stiffness with increasing water content is small. If the value is large, the loss in stiffness is large.

It follows for Regime I that:

$$\ln[E_0]^{I} = \ln[E_{(w)}]^{I} + w \quad (7)$$

and for Regime II that:

$$\ln[E_0]^{II} = A - D \quad (8)$$

$$= A - (1/3) + 2w_c \quad (9)$$

where A is the intercept of In[E] vs. w on the ln[E] ordinate with

$$\ln[E_0]^{I} = \ln[E_0]^{II} \quad (10)$$

To render these equations predictive rather than merely descriptive it is postulated that:

$$w_c = w_m \quad (11)$$

Where w_m is the value of w for adsorption of a "monomolecular" layer of water on cellulose, given by the B.E.T. analysis.

When the natural logarithm of modulus values obtained by quasi-static methods, ln[$E_{(w)}$]$_s$, is plotted against w [for many papers reported in the literature] two straight lines, intersecting at a critical water content, w_c, are obtained *(2).* Modulus values at $w > w_c$ taken from the literature and fitted by a straight line, using Eq. 4, yield negative slopes with values ranging from -5.7 up to -8.2, with a mean of -6.7 ± 0.9 *(2).* The mean value of w_c appears to be about 0.04 to 0.05, which agrees with experimental values of w_m of water adsorption in paper. Calculated values of 6.4 for *(C.I.)*$_s$ and 0.24 for D_s, obtained applying the cluster integral concept of water *(17),* agree with the experimentally derived values of 6.7±0.9 and 0.26±0.06, respectively *(2).*

Only a limited number of data have been availabie to date for ultrasonic modulus measurements over an extended region of water content *(3, 6, 22).* Applying the equations of the H-bond theory to these data one finds the slope values in Regime II to lie between -5 to -6 instead of -6 to -7. There is a noted difference in the response of the MD and CD moduli to increasing water content, expressed by a different slope value for MD and CD *(3).* To date, a fundamental, quantitative explanation for these discrepancies is lacking.

THE ISSUE OF [E_0]$_u$ AND [E_0]$_s$

It is postulated that in cellulose at 0% water content the two values of E_0 obtained by ultrasonic and by quasi-static methods reflect two different forms of energy storage and propagation. This hypothesis will be discussed below in the framework of the H-bond theory which postulates that the elastic properties of paper are primarily governed by the effective number density of an average type H-bond. However, there are different types of H-bonds in the crystalline regions of cellulose as primary and secondary hydroxyl groups join to each other or to the oxygen atoms in the glycosidic chains. Furthermore, in the disordered portion, amorphous regions, the distances at which OH- groups approach each other are constrained by other parts of the network and are mostly not at the equilibrium distance R_0 but at longer distances. Hence $U_{(R)}$, and therefore also $k_{(R)}$, is smaller, i.e., less than the maximum which may occur at the shorter R_0,

Thus the network will consist of a wide range of values of $U_{(R)}$, R, $k_{(R)}$ and n_e. For simplicity in the argumentation this wide spectrum will be divided into two classes. Class I comprises crystallites, regions of high order, where $U_{(R)}$ *is* of large negative value and hence $k_{(R)}$ is high. This will include the surfaces of the crystailites where bonds are accessible. Since the crystallites are of the order of 0.35 nm in width, i.e., about 7-8 molecules across, some 44-49% are therefore on the surface and accessible to bonding with other molecules or water. Class II consists of less ordered portions with bonds strained to various degrees. Their energy values and those of $k_{(R)}$ will be lower. Thus, in this model paper and other cellulosics consist of stiff elements (Class I) having high modulus values embedded in a matrix of less ordered elements (Class II) of low modulus values.

When such a system is subjected to a constant, low stress the system will deform with all elements contributing their share to deformation, according to the appropriate rule of mixtures. Whether or not the different elements are in series or in parallel, the average strain will be greater than the strain suffered by the stiffest elements and smaller than the strain suffered by the more compliant disordered elements. Thus, if the overall modulus for the ordered portion is E_{od} and that of the amorphous region is E_{amorph} then the E_s measured by a quasi-static method at 0% water content will be characterized in general by:

$$[E_0]_{amorph} < [E_0]_s < [E_0]_{ord} \quad (12)$$

In ultrasonic measurements, a wave is sent through the paper and its time of travel from the origin to the reception point is measured. The wave of stress will have different velocities in the different elements but the measured time is ideally that of the fastest (not necessarily shortest) path, i.e., the path through the stiffest elements. This is therefore a direct measure of $[E_0]_{ord}$. Thus,

$$[E_0]_u = [E_0]_{ord} > [E_0]_s \quad (13)$$

For real paper, of lower density than that of a cellulosic crystal, Eq. 1 for the elastic modulus should be modified to read

$$E = \langle k_{(R)} \rangle \cdot [(1/3) \cdot n_e]^{1/3} \cdot f(\rho,\gamma) \quad (14)$$

Where the function $f(r,g)$ accounts for the structural and chemical properties of real papers. ρ is the apparent density of paper and γ is an activity coefficient to allow for differences in composition or additives which modify the degree of bonding from that of ideal paper *(19)*. Thus, we get:

$$[E_0]_u = \langle k_{(R)} \rangle_u \cdot \{[(1/3) \cdot n_e]^{1/3}{}_0\}_u \cdot f(\rho,\gamma) \quad (15)$$

$$[E_0]_s = \langle k_{(R)} \rangle_s \cdot \{[(1/3) \cdot n_e]^{1/3}{}_0\}_s \cdot f(\rho,\gamma) \quad (16)$$

To derive a rigorous relationship between Eqs. 15 and 16, it is necessary to know both, the exact distribution of lengths, R, of the H-bonds and the density of the bonds, n_e, in paper. Lacking this knowledge an average value of $\langle k_{(R)} \rangle$ = 18.4 N/m, as applying to both the ordered and the amorphous regions, is adopted. It then can be assumed that all ordered regions have an equivalent density of effective H-bonds, $(n_{equ})_s$, normalized to the average bond stiffness, $\langle k_{(R)} \rangle$. Accordingly, all H-bonds (ordered and amorphous) average to an equivalent bond density of $(I > {}_{nequ})_s$ and one obtains:

$$\{[E_0]_u/[E_0]_s\}^3 = [n_{equ}]_u/[n_{equ}]_s > 1.0 \quad (17)$$

There is no theoretical prediction for how much the ratios in equation *(17)* exceed unity. For a real paper, the actual value depends on the morphology of the fibers, the manufacturing process and the characteristic duration of the modulus measurement in each of the two methods. Thus, in summary, it is postulated that the difference between $[E_0]_u$ and $[E_0]_s$ arises from different types and different densities of effective H-bonds activated in each of the two measurement methods.

THE ISSUE OF *(C.I.)* AND w_c

To have an influence on E_s, a water molecule may interact with any H-bond to which it is accessible. But to affect E_u, it must effectively interact with an H-bond in a more ordered region, as, for example, at the surface of a crystallite and, to achieve a critical water content in the ordered regions, more water is needed than predicted by $(w_c)_s$. For the present discussion it is postulated that the critical water content is proportional to the equivalent H-bond density. The ratio of equivalent H-bond densities, for ultrasonic and quasi-static measurements, is therefore equal to the ratio of critical water contents:

$$\{[E_0]_u/[E_0]_s\}^3 = [w_c]_u/[w_c]_s = [n_{equ}]_u/[n_{equ}]_s \quad (18)$$

This yields, applying Eq. 5:

$$\{[E_0]_u/[E_0]_s\}^3 = [(C.I.)_s + 1]/[(C.I.)_u + 1] \quad (19)$$

Equation 19 postulates that the modulus ratio at 0% water content is predictable from values of the slope of In $[E]$ vs. w in Regime II and *vice versa.*

CONCLUSIONS

The extension of the H-bond theory developed above, postulates that the equivalent number density of effective H-bonds, which is normalized to an average H-bond with an average bond stiffness of $\langle k_R \rangle$ = 18.4 N/m, is higher for ultrasonic measurements than it is for static measurements. This difference in equivalent number densities may be explained by the view that there exist two different forms of energy storage and propagation in cellulose, dependent on the

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Elastic strength, equations, hydrogen bonds, forecasts, measurement, moisture content, paper, solids content, theories, water.

method of modulus measurement. It is demonstrated that the ratio of these equivalent H-bond densities can be predicted ultimately from the ratio of the slopes of ln[E] vs. w of Regime II and therefore from *(C.I.)*. Although the present work focuses on paper, similar analyses should hold for other hydrogen-bond-dominated solids.

Next it is necessary to test the internal consistency of this extension to the theory of hydrogen-bond-dominated solids. It will be necessary to account for paper anisotropy, since the H-bond theory, in the form developed above, holds only for isotropic papers. These tasks will be undertaken in Part 2 of this paper *(14)*. **TJ**

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LITERATURE CITED

1. Weatherwax, R. C. and Caulfield, D. F., *Tappi* 59(8): 85(1976).
2. Nissan, A. H., *Lectures on Fiber Science in Paper*, Pulp and Paper Technology Series, No.4, Joint Textbook Committee of the Paper Industry, TAPPI PRESS, Atlanta, 1977.
3. Baum, G. A., Brennan, D. C., and Habeger, C. C., *Tappi* 64(8): 97(1981).
4. Caulfield, D. F., in *Solid Mechanics Advances in Paper and Related Industries*, Proceedings of NSF Workshop, 1986, (Perkins, R. W., Mark, R. E. and Thorpe, J. L., Eds.), Syracuse University, NY, 1990, p. 50.
5. Nielsen, L. F. and Landel, R. F., *Mechanical Properties of Polymers and Composites*, Marcel Dekker, Inc., NY, 1994, p.19.
6. Caulfield, D. F. and Weatherwax, R. C., in *Fibre–Water Interactions in Paper-Making*, Vol. 2, Technical Division British Paper and Board Industry Federation, London, 1978, p.741.
7. Nissan, A. H., in *Fibre–Water Interactions in Paper-Making*, Vol. 2, , Technical Division British Paper and Board Industry Federation, London, 1978, p. 609.
8. Nissan, A. H., in *Fibre–Water Interactions in Paper-Making*, Vol. 2, Technical Division British Paper and Board Industry Federation, London, 1978, p.710.
9. Batten, G. L., in *Materials Interactions Relevant to the Pulp, Paper, and Wood Industries* (D. F. Caulfield, J. D. Passaretti and S. F. Sobczynski, Eds.), Materials Research Society Symposium Proceedings, Pittsburgh, Vol. 197, 1990, pp. 163–172.
10. Habeger, C. C., Mann, R. W. and Baum, G. A., *Ultrasonics* 17(2): 57(1979).
11. Pankonin, B. and Habeger, C., *J. Polym. Sci., Polym. Phys. Ed.* 26: 339(1988).
12. Berger, B. J., Habeger, C. C. and Pankonin, B. M., *JPPS* 15(5): 170(1989).
13. Bradley, S. A. and Carr, S. H., *J. Polym. Sci., Polym. Phys. Ed.* 14: 111(1976).
14. Zauscher, S., Nissan, A. H. and Caulfield, D. F., submitted *TAPPI J.* (1995).
15. Nissan, A. H., *Trans. Faraday Soc.* 53: 700, 711(1957).
16. Nissan, A. H., Byrd, V. L., Batten, G. L., and Ogden, R. W., *Tappi J.* 68(9): 118(1985).
17. Batten, G. L. and Nissan, A. H., *Tappi J.* 70(9): 119(1987).
18. Nissan, A. H. and Batten, G. L., *Nord. Pulp & Pap. Res. J.*, special issue, August 6 (1987).
19. Batten, G. L. and Nissan, A. H., *Tappi J.* 70(11): 137(1987).
20. Nissan, A. H. and Batten, G. L., *Tappi J.* 70(10): 128(1987).
21. Nissan, A. H. and Batten, G. L., *TAPPI J.*, accepted 1995.
22. Craver, J. K. and Taylor, D. L., *Tappi* 48(3): 142(1965).

NOMENCLATURE

C.I.	= Cooperative Index
I	= superscript, referring to Regime I
II	= superscript, referring to Regime II
ρ	= apparent density of the paper at time of test, kg/m^3
$_0$	= subscript referring to 0% water content
A	= intercept of ln[E] vs. w on the ln[E] ordinate
$_{amorph}$	= subscript referring to the amorphous regions of cellulose
D	= intercept at 0% water content from regression analysis of ln[E] vs. w = in Regime II
E	= modulus of elasticity, N/m^2
$k_{(R)}$	= force constant for stretching the H-bond, N/m
n_e	= total number of effective H-bonds per unit volume, 1/m^3
n_{equ}	= total number of equivalent, effective H-bonds per unit volume, 1/m^3
o_d	= subscript referring to the ordered regions of cellulose
R_0	= H-bond length at equilibrium, m
$_s$	= subscript, pertaining to quasi-static measurements
T	= absolute temperature, K
$_u$	= subscript, pertaining to ultrasonic measurements
$U_{(R)}$	= potential energy of an H-bond, kJ/mole
w	= water content, mass of water per unit mass of paper
w_c	= critical water content
w_m	= water content after adsorption of a monomolecular layer of water