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TENSILE MODULUS OF PAPER WET-STIFFENED BY CROSSLINKING

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Synopsis The mechanism of the wet tensile performance of paper is described in terms of the hydrogen bond theory of paper. Distinctions are made between the action of wet strength agents and the stiffening action of crosslinks. Chemical crosslinks improve the wet stiffness of paper by reducing the moisture sensitivity of the cellulose network to the swelling action of water. Below the fibre saturation point, the effect of water in reducing the tensile modulus of crosslinked paper is quantitatively the same as in uncrosslinked paper. Wet stiffening arises only from the reduction in the fibre saturation point that the crosslinks create. The role of crosslinks as load-carrying elements is not important in wet stiffening. Rather, crosslinks function as swelling restraints to the network, so that a larger fraction of the pre-existing hydrogen bonds function to retain a larger fraction of the paper's dry tensile modulus. In this respect, even crosslinked paper can be considered a hydrogen-bond-dominated solid.

Introduction

THE interaction of cellulose and water is of prime technological concern, not only as the foundation of every step in the manufacture of paper, but also as the cause for many of paper's shortcomings. The major technical obstacle preventing the realisation of the full potential of paper and fibre products in structural applications is the serious effect water has on two desirable engineering properties. Hygroexpansivity, or the dimensional instability of paper on exposure to moisture, discourages engineers who prefer dealing with materials whose dimensions do not change markedly with environment. (They must, of course, deal with thermal expansion.) The second drawback to the consideration of paper as an engineering material is the serious loss in elasticity or stiffness that water causes.

Under the chairmanship of Dr N. K. Bridge

These problems of wet stiffness and dimensional instability are intimately related, and it is believed that the solution to one will automatically resolve the other. Crosslinking appears to be a promising solution to the duel problems of poor dimensional stability and poor stiffness of wet paper. This report is an attempt to provide an explanation of the mechanism by which crosslinks function to improve the stiffness of wet paper.

Background

Definitions

ALTHOUGH the wet strength properties of paper can be greatly improved by several methods, these methods may cause no, or only modest, improvements in wet stiffness. Setterholm(1) has pointed out the confusion that results from thinking of stiffness and strength as synonymous. Similarly wet strength and wet stiffness, although often correlated, should be considered as distinct properties. Wet-strength papers have been defined(2) as papers which have 'extraordinary resistance to rupture or disintegration when saturated with water . . . Normally, a paper loses most of its strength when truly wetted with water. A paper which retains more than 15 per cent of its dry strength when completely wetted with water may properly be called a wet-strength paper.'

Commonly, stiffness is defined(2) as the product of modulus of elasticity and the moment of inertia of the section of the test member. The moment of inertia depends upon the configuration of the test specimen; the modulus of elasticity is the only material property. Therefore, wet-stiff paper can be defined much like wet-strength paper. *Wet-stiff paper is paper which, when truly wetted with water, exhibits an extraordinary resistance to deformation under stress. It is paper which retains over 15 per cent of its dry modulus of elasticity, E, when fully saturated with water.*

Mechanisms of wet tensile performance

THE problems of wet strength and wet stiffness are closely related. Steenberg(3) proposed that a wet-strength agent functions by interacting in some way with the existing interfibrillar bonds, making them less sensitive to the swelling and dissolving action of water.

Stannett(4) has reaffirmed that view indicating that the action of a wet-strength agent is more than that of a waterproof glue; it somehow reduces the interaction between water and the hydrogen-bonded cellulosic network. To understand how the interaction between water and cellulose can be altered, it is first necessary to understand the mechanism of that interaction.

Hydrogen bond theory explanation of tensile modulus

THE mechanism by which water reduces the tensile modulus of paper is

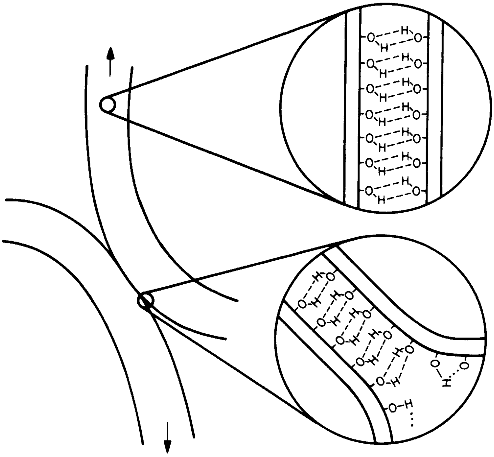

Fig. 1—Schematic of two cellulosic fibrils in contact, showing hydrogen-bonded nature in the interfibre region and within the cell wall

most readily explained in terms of the hydrogen bond theory of paper. This theory, developed by Nissan,(5–8) explains the rheological properties of tensile modulus and creep in terms of the chemical kinetics of the dissociation of hydrogen bonds. This theory has been well tested by its ability to explain, both qualitatively and quantitatively, most of the experimental measurements of paper's tensile properties as affected by moisture.

This elegant hydrogen bond theory can be reviewed in general terms with the aid of some grossly simplified pictures.

Fig. 1 is a schematic of two dry pulp fibres in contact It is clear why paper is considered a hydrogen bond dominated solid.(7) Within the fibre, the stiff cellulose molecules are connected in long chains by strong chemical covalent bonds. But these long chains are held side-by-side by hydrogen bonds that are much weaker than the chemical bonds along the chains. Within the cellulose structure there is little chain entanglement. Between the fibres there are no covalent chemical bonds either. They, too, are held together only by weak hydrogen bonds. The hydrogen bond is so much weaker than the covalent bond that its energy is of the same order of magnitude as the thermal kinetic energy associated with molecules at ordinary room temperature:

Covalent bond energy	340 kJ/mole °K (82 kcal/mole °C)
Hydrogen bond energy	~19 kJ/mole °K (~4·5 kcal/mole °C)
Thermal kinetic energy at R.T.	3·8 kJ/mole °K (0·9 kcal/mole °C)

The fraction of molecules that have thermal energies greater than the energy associated with the hydrogen bond can be estimated by Boltzmann statistics to be about 0·01—that is, the hydrogen bonds in the cellulose system are experiencing interactions with surrounding molecules, 1 per cent of which have energies greater than the hydrogen bond energy. This can only mean that these hydrogen bonds are breaking and forming very quickly at room temperature just as they are presumed to do in water. What holds fibres together, therefore, is not a locked array of hydrogen bonds, but rather a flickering array of bonds. At any one instant, a small fraction of the hydrogen bonds is open.

It has been calculated from the structure of the cellulose molecule that the tensile modulus along the chain of the molecule is about 90 GPa.(9) Setterholm has reported preparing handsheets with a tensile modulus of 26 GPa.(1). But one cellulose chain does not run from one end of a sheet of paper to the other. The question answered by the hydrogen bond theory is, 'How can a large fraction of the stress borne by one cellulose chain in one fibre be transmitted to another cellulose chain in another fibre across a flickering array of very weak hydrogen bonds?'

The answer, of course, is to spread that load over a large area. The rule for making good paper is to increase the area of contacts between fibres. That is why conformable fibres make better papers than do stiff fibres, why beating is an important step in papermaking, why press-drying improves paper strength, etc. The flickering array is effective when spread over a large enough area, because the cellulose chains are stiff and the hydrogen-bonded atom pairs tend not to move even though the hydrogen bonds may flicker. Even if a number of hydrogen bonds open cooperatively(7) while the dry fibre assembly is stressed, the resultant strain can be small because the hydrogen bond array tends to reform quickly with the same atoms paired.

When paper is exposed to moisture or high humidity, the cellulose adsorbs water between fibres and within the cell walls. This water does two things: it separates the cellulose chains from one another, and plasticises them, making them more flexible (Fig. 2). If a load is applied when water is present, the hydrogen bond array still flickers open and closed. But on closing, the array need not re-form with all its original partners paired, because there is competition among sites. The flickering array can re-form with some hydrogen bonds in stress-relaxed configurations, and those unrelaxed in a state of increased strain. The resultant measured modulus will be thereby decreased.

Wet strength and wet stiffness

SUCCESSFUL attempts at improving the wet stiffness and the wet strength of

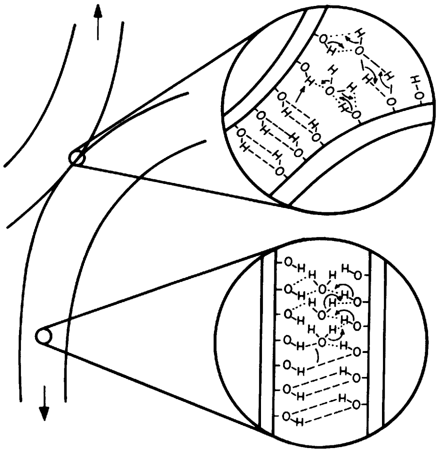

Fig. 2—Two wet cellulose fibrils. Hydrogen-bonded array may flicker more easily into new configuration of bonds, in which some bonds are stress relaxed. A greater strain is experienced by those bonds that do not relax

paper involve protecting the hydrogen bond arrays or augmenting or replacing the flickering arrays of hydrogen bonds with bonds of greater strength.

Most solutions to the problems of wet strength have involved augmenting hydrogen bonds with synthetic resins. The mechanism by which these polymetric materials function as wet-strengthening agents has been reviewed.(4, 10, 11) When these polymeric additives do not enter the cell wall, their reinforcing action occurs only on the flickering arrays in the interfibre regions. In these cases the mechanism of failure tends to be failure within the wet cell wall.(10) Whereas wet strength can be improved to 40 or 50 per cent of the dry tensile strength, there may be little or no improvement in the wet tensile modulus.(10, 12) This action of a nonpenetrating wet-strengthening resin is understandable in terms of the hydrogen bond theory. Consider stressing a wet paper, bonded only in the interfibre regions with covalent bonds (spot-welded, so to say), to transfer a load from one fibre to another. Because the cellulose chains inside the wet cell walls, behind the bonded interface, are held together by hydrogen bonds, hydrogen bond arrays inside the stressed cell wall can still flicker into configurations where some bonds are relaxed and fewer bonds experience greater strains. The network thereby exhibits a lower tensile modulus. Paper, resin-treated at the interfaces between fibres only, although wet strengthened, still exhibits a low modulus when wet.

In terms of the hydrogen bond theory, intrafibre bonding (excluding hydrogen bonds within crystallites) and interfibre bonding are identical, because the hydrogen bonds are identical in respect to their sensitivity to water and differ only in concentration. The morphology of the network determines how the tensile stress is distributed among the different hydrogen bonds. But the mechanism by which a tensile stress is transmitted is the same in principle, whether the ultimate failure occurs in the interfibre region or within the cell wall.

The tensile modulus, according to the hydrogen bond theory, is proportional to the cube root of the number of effective hydrogen bonds per unit volume. Because most of these hydrogen bonds are within the cell wall, protecting only interfibre regions can have little effect in wet stiffening. Augmenting or protecting hydrogen bonds within the cell wall is also needed. This can be accomplished by a number of methods: Polymers small enough to enter the cell walls may be employed,(13) monomers may be polymerised within the cell wall,(14) the cell walls may be impregnated with waxes or other moisture insensitive hydrocarbons,(15) or the cellulose itself may be crosslinked.(16)

Crosslinking

Of all the methods known for improving wet stiffness, crosslinking is the most effective—that is, the greatest improvements in wet stiffness are possible with the smallest chemical addition. Several reviews have been prepared on the subject of crosslinking of cellulose.(16–18) True chemical crosslinking involves the formation of new covalent bonds between cellulose chains. Such a covalent bond can arise from the reaction of a bifunctional molecule and two cellulose chains, or from the direct bonding between two cellulose chains (autocrosslinking). Molecules of primary interest capable of reacting bifunctionally that have been used for crosslinking paper include aldehydes (primarily formaldehyde), glyoxal, epoxides, and diisocyanates. Many other reagents have been investigated as crosslinking agents for cotton fabrics,(18) and the chemistry of these reactions discussed.

Investigations of the effect of crosslinking on the properties of paper were pioneered by A. J. Stamm and co-workers.(19–21) That research studied in detail the effects of both formaldehyde crosslinking and heat treatment (autocrosslinking) on the mechanical properties and the swelling properties of paper. In all cases in which the wet stiffness of the material was improved greatly, there was observed a similarly marked improvement in dimensional stability.

The suggestion that heat treatment causes autocrosslinking in cellulose was proposed by Back and Klinga.(22) Back and co-workers(23) reported increases in both wet modulus and wet strength on heat treatment (autocrosslinking) that also reduced swelling. Autocrosslinking by heat treatment is still being actively investigated as a potential means for producing wet-stiff corrugated board,(24) a goal of great interest to the corrugated board industry.

Much of the research on crosslinking of cotton fabrics by formaldehyde indicated that the amount of water and the swollen conditions of the cellulose network greatly influenced the resultant properties.(25) A detailed investigation(26) was made of the changes in the colloidal structure of paper upon crosslinking with formaldehyde. These structural changes were related to the wet stiffness of the paper. A number of findings resulted that seem consistent with the hydrogen bond theory of tensile modulus. Dimensional stabilisation was determined by measuring both linear swelling and fibre saturation points of crosslinked papers. The state of swelling at the time of crosslinking determined the degree of stabilisation. It was found that there is an unmistakable linear correlation between the logarithm of the wet tensile modulus and the fibre saturation points of the crosslinked papers. It was clear that those crosslinks effective in improving the wet modulus of paper are the same crosslinks that restrain the swelling and restrict the entry of water into the structure.

A most important connection was also revealed between the wet modulus and the colloidal surface structure of crosslinked papers.(26) The surface areas and pore structures of several swollen crosslinked papers were determined by N_2 sorption. The modulus ratios (ratio of wet tensile modulus to modulus at 50 per cent RH) of the crosslinked papers decreased with increasing specific swollen surface in a way predicted by Nissan's hydrogen bond theory. According to this theory, the modulus of paper is proportional to the cube root of the number of effective hydrogen bonds per unit volume. If the hydrogen bond sites are uniformly distributed on the bonded cellulosic surfaces, then, as these surfaces are separated by the swelling action of water, fewer hydrogen bonds are functional. The tensile modulus should vary inversely as the cube root of the swollen specific surface. This relationship was verified.(26)

It seems, then, to retain in wet paper the largest possible fraction of its dry modulus, it is necessary to crosslink cellulose in the collapsed state so that the maximum number of hydrogen bonds can function. But in the fully collapsed state, the interior cellulosic surfaces are inaccessible to even the smallest crosslinking molecule. Only if the cellulose is first swollen are internal surfaces made accessible. But crosslinking in the swollen state results in fewer functional hydrogen bonds. This problem can be circumvented by crosslinking the cellulosic structure during a dehydration process.(27) When formaldehyde vapour and SO_2 are introduced into moist paper and the paper is then dried in an atmosphere in which a high partial vapour pressure of formaldehyde is maintained, crosslinking results throughout the cellulosic structure. Using this SOFORM method crosslinks are introduced both in the interfibre regions and within the collapsed cell wall and result in papers with dimensional stabilisations that can exceed 90 per cent. These most highly stabilised papers have wet tensile moduli that exceed 90 per cent of the dry tensile moduli.

For the crosslinked papers investigated, the logarithm of the tensile modulus ratio decreased linearly with the fibre saturation point of the paper. The slope of this loss in natural logarithm of modulus ratio with fibre saturation point was equal to the fractional loss in modulus that *uncrosslinked* paper exhibited with added moisture.

These results led to the proposal that the mechanism by which crosslinks function to impart high wet tensile modulus to paper results from the swelling restraints that the crosslinks afford. The action of crosslinks as load-bearing elements is not an overriding factor. Rather, the restraints that the crosslinks afford protect the pre-existing hydrogen bonds from competition with and disruption by water. As a result, it was proposed that the number of hydrogen bonds protected by the covalent crosslinks should be considered the determining factor in retention of wet stiffness.(27)

Effect of moisture on E for crosslinked paper

It is desirable now to evaluate in quantitative terms the effect that water has in reducing the tensile modulus of crosslinked paper both above and below the fibre saturation point (FSP), and to compare this with the effect that water has on the tensile modulus of uncrosslinked paper.

Static methods for measuring the effect of moisture on tensile modulus are convenient only when the moisture can be held constant by equilibrating the sample and surroundings at set relative humidities. The convenient range of working relative humidities is between 30 and 90 per cent RH. This results in a limited range of equilibrium moisture contents that can be investigated. Sonic pulse propagation measurements, which can be made quickly, can be made under non-equilibrium conditions in which the moisture content does not change much. This enables the effect of moisture on tensile modulus to be measured over a very wide range of moisture contents from dry to soaking wet.

Experimental

Materials and methods

The paper used in this investigation was a 186-g/m^2 (38 pounds) kraft linerboard prepared from unbleached southern pine on the Forest Products Laboratory paper machine (Run No. 6981). The fibre saturation point was measured by the polymer exclusion method.(28) The moisture content at the fibre saturation point for this uncrosslinked paper was 78·4 per cent of its dry weight.

Sheets of the same stock were crosslinked using the SOFORM method at a temperature of 126° C for a period of 5 minutes using the reactor described previously.(27) The doubly bound formaldehyde content was 1·6 per cent, measured by the chromotropic acid method.(29) The fibre saturation point of the crosslinked paper 17·4 per cent.

The group velocity of compressional wave propagation was measured in both machine and cross-machine directions in crosslinked and uncrosslinked papers at a frequency of about 5 kHz, using the multipoint method and the planar mount on the H. M. Morgan Co. Dynamic Modulus Tester PPM-5R. Measurements of sonic pulse velocity were obtained over a wide range of moisture contents. The moisture contents in the lower range were obtained by equilibrating the paper in atmospheres of controlled relative humidity. Moisture contents corresponding to relative humidities greater than 90 per cent RH were obtained by slowly drying saturated samples between damp sheets of paper towelling to selected moisture contents and then sealing tightly in aluminium envelopes and equilibrating for several days to remove drying gradients. All moisture contents were obtained on a descending isotherm. Moisture contents were determined by weighing specimens before and after sonic measurements were made and then drying to oven dryness. Density values were obtained from measurements of weight and volume at the time the sonic measurements were made. Thickness measurements were generally obtained with the Forest Products Laboratory's thickness tester.(30) Uncrosslinked samples at high moisture content, which were too soft and too fragile to be measured on the thickness tester, were measured by a mercury displacement procedure.

Results

THE sonic velocity measurements in the machine and cross-machine directions are presented in Figs. 3 and 4. The natural logarithm of the square of the compressional wave velocities is plotted against the moisture content of the samples. Each plot shows two linear segments which intersect at about the fibre saturation point of the paper. The equations of the regression lines are given in Table 1 with the moisture content at the intersection of the lines. The means of the intersection of the lines, 74·4 and 19·2 per cent, do not differ significantly from the corresponding fibre saturation points measured by the polymer exclusion method on the untreated and crosslinked kraft paper, 78·4 and 17·4 per cent, respectively.

Taylor and Craver(31) have reviewed in detail the theory of elastic behaviour of anisotropic paper. They have shown for anisotropic paper how Young's modulus, E, is related to sonic velocities. In the machine direction, Young's modulus is given by

$$E_{11} = \rho(C_{11}^2 - \nu_{12}C_{12}^2) \quad . \quad . \quad . \quad . \quad (1)$$

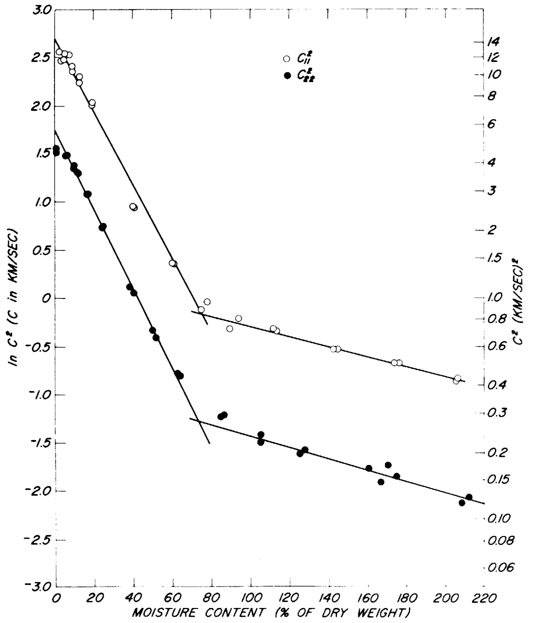

Fig. 3—Dependence of sonic velocity on moisture for uncrosslinked kraft linerboard in the machine and cross-machine direction

TABLE 1—CONSTANTS OF THE REGRESSION EQUATION,* $\ln C^2 = A + Bm$, FOR UNTREATED AND FOR CROSSLINKED KRAFT LINERBOARD

Paper	*Direction of measurement*	*Moisture content range*	*A*	*B*	*Moisture content at the intercept of the line segments*	
					(%)	(Mean %)
Untreated kraft linerboard	Machine	< FSP	2·691	−0·0379	75·3	74·4
		> FSP	0·231	−0·00526		
	Cross-machine	< FSP	1·736	−0·0411	73·4	
		> FSP	−0·846	−0·00590		
Crosslinked kraft linerboard	Machine	< FSP	2·649	−0·0403	19·4	19·2
		> FSP	1·980	−0·00573		
	Cross-machine	< FSP	1·716	−0·0416	18·9	
		> FSP	1·050	−0·00629		

* *C* is sonic velocity in km/sec; *m* is moisture content as per cent of dry weight.

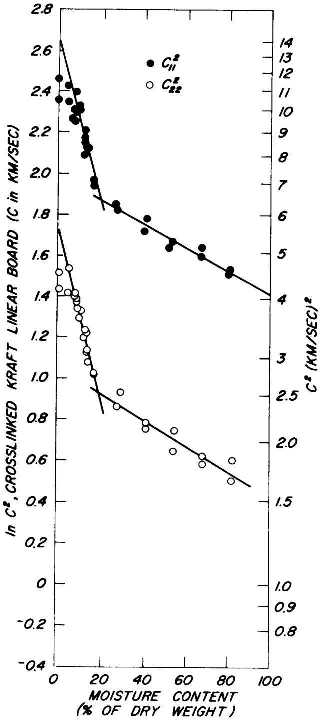

Fig. 4—Dependence of sonic velocity on moisture for crosslinked kraft linerboard in machine and cross-machine direction

and in the cross-machine direction

$$E_{22} = \rho(C_{22}{}^2 - \nu_{21}C_{12}{}^2), \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where ρ	is density,
C_{11} and C_{22}	are sonic velocities of a compressional wave in the machine and cross-machine direction, respectively,
ν_{12} and ν_{21}	are corresponding Poisson's ratios, and
C_{12}	is velocity of a shear wave generated in the plane of the sheet by a compressional wave in either the machine or cross-machine direction.

C_{12} is not measurable directly but may be calculated from equations given by Taylor and Craver.

Taylor and Craver have also shown that the contribution of the second term on the right hand side of either equation (*1*) or (*2*) amounts to about 10 per cent of the first term. If the second terms are ignored, a modulus almost equal to Young's modulus results:

$$(E_{11})_S = \rho C_{11}^2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$(E_{22})_S = \rho C_{22}^2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This new modulus, E_S, called the sonic tensile modulus, adequately represents the elastic tensile modulus.

The sonic tensile modulus at each moisture content was obtained from the sonic velocity. The modulus ratio was obtained by dividing the modulus at

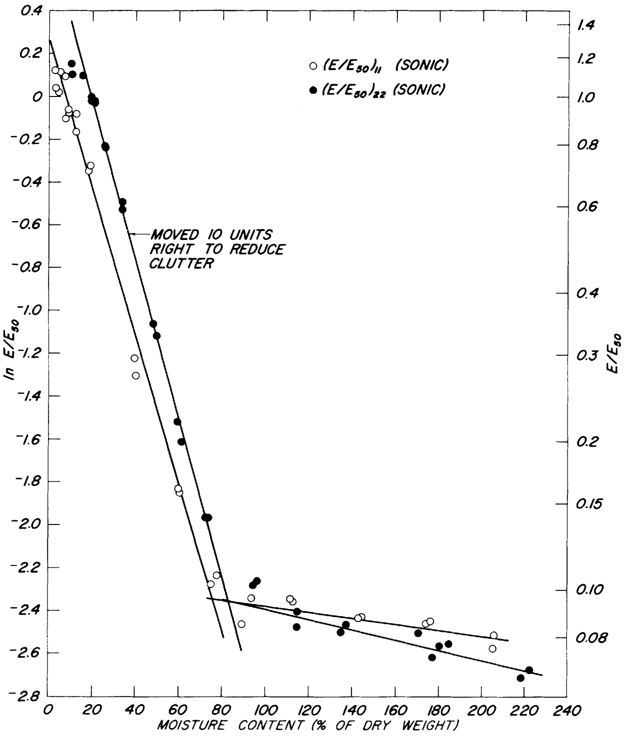

Fig. 5—Dependence of sonic modulus on moisture for uncrosslinked kraft linerboard in machine and cross-machine direction

each moisture content by the modulus that the same paper has at 50 per cent RH. Figs. 5 and 6 are plots of the natural logarithm of the modulus ratios ($ln(E/E_{50})_S$) *versus* moisture content. Again, the results are straight lines intersecting at the fibre saturation point. The constants of the regression lines are given in Table 2. In this case, the intersection of the lines has mean values of 74·4 and 18·7 for the uncrosslinked and crosslinked linerboards, respectively.

It should be recalled that the original concept of fibre saturation point arose from an explanation of the effects of moisture on the properties of

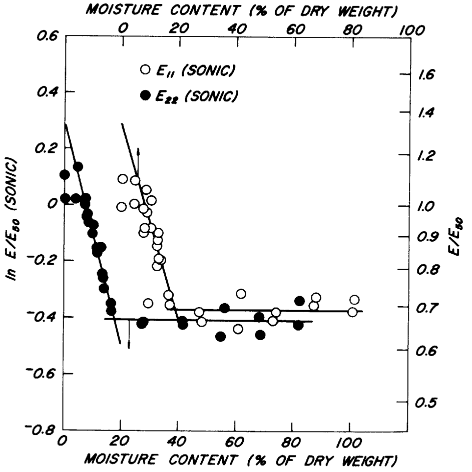

Fig. 6—Dependence of sonic modulus on moisture for crosslinked kraft linerboard in machine and cross-machine direction

TABLE 2—CONSTANTS OF THE REGRESSION EQUATION, $\ln(E/E_{50})_S = A+Bm$, FOR UNTREATED AND FOR CROSSLINKED KRAFT LINERBOARD

Paper	*Direction of measurement*	*Moisture content range*	*A*	*B*	*Moisture content at the intercept of the line segments* (%)	(Mean %)
Untreated kraft linerboard	Machine	<FSP	0·264	−0·0344	75·8	74·4
		>FSP	−2·242	−0·00136		
	Cross-machine	<FSP	0·350	−0·0370	73·0	
		>FSP	−2·179	−0·00239		
Crosslinked kraft linerboard	Machine	<FSP	0·2879	−0·0341	19·3	18·7
		>FSP	−0·3704	0		
	Cross-machine	<FSP	0·3019	−0·0393	18·1	
		>FSP	−0·4071	0		

wood.(32) When the logarithms of the strength properties of wood were plotted against moisture content, two intersecting straight lines were obtained. The intersection point of the lines corresponded to a moisture content obtained by extrapolating adsorption isotherms to unit relative vapor pressure.

The most important result of crosslinking is the great reduction in the fibre saturation point of the paper (Figs. 3–6). Crosslinked paper gains only a fraction of the moisture that uncrosslinked paper regains at the same relative humidity. In the wet state, it is the great reduction in fibre saturation point on crosslinking that is responsible for the large retention of tensile modulus of the paper. It is also clear from Tables 1 and 2 that crosslinking does not change significantly the slopes of the line segments for compressional wave velocity, or tensile modulus either above or below the fibre saturation point.

The fractional reduction in the tensile modulus of crosslinked paper at any moisture content below its fibre saturation point equals the fractional loss in tensile modulus that the uncrosslinked paper exhibits at the same moisture content.

If the wet stiffness were due to a direct load-bearing contribution of the crosslink bonds, a unit increment of water to the crosslinked paper would cause a smaller drop in tensile modulus than it would in uncrosslinked paper. However, the slope of the line for crosslinked paper below its fibre saturation point is essentially the same as the initial slope of the uncrosslinked paper. Therefore, the direct load-bearing contribution of crosslinks to wet stiffening must be negligible.

The average slope of the lines in Figs. 5 and 6 below the fibre saturation points are approximately one-half of the value of slopes of ln E vs. moisture content reported by others at low rates of loading.(7) They are not, however, in disagreement with data obtained sonically by other investigators on different cellulosic materials (Table 3, (33–37)). The differences between slopes obtained statically and dynamically may be due to the great differences in the rates of loading and the relaxation processes involved. They may also be due to the different averages obtained by both methods. A static method measures the average modulus of the material between the tester's jaws. The sonic method measures a modulus that corresponds to the fastest route that a compressional wave can travel through the material.

The mechanism by which crosslinked paper, when wet, retains a high proportion of its dry tensile modulus seems clearly to result only from the reduction in swelling that the crosslinks provide and not from a load-bearing contribution of the added covalent bonds. The crosslinks limit the access of water into the cellulose so that the flickering arrays of hydrogen bonds responsible for the dry tensile modulus of paper can still function. This mechan-

TABLE 3—EFFECT OF MOISTURE ON DYNAMIC AND ON STATIC MODULI OF ELASTICITY OF CELLULOSIC MATERIALS CALCULATED FROM THE DATA OF OTHER INVESTIGATORS

	Slope of ln E vs. m		
Material	*Dynamic*	*Static*	*Investigator*
Cotton	0·055	0·080	Andersen(33)*
Rayon staple fibre	0·020	0·060	
Rayon	0·018	0·082	
Cellophane†	0·038		Bradley and Carr(34)
Cellophane†	0·035		
Cellophane‡	0·024		
FORTISAN	0·045		de Vries(35)
Southern pine kraft pulps	0·033		Chatterjee(36)*
Mean	0·033	0·074	

* Combined with water adsorption data of Stamm(37) for similar materials.
† Machine direction.
‡ Cross-machine direction.

ism of protection of pre-existing hydrogen bonds is probably the mechanism by which all other wet-stiffening treatments function. Penetrating resins, *in situ* polymerisations, and non-reactive bulking agents, to the extent that they function as wet-stiffening agents, probably function by preventing access of water into hydrogen-bonded regions within the cellulose.

When large quantities of these additives are used to improve stiffness, the material should no longer be considered paper but a paper composite. The properties of a composite are determined by an averaging of the properties of the individual components. Several types of averages have been proposed.(38) If water greatly reduces the tensile modulus of one component, water's effect on the modulus of the composite can be reduced by greatly increasing the proportion of the moisture-insensitive component. These should not properly be considered wet-stiffening agents. If, however, the resin functions to reduce the natural moisture sensitivity of the cellulosic component, it functions as a true wet-stiffening agent. Crosslinking is clearly the most effective wet-stiffening agent because it directly reduces the inherent moisture sensitivity of cellulose.

Crosslink embrittlement

Crosslinking improves the stiffness of paper, but unfortunately has detrimental effects upon another desirable property of paper. Paper is severely embrittled by crosslinking and cannot be folded if it is substantially wet stiffened.(26) Although this embrittlement has sometimes been explained to be a result of hydrolysis due to the acid conditions usually required for crosslinking,(39) it seems more likely to stem from the same mechanism by which crosslinks improve wet tensile modulus. The improvement in wet stiffness occurs with a necessary reduction in elongation to break. As a fold is created in ordinary paper, the severe local stresses are relaxed by a series of flickering rearrangements of hydrogen bonds. Fibres and fibrils may slip past one other to be rebonded in their new positions. Crosslinks in paper prevent relative movement between linked chains. As a fold is applied, the flickering hydrogen bonds do not relieve the severe local stress so that strains increase until the covalent bonds rupture, resulting in fibre failure.

Conclusion

The mechanism proposed by which crosslinks improve the modulus of wet paper is quite different from the mechanism by which crosslinks improve the tensile modulus of elastomers.(40) That there must be a difference in mechanisms is clear because crosslinks in paper do not produce any marked improvement in dry tensile modulus. The crosslinks in paper do not function by making a larger fraction of the cellulosic chains load bearing. The introduction of crosslinks in cellulose limits the swelling of the bonded network and protects the pre-existing hydrogen bonds from the disrupting and dissolving action of water. The retention of the tensile modulus of wet paper is dependent upon the number of effective hydrogen bonds remaining. In this respect, even crosslinked paper should be considered a hydrogen-bond-dominated solid.

References

1. Setterholm, V. C., 'Factors that affect the stiffness of paper'. In *The Fundamental Properties of Paper Related to its Uses*, Ed. F. Bolam (Technical Division of the British Paper & Board Industry Federation, London, 1976), 253–268
2. American Pulp and Paper Association, *The dictionary of paper, 1965*, American Pulp and Paper Association, N.Y.
3. Steenberg, B., *Svensk Papperstidn.*, 1946, **49** (14), 311–323
4. Stannett, V. T., 'Wet strength development in paper'. In *Surfaces and Coatings Related to Paper and Wood*, p. 269–299. R. H. Marchessault and C. Skaar, Eds., 1967, Syracuse University Press, Syracuse, N.Y.
5. Nissan, A. H., *Trans. Faraday Soc.*, 1957, **53**, 700–721
6. Nissan, A. H., 'The significance of hydrogen bonding at the surfaces of cellulose network structure'. In *Surfaces and Coatings Related to Paper and Wood*, p. 221–265. R. H. Marchessault and C. Skaar, Eds., 1967, Syracuse University Press, Syracuse, N.Y.
7. Nissan, A. H., *Macromolecules*, 1976, **9** (5), 840–850
8. Nissan, A. H., 'The cooperative rupture of bonds in hydrogen bond dominated solids on adsorbing water'. (This conference, in press)

9. Meredith, R., *The Mechanical Properties of Textile Fibres*, 1956, North Holland Publishing Co., N.Y.
10. Taylor, D. L., *Tappi*, 1968, **51** (9), 410–413
11. Weidner, J. P., 'Wet Strength in Paper and Paperboard'. TAPPI Monograph No. 29, 1965, Technical Association of the Pulp and Paper Industry, Atlanta, Ga.
12. Jenkinson, P. M., 'Effect of core thickness and moisture content on mechanical properties of two resin treated paper honeycomb cores'. U.S. Forestry Serv. Res. Pap. FPL 35, 1965, Forest Products Laboratory, Madison, Wis.
13. Becker, J. J., Hoffman, G. R. and Swanson, J. W., *Tappi*, 1961, **44** (4), 296–299
14. Schwab, E., Stannett, V., Rakowitz, D. H. and Magrane, J. K., *Tappi*, 1962, **45** (5), 390–400
15. Olsson, L. A., 'Improving moisture resistance of paper'. FEFCO Bulletin No. 87, 1974, Federation Européenne des Fabriquants du Carton Ondulé, Paris
16. Ward, D., Jr., Chemical modification of paper fibres, 1973, Marcel Dekker, Inc., N.Y.
17. Tesoro, G. D. and Willard, J. J., 'Crosslinked cellulose'. In *Cellulose and Cellulose Derivatives.* Volume V, Part V, pp. 835–875, Eds., N. M. Bikales and L. Segal, Wiley Interscience, N.Y.
18. Petersen, H., 'Crosslinking chemicals and the chemical principles of resin furnishing of cotton'. In *Chemical After-Treatments of Textiles.* Ch. 5A, pp. 135–234, Eds., H. Mark, N. S. Wooding and S. Atlas, 1971, John Wiley & Sons, Inc., N.Y.
19. Stamm, A. J. and Cohen, W. E., *Australian Pulp and Paper Ind. Tech. Assoc. Proc.*, 1956, **10**, 346–366
20. Stamm, A. J., *Tappi*, 1959, **42** (1), 44–50
21. Cohen, W. E., Stamm, A. J. and Fahey, D. J., *Tappi*, 1959, **42** (12), 934–940
22. Back, E. L. and Klinga, L. O., *Svensk Papperstidn.*, 1963, **66** (19), 745–753
23. Back, E. L., Htun, M. T., Jackson, M. and Johanson, F., *Tappi*, 1967, **50** **(11)**, 542–547
24. Anderson, R., *Svensk Paperstidn.*, 1976, **79** (7), 212–214
25. Rowland, S. P., Cousins, E. R. and Mitcham, D., *J. Appl. Polymer Sci.*, 1965, **9** (12), 3869
26. Caulfield, D. F. and Weatherwax, R. C., *Tappi*, 1976, **59** (7), 114–118
27. Weatherwax, R. C. and Caulfield, D. F., *Tappi*, 1976, **59** (8), 85–87
28. Feist, W. C. and Tarkow, H., *For. Prod. J.*, 1967, **17** (10), 65
29. Moore, W. E. and Johnson, D. B., 'Laboratory procedures for chemical analysis of wood and wood products', 1967, For. Prod. Lab. Madison, Wis.
30. Setterholm, V. C., *Tappi*, 1974, **57** (3), 164
31. Taylor, D. L. and Craver, J. K., 'Anisotropic elasticity of paper from sonic velocity measurements'. In *Consolidation of the Paper Web*, Vol. 2, Ed., F. Bolam (Technical Section of British Paper and Board Industry Federation, London, 1966) 852–872

32. Tiemann, H., 'Effect of moisture upon the strength and stiffness of wood', 1906, USDA For. Serv. Bull. No. 70
33. Anderson, F., 'Studies of the mechanical properties of cellulose fibres in relation to internal structure', 1950, Akademie fur de Tehueske Viden skuber, A.T.S., No. 3, Copenhagen
34. Bradley, S. A. and Carr, S. H., *J. Poly. Sci.*, 1976, Poly. Phs. Ed., **14**, 111–124
35. de Vries, quoted by R. Meredith, *Mechanical Properties of Textile Fibres*, 1956, North Holland Publishing Co., N.Y., 119
36. Chatterjee, P. K., *Tappi*, 1969, **52** (4), 599–704
37. Stamm, A. J., *Wood and Cellulose Science*, 1964, Ronald Press Co., N.Y., 156
38. Nielsen, L. E., *Mechanical Properties of Polymers and Composites*, 1974, Mercel Dekker, Inc., N.Y.
39. Cohen, W. E., *Appita*, 1967, **20** (3), 95–103
40. Treloar, L. R. G., *The Physics of Rubber Elasticity*, 2nd ed., 1958, Oxford Univ. Press, London

Transcription of Discussion

Discussion

Dr. E. Back—Prepared discussion contribution

Dr Caulfield, let me add a few results on auto-crosslinking of paper products, which could modify some of your conclusions, especially in respect to the difference in cross-linking of cellulose as compared to other polymers.

Auto-crosslinking in hot air is supposed to produce very short crosslinks. The modulus of elasticity in the dry state can be considerably increased. This is illustrated in Fig. 1(1) for heat treated bleached kraft liner evaluating the modulus of elasticity with sonic pulse technique. The increase in modulus of elasticity is significant over the range of temperature evaluated.

Fig. 2 illustrates the increase in bonding strength as evaluated by Derek Page's bonding index due to such auto-crosslinking, here achieved by a

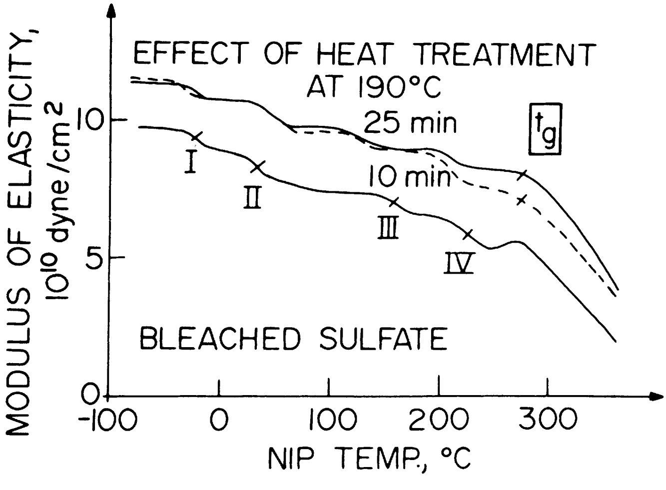

Fig. 1—Modulus of elasticity in the dry (water free) state of untreated and auto-crosslinked paper of bleached kraft as a function of uncorrected temperatures (1)

Under the chairmanship of Dr N. K. Bridge

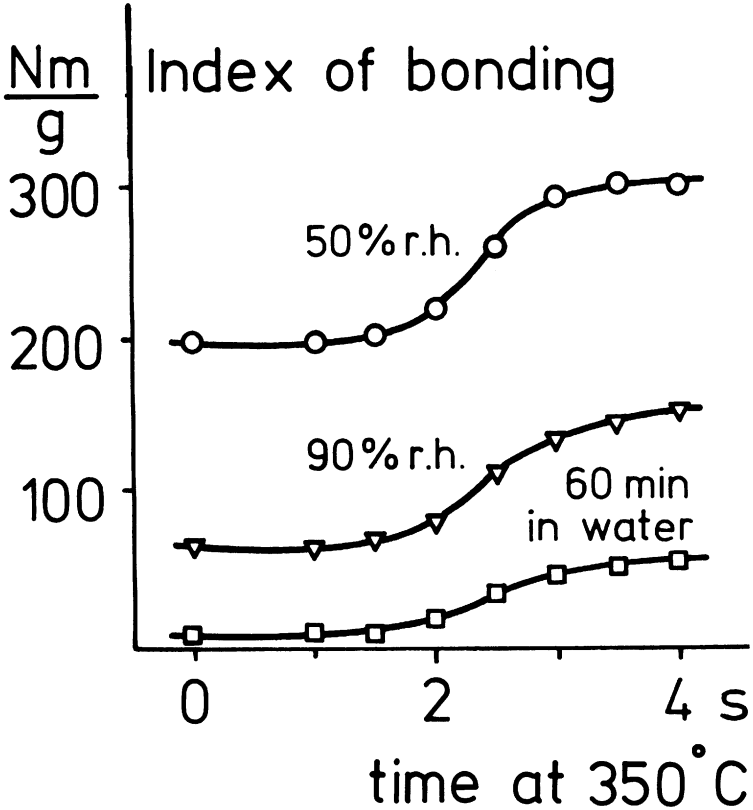

Fig. 2—The Page bonding index of unbleached kraft paper in the moist and wet state as a function of heating period at 350° C employed to cause auto-crosslinking. Data by E. Stenberg (2)

more rapid heat-treatment at a higher temperature. These data are from a paper of my earlier co-worker Ebbe Stenberg.(2) As is seen, the increase in bonding index is considerable also in the dry state. On a relative basis, on the other hand, the increase is much larger in the wet state. Data refer to kraft liner.

It is evident that due to the structural arrangement of bonding areas in the paper and within the fibres, the auto-crosslinking will especially increase the *z*-direction strength. This is illustrated in Fig. 3, referring to hardboard of density 1 000 kg/m^3 with heat treatment carried out during hours in the temperature range of 170 to 210° C, which temperatures are commercially

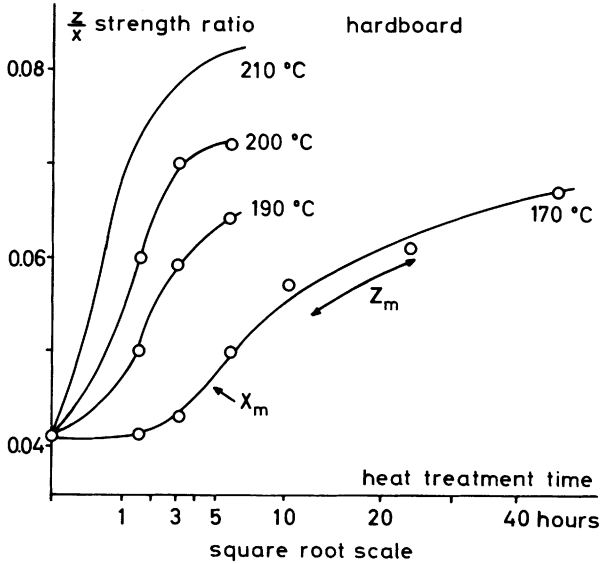

Fig. 3—The strength ratio in the z- to x-direction (perpendicular to sheet relative machine direction) for hardboard of a thermo-mechanical pulp without a resin binder. The strength ratio is given versus the heat treatment time at a few commercially used temperatures (3)

employed for such boards. In the lower curve is indicated by arrows the time period at which the tensile strength in the direction of the board (the x-direction strength) and the z-direction strength respectively, achieve a maximum.

Apparently, the ratio of z- to x-direction strength can be doubled by such a heat treatment in the dry state.

This pronounced increase in z-direction bonding and cross-linking also is the main cause for embrittlement of paper and board in the dry state occurring in such a treatment.

(*Comment at the symposium*) Have you in your studies examined the swollen and non-swollen polymers of other kinds which are cross-linked and non-cross-linked? If so, what does the logarithmic plot of E against adsorbed swelling agent look like? Secondly, I would say that cross-linking in cellulose is similar to cross-linking in other polymers with one exception. That is that hydrogen bonds have a high energy compared to the covalent bonds; so that initially the addition of covalent bonds across the polymers will not as easily be observed, that is, not as easily as it would be observed with polymers that do not have hydrogen bonding. Also the length of the cross-link will effect considerably the amount of strength and swelling properties achieved.

Caulfield I agree with you that in some respects cross-linking in cellulose is like cross-linking in other polymers. I tried to show that cross-linking in cellulose is like cross-linking in other crystalline or polymeric materials—materials below their glass transition temperatures. Here, cross-linking typically is not effective in improving tensile modulus. And crosslinks do not improve markedly the modulus of dry paper. You made a point about embrittlement. This is of practical concern in the property of fold where restraints between two adjacent polymer molecules are more important than in a typical stress test. We have not investigated cross-linking in other polymer systems and the effect of water on the cross-linked system. We are presently investigating polymer addition to paper for the purpose of wet-stiffening and it seems in that case too that polymer treatments that are effective in wet stiffening are also the ones which are effective in restraining the access of water into the cellulose system.

Dr N. K. Bridge Dr Back, have you published those autocrosslinking results elsewhere?

Back Some have been recently published, some several years ago.

Caulfield Dr Back, how big is the increase in dry modulus in your autocrosslinked samples?

Back Up to 50 per cent.

Caulfield I find it difficult to explain the large difference between your results and ours. Our paper was cross-linked to the extent of a formaldehyde content of 1·6 per cent by a very gentle method which consisted of heating at 120° C in the formaldehyde/SO_2 atmospheres for only six minutes. Your autocrosslinks are exposed to higher temperatures and much longer lengths of time. There must be considerable chemical changes going on.

Dr H. Corte Just a point of clarification. I am not opposed to the concept of hydrogen bonding in paper as Dr Caulfield said at one point. On the contrary, to the best of my knowledge I was the first to prove that the mechanical strength of paper is derived from hydrogen bonds developed between the fibres; not by a theoretical concept but by experimentation. We also proved that between 0·5 and 2 per cent of all hydroxyl groups present in the cellulose are additionally bonded between the fibres to form hydrogen bonds in the drying stages of the papermaking process, and that the average energy of these hydrogen bonds is 4·5 kilocalories per mole OH. What I am opposed to is the generalisation to consider paper as a three-dimensional continuum of hydrogen bonds without regard to its discontinuous fibrous structure.

Caulfield I apologise if I misquoted you.

Dr D. H. Page I would like to second what Dr Corte said there. I published a paper in Tappi in 1963 in which I said that we must have the freedom to accept that hydrogen bonds are important in paper without accepting the theories of Dr Nissan on the subject. I would like to congratulate you, Dr Caulfield, on your interpretation. Could I ask you a question about your Figure 3? There are two slopes on this graph, an initial slope at low moisture content and then a further gradual decrease in the sonic velocity at high moisture content. I suspect this second slope corresponds to a situation where the stress is being borne not by the water but by the cellulose component whereas the mass is being contributed to by both the cellulose and the water. In other words as we add more water, the sonic wave will travel more slowly, simply because of the larger mass.

Caulfield I think you are probably right about that. We have recently found better agreement with a line of zero slope above the fibre saturation point when we use wet volume and dry weight.