

Prepared contribution

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THE authors' work with high frequency offers an interesting extension of the work of Kurath to which they refer. Kurath found G' increasing by a factor of about 2.5 as test frequency increased about 2.5 orders of magnitude. (5–1 500 cps). Now, in Fig. 11, we have resistance R^2 , closely related to G' , increasing by up to a factor of 4 as frequency increases 4 orders of magnitude. The obvious relationship between G' and frequency may possibly extend to lower shear rates as well, giving us a crude but ready rule of thumb. If one can think of paper as a network of jointed rods so that *any* paper deformation is a shearing of joints, then the utility of such a relationship for shear would be considerable.

It is not clear to me whether we have here seen measured a property of cellulose or a property of the entire wet paper sheet. At megacycle frequencies, we know we sense only molecular properties, yet experimentally we find we need layers 50–100 fibres deep in order to escape interface effects. What value of ρ should be used in equation (10) to convert from resistance to modulus—a cellulose density?—a density weighted for the fraction of the quartz surface that is in contact?—or a density weighted according to the amount of water present? Should the inertia of water be involved, since equation (2) is inertial?—even though water has no shear stiffness at these frequencies, must not its molecules move if they are adjacent to cellulose ones?

One interpretation of the curve in Fig. 9 is that the attenuation growth rate falls away between 55 and 85 per cent solids, after which it resumes the identical trend it earlier followed, however displaced. Could not this falling away be due to a gradual decrease of cellulose-quartz contact area as the paper dries? The affinity of quartz for wetted cellulose could be studied by chemisorbing surfactants on the impedometer bar and observing changes in curves like Fig. 9.

Does ultrasonic vibration itself change the structure of paper as it consolidates and dries? Could a part of what has been measured be a reflection of the technique used?

I suspect that the paper by Craver & Taylor is an important contribution to cellulose physics. For those of us with the coarser nature of paper mechanics at interest, it is a pity that reflection wave phase shift φ could not have been measured so that G' and G'' could replace the less familiar quantities Δdb , X and R .

Transcription of Discussion

Discussion

Mr J. K. Craver—Wilder asks whether the obvious relationship of G' increasing by 4 magnitudes as frequency increases by 4 may possibly extend to other shear rates as well, giving us a crude but ready rule of thumb. I would point out that G' is independent of frequency (f) for solids of high modulus, whereas liquids will have no shear resistance below a frequency that is characteristic for that liquid; above that point, it will begin to behave as an elastic solid. With a drying pulp mat, therefore, there will be all degrees of response from that of liquid water to that of an elastic solid. We are using a frequency band that permits study of this very behaviour. So it is not entirely correct that the relationship will hold between G' and frequency; it will not. This is a useful technique, but not in the way that Wilder implies.

In his second paragraph, Wilder asks what value of ρ should be used to convert from resistance to modulus—the density of cellulose or, should the inertia of water be involved, even though water has no shear stiffness at the frequencies, must not its molecules move if they are adjacent to the cellulose? The answer is yes, they must, if they are adjacent. We have used $\rho = 1.55$ for dry cellulose. At intermediary stages, we do not know how much water is associated with fibres. The value is continually changing, hence we do not derive G' for the intermediary stages.

The question whether the changes noted could be caused by changes in cellulose-quartz contact can be answered in the negative. We can observe the contact areas by using polarised vertical illumination and there is no change in contact area from about 40 per cent solids on up to dryness. We have treated our test surface with Kel-F emulsion (which has no stickiness), yet the fibre-quartz contact—hence, the signal—is unaffected until one gets to 60–70 per cent solids. At this point, the fibre contact disappears: in other words, a partly dry mat will not stick to a Kel-F surface. With clean quartz, this is never observed.

Incidentally, very thin films of metals can be put on to the quartz bar. If in the range of a micron or so, they are transparent to the ultrasonic pulse, so you can examine the drying of cellulose on various surfaces if you so choose.

'Does ultrasonic vibration itself change the structure of paper as it consolidates and dries?' (paragraph 4). No, we have left a sample on the bar for 18 h with the signal going through and observed no change in attenuation. The actual physical movement is so small that there is no change in attenuation.

Wilder says that it is a pity that the reflection wave phase shift φ could not have been measured so that G' and G'' could replace the less familiar quantities Δdb , X and R . We agree, though to measure phase shift requires very precise control over the temperature at any given point, since temperature has a larger effect on ϕ than anything else we are measuring. To do this and, at the same time, evaporate water out of the system presents many experimental difficulties. It is for this reason that we use the Δdb notation, not G' and G'' .

Dr J. Kubát—Transient effects similar to those shown in Fig. 18 have been observed in our laboratory* (Paper Technology Dept., Swedish Forest Products Research Laboratory, Stockholm). We found that, on changing the humidity of the atmosphere surrounding the sample, there was a transient increase in damping. This effect was observed both when the humidity was raised and when it was lowered. Besides being clearly developed in the system paper (cellulose)/water, it was observed also with paper (cellulose)/ammonia and with a number of polymer and solvent vapour systems. The damping capacity was measured by means of the torsion pendulum technique.

Prof. B. G. Ranby—I would just point out that the ultrasonic methods of Craver & Taylor appear to be more powerful than those developed previously for studies of cellulose/water interaction. In the data presented today, we can see several steps in the curve for damping against modulus when water is gradually removed. It should be observed that we have here a new means of studying just the very same effects we discussed in the first session—what do the hemicelluloses do in the fibres at different water contents?

* Kubát, J. and Lindbergson, B., *J. appl. Polymer Sci.*, 1965, **9**, 2 651