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ULTRASONIC IMPEDOMETRIC STUDIES IN THE CELLULOSE PULP/WATER SYSTEM

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Synopsis—The high frequency shear mechanical behaviour of cellulose pulp/ water systems during the process of drying from 3 per cent solids to total dryness has been non-destructively and continuously monitored by the technique of ultrasonic impedometry. Unusual fibre/water interactions have been detected at both extremes of the concentration range studied. These interactions are given interpretation in molecular terms.

Introduction

IN MANY ways, the formation of paper from a dilute water slurry of fibres is analogous to the drying of synthetic latices to form coherent polymer films. In both systems, a dispersed, deformable solid phase is caused to coalesce under the action of surface tension forces that arise during the removal of water from the system. The principal differences reside in the nature of the solid phase. The papermaking fibres are swollen and plasticised by water and cohere mainly by means of hydrogen bonds. The latex particles are hydrophobic and require thermal energy or internal plasticisers for the deformability necessary to coalescence.

This analogy suggested that the methods developed for monitoring the drying of latex films should be applicable to a study of the consolidation of wet pulp webs to form paper. Our attention was called to ultrasonic impedometry, $^{(1,2)}$ which was most attractive, because it had the potential of monitoring the complete transition from dilute slurry to dry web in a non-destructive manner. The changes in mechanical properties of the web during drying could thus be determined on a single specimen, without disturbing the system or interrupting the drying process. This technique has exceeded our expectations on all counts.

Ultrasonic impedometry

History—The choice of experimental method for measuring dynamic mechanical properties depends in part on the physical state of the material

being tested. Obviously, a technique applicable to hard solids might not be suitable for visco-elastic liquids. A large number of dynamic mechanical test methods has arisen in the past to satisfy particular requirements of test material and test frequency. Among these are free and forced resonance vibration (torsion pendulum, vibrating reed), wave propagation methods and electromagnetic transducer techniques. Methods that measure shear mechanical properties (as opposed to tensile or compressional properties) deserve particular attention, because, as Ferry has stated, 'Simple shear is by far the most important type of deformation in studies of visco-elastic bodies, because it can be performed on liquids and solids alike, and on materials with all degrees of intermediate character...Moreover, the absence of a volume change facilitates interpretation of the behaviour in molecular terms.' (p. $6^{(3)}$)

Ultrasonic impedometry was developed by Mason & McSkimin in the late forties for measuring the complex mechanical shear modulus of polymer liquids.⁽⁴⁾ This method has two important features to distinguish it from most other approaches to dynamic mechanical testing—

- 1. Transitions between liquid and solid states can be continuously monitored on a single sample.⁽²⁾ This is most important in studies of resin curing, pain drying, paper formation, etc.
- 2. The very high frequencies used cause vibration of small structural elements (with short relaxation times). This permits examination of short range molecular phenomena such as hydrogen bonding and local chain stiffness of polymers.

In the original work of Mason and co-workers,⁽⁴⁻⁶⁾ the shear behaviour of low molecular weight polymer liquids (polyisobutylene and poly- α methylstyrene) was examined over the frequency range of 5–25 Mc (1 Mc = 10^6 c/sec). These liquids exhibited a shear elasticity approaching that of crystalline solids suggesting that only small segments of the polymer chain were being displaced from equilibrium positions. Litovitz and co-workers have used ultrasonic impedometry in their investigations of the visco-elastic properties of associated liquids.^(7,8) Myers & Schultz have monitored the liquid-solid transitions associated with coalescence of lattices and autoxidative polymerisation.^(1, 2) Barlow & Lamb have examined the high shear rate behaviour of lubricating oils at pressures up to 1 000 atm and frequencies up to 85 Mc.^(9,10) Recently, the visco-elastic constants of short-chain polymers have been evaluated by ultrasonic impedometry at 300 Mc.⁽¹¹⁾

General principles—In ultrasonic impedometry, the test sample is subjected to a rapid cyclic shear strain by a plane polarised ultrasonic shear wave (particle displacement perpendicular to direction of propagation). Since shear waves are rapidly damped out in liquids, it is necessary to use a surface reflectance technique (Fig. 1). The test material is placed on top of the fused quartz bar. A pulsed ultrasonic shear wave (with displacement parallel to the top surface) is generated in the bar by means of a piezoelectric crystal suitably bonded to one end of the bar and driven at resonance frequencies by an electrical signal from a pulsed oscillator. The vibration lasts only 5 μ sec and is repeated 400 times a second. The pulse or packet of ultrasound is reflected from the test surface, with negligible mode conversion and is received at the other end of the bar by a second piezoelectric crystal. The mechanical pulse is reconverted to an electrical signal and is displayed on an oscilloscope as a series of peaks of decreasing amplitude, which represent the echo intensity



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S = Reflecting surface
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T_1, T_2 = Transmitting and receiving transducers, Y-cut quartz, thickness shear mode of vibration
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W = Path of ultrasonic beam, polarised parallel to reflecting surface S
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Fig. 1-Ultrasonic impedometer bar

after successive odd-numbered reflections from the test surface. Since the shear wave packet strikes the receiving end of the bar at normal incidence, it is reflected again at the test surface, retracing its original path back and forth and creating the pulse echo pattern shown on the oscilloscope trace of Fig. 2a. As many as 50 echoes are observed in favourable cases.

With a test sample on the optically flat surface of the bar, the pulse echo train is reduced in amplitude (Fig. 2b). This attenuation is due to refraction of part of the sound wave into the test material at the bar surface. This energy is absorbed and converted to heat, which is immediately dissipated.

The behaviour of the sound wave at the reflecting surface is analogous to the reflection and refraction of light at an interface of two materials of different refractive indices. In the acoustic case, the shear mechanical properties of the fused quartz and the test material are the governing factors. As the shear modulus of the test material approaches that of fused quartz, more energy is lost through refraction, less is received at the second transducer and a greater attenuation of pulse echo height results.

To characterise both components of a complex shear modulus completely, two independent experimental quantities must be determined. One is attenuation and the other is the small shift in phase in the mechanical wave that occurs upon reflection at the test interface. This phase shift is the time delay resulting from a slight penetration of the reflected mechanical wave through the acoustical interface. The phase shift depends directly on the viscosity of the test material.





(b)

Fig. 2—(a) Pulse echoes, empty bar—sweep rate 50 msec/cm (b) Pulse echoes, loaded bar—sweep rate 50 msec/cm, $\Delta db = 2.7$

In our work so far, we have not measured phase shifts and so do not have a complete measure of the complex shear modulus, but the attenuation data alone permit an accurate calculation of the real part of the complex mechanical impedance (see *Theory*). This quantity in turn determines liquid viscosity in the limit of zero shear elasticity and the shear modulus in the limit of pure elasticity. The change of attenuation with time or composition can be used for monitoring physical changes with converting to basic units.

Theory—The development of the descriptive equations for ultrasonic impedometry presented below is a simplification of the full mathematical treatment published by O'Neil⁽¹²⁾ and reviewed by Schultz.⁽¹⁴⁾ The object of the theory is to relate the measured quantities of attenuation and phase shift per reflection to the components of the complex shear modulus. In the development, use is made of the impedance method of representing complex

moduli as described by Alfrey.⁽¹³⁾ A brief description of this treatment of complex moduli is also given. A general discussion of visco-elasticity and dynamic moduli as they pertain to ultrasonic impedometry is given in the appendix.

Consider a small volume of material with dimensions dx, dy, dz through which is travelling a mechanical shear wave propagated in direction z and polarised in direction x (particle displacements in x direction). The only forces acting on the unit cube are the shear stresses acting on the xy faces. The net force F acting on the cube is the difference in stress (T) acting on the two xy faces multiplied by the area over which the stress is acting—

$$F = \left(\frac{\partial T}{\partial z}\right) dz (dxdy) \qquad . \qquad . \qquad . \qquad (1)$$

If u is the particle displacement, then Newton's second law gives—

$$F = (dx \, dy \, dz \rho) \, \partial^2 u / \partial t^2 \qquad . \qquad . \qquad (2)$$

where ρ is the density of the material and t is time. The strain is small and therefore stress and strain are proportional—

$$T = G^* \frac{\partial u}{\partial z} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

where G^* is the complex shear modulus. (Obviously, $\partial u/\partial z$ is the strain and not u alone, as a uniform displacement u results only in translation of the body as a whole.) Combining equations (1), (2) and (3), we obtain—

$$\rho(\partial^2 u/\partial t^2) = G^*(\partial^2 u/\partial z^2) \qquad . \qquad . \qquad . \qquad (4)$$

which has the solution-

$$u = u_0 \exp(i\omega[t - z(\rho/G^*)^{\frac{1}{2}}])$$
 . . . (5)

where ω is the circular frequency and u_0 is the maximum displacement.

As mentioned earlier, a mechanical wave interacts with an interface in much the same manner as does light: reflection and refraction phenomena are common to both. The physical quantity governing the behaviour of the mechanical wave at an acoustical interface is the mechanical impedance Z just as the refractive index determines the electromagnetic wave behaviour at an optical interface. For *perfectly* elastic materials, Z is given by—

$$Z = \rho c \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

where c is the velocity of sound through the material. Similarly, the refractive index of a substance is related to the speed of light through the substance. Fundamentally, Z is defined as a force per unit velocity [p. $90^{(3)}$]—

$$Z = -T/(\partial u/\partial t) = -G^*(\partial u/\partial z)/(\partial u/\partial t) \qquad . \qquad . \qquad (7)$$

Differentiation of equation (5) and substitution into (7) gives-

Both the shear mechanical impedance Z and the shear modulus G^* are, in general, complex and can be expressed as—

where R and X are the resistance and reactance components of the impedance (in analogy with electrical nomenclature). Expanding equation (8) in terms of (9) and equating real and imaginary parts, we obtain the desired impedance representation of the complex shear modulus—

$$\begin{cases} G' = (R^2 - X^2)/\rho \\ G'' = 2RX/\rho \end{cases}$$
 (10)

Typically, G^* is expressed in units of dyn/cm² and Z in 'mechanical ohms' (dyn sec/cm³ or g/sec cm²). The viscous component of G^* is often reported as a dynamic viscosity, $\eta' = G''/\omega$, which equals the ordinary shear viscosity as the frequency ω approaches zero.

We must now develop the relationships between the experimentally measured quantities and the mechanical impedance from which the complex modulus follows by equation (10). The data obtained from the impedometer are—

- (a) The absolute reflection coefficient \overline{R} , which is the ratio of the amplitude of the reflected and incident waves (ranging from 0 to 1).
- (b) The phase shift ϕ , which is the shift in phase in excess of 180° suffered by the reflected wave.

Freshel's law of reflection, applicable to acoustical phenomena as well as to electromagnetic waves, gives the complex reflection coefficient r as a function of the angle of incidence and reflection θ_i and the angle of refraction θ_0 (Fig. 3)—

$$r = \tan \left(\theta_i - \theta_0\right) / \tan \left(\theta_i + \theta_0\right) \qquad . \qquad . \qquad (11)$$

The quantity \overline{R} is the absolute value of the complex r and the two are relatable through the usual exponential form of complex numbers—

$$r = R \exp(-i\phi)$$
 (12)

450

Snell's law relating angle of incidence of light to angle of refraction is applicable to acoustic refraction, if refractive indices are replaced by reciprocal Z, to give—

$$Z_2 \sin \theta_i = Z_1 \sin \theta_0 \qquad . \qquad . \qquad . \qquad (13)$$

Combining equations (11) and (13), with appropriate trigonometric manipulation, gives—

$$Z_{2} = Z_{1} \frac{\cos \theta_{i}(1-r)}{\cos \theta_{0}(1-r)} \qquad . \qquad . \qquad (14)$$



Fig. 3-Reflection and refraction of sound

The shear mechanical impedance of fused quartz Z_1 is much higher than that for most conceivable test materials and $\cos \theta_0$ will nearly always be greater than 0.988.^(12,14) Substituting equation (12) into equation (14), setting $\cos \theta_0$ equal to unity (θ_0 is not directly measurable) and separating the resulting equation into real and imaginary parts, we obtain—

$$\left. \begin{array}{l} R_2 = Z_1 \cos \theta_i (1 - \bar{R}^2) / (1 + \bar{R}^2 + 2\bar{R} \cos \phi) \\ X_2 = Z_1 \cos \theta_i (2\bar{R} \sin \phi) / (1 + \bar{R}^2 + 2\bar{R} \cos \phi) \end{array} \right\} \qquad . (15)$$

Equation (15) relates the components of the mechanical impedance of the test material to the measurable quantities \overline{R} and ϕ and to the fixed instrument constants Z_1 and θ_i . The mechanical impedance can then be converted to the shear modulus through equation (10).

In practice, the absolute reflection coefficient \overline{R} is evaluated by measuring the change in the rate of decay of echo amplitude upon application of the test material (Fig. 2). If the amplitude of the original incident ultrasonic

wave is A_0 , then the amplitude after the first reflection from the test surface is $\overline{R}A_0$. The amplitude after two reflections is \overline{R}^2A_0 and after *n* reflections is \overline{R}^nA_0 . The decay rate is therefore logarithmic with regard to *n* and the ratio of successive echo amplitudes is a constant.

The decibel (db) notation is convenient in such situations-

$$db = 20 \log (amplitude ratio) \qquad . \qquad . \qquad (16)$$

The actual decay rate observed on an empty bar is not always perfectly logarithmic, but this is of no concern, because it is the amplitude difference before and after application of test sample to the bar that is related to physical properties of the sample. The amplitude differences, expressed on a decibel scale, are indeed linear with n, regardless of the original decay pattern.

Only the odd-numbered reflections are observed as explained earlier. If n is the observed echo number, then the total number of reflections i from the test surface is given by—

Let the amplitude of the *n*th observed echo (or 'peak') be A_n^0 before and A_n after application of sample: then we have—

$$A_n = A_n^0 \bar{R}^i$$
 (18)

which gives, upon substitution of (16) and (17)-

$$(db)_n = -20(2n-1)\log \bar{R}$$
 . . . (19)

A plot of $(db)_n$ against *n* should be linear with a slope, designated Δdb , given by—

$$\Delta db = -40 \log \overline{R} \quad . \quad . \quad . \quad (20)$$

Experimentally, Δdb is readily determined by measuring peak amplitudes in decibels (relative to any arbitrary standard) before and after application of sample. Decibel differences for several peaks are plotted against peak number *n* to give a straight line of slope Δdb .

If the sample properties are changing with time, the Δdb can be evaluated from the amplitude change of a single peak. Combining equations (19) and (20), we have for this case—

$$\Delta db = 2(db)_n/(2n-1)$$
 . . . (21)

In our work, we have not measured the phase shift ϕ , therefore we are not able to separate the real and imaginary components of the complex shear modulus, but it is predictable in all practical cases that ϕ will be less than 5°.⁽¹⁴⁾ The denominator of equation (15) then reduces to $(1+\bar{R})^2$, because $\cos \phi$ is nearly unity: in this case—

$$R = Z_1 \cos \theta (1 - \bar{R}) / (1 + \bar{R})$$
 . . . (22)

and the real component of the complex mechanical impedance can be accurately evaluated in the absence of a value for ϕ .

Liquids of viscosity less than 10 poise are unlikely to show any shear stiffness at frequencies up to 100 Mc, because of the short relaxation times characteristic of such liquids. For zero shear stiffness (G' = 0), we have R = X by equation (10). Hence, for light liquids, the ultrasonic impedometer is a viscometer, because we then have—

$$\eta = 2R^2/\omega\rho \qquad . \qquad . \qquad . \qquad (23)$$

Typical values of Δdb for non-relaxing simple liquids [for $\theta = 79^{\circ}$, $Z_1 = 8.29 \times 10^5$ mechanical ohm, $\omega = 9.4 \times 10^7$ (15 Mc)] at 20°C are—water, 0.15 and mercury, 0.69.



Fig. 4—Impedometer shear modulus relationship

Fig. 7—Thickness dependence of attenuation—bleached sulphite wood pulp 430 CSF, dried from water

When the material adhering to the surface of the impedometer bar is a solid, the reflection coefficient \overline{R} becomes quite small and correspondingly Δdb becomes large. For perfectly elastic solids, X = 0, so that G'' = 0 and $G' = R^2/\rho$ from equation (10). Because ϕ in any case will be small, it follows from equation (15), however, that the measured Δdb for rigid materials (shear modulus greater than about 5×10^8 dyn/cm²) provides a good measure of 30—c.p.w. 1

the elastic shear modulus G'. This is illustrated by Fig. 4, in which is plotted $\rho G'$ calculated from equations (10) and (15) for $\phi = 0$ and 5°. For Δdb greater than 5, an assumption of $\phi = 0$ results in a good estimate of $\rho G'$.

In summary, without measuring the phase shift ϕ , we can obtain the real part R of the complex shear impedance Z. For non-relaxing liquids, R is determined by the viscosity η ; for rigid solids by the shear elasticity G'. R is evaluated experimentally by measuring Δdb .



Fig. 5-Ultrasonic impedometer

Equipment—Our instrument is of the design of Myers & Schultz,⁽¹⁾ with modifications to permit recording the signals: a block diagram of the apparatus is shown in Fig. 5. The pulse generator emits a radiofrequency electrical pulse of 2–80 Mc, lasting about 5 μ sec and repeating about 400 times a second. The shape of a single pulse is shown in the oscilloscope photograph of Fig. 6. The radiofrequency is tuned to the natural resonant frequency of the piezoelectric crystals on the quartz rod or an odd harmonic thereof. The crystal receives the electrical pulse and vibrates in a thickness shear mode parallel to the top surface of the bar. The reflected pulse received by the second crystal is amplified, sent through a calibrated attenuator and displayed on an oscilloscope. The oscilloscope is triggered directly by the

pulsed oscillator. The attenuator permits measurement of pulse echo amplitudes directly in decibels. The amplitude of any echo peak displayed on the oscilloscope may be continuously recorded as indicated in Fig. 6.



Fig. 6—A single ultrasonic pulse—sweep rate 0.5 msec/cm, frequency 10.5 Mc/s

The test bar is of highest quality fused quartz, 4 in long and 1 in square in cross-section, polished to standard optical flatness both top and bottom to permit visual examination of the test surface. The piezoelectric transducers used are Y-cut or BT-cut quartz, gold-plated, with a fundamental resonance of 5 or 10 Mc. They are positioned and bonded to the fused quartz rod by standard delay-line techniques.

To contain dilute (2 per cent) pulp slurries on the impedometer bar surface, a glass rod retaining wall was cemented to the outer perimeter of the test surface. This in no way affected the reflection behaviour of the acoustic beam, because the wall was outside the well-defined beam path.

Results and discussion

Comments and procedures—An important question to consider is to what extent the measured Δdb values give information about the bulk mechanical properties of the sample in distinction to the properties at the quartz-sample interface only. Mason & McSkimin⁽⁴⁾ noted that the measured shear impedance was independent of sample thickness for thicknesses greater than 10 μ , but they worked with liquid polymers and the critical thickness should be greater for solids, which are poorer dissipaters of acoustic energy. To answer the question of critical thickness in the case of pulp mats, we dried various amounts of a beaten bleached sulphite pulp on the impedometer bar and measured Δdb in the air-dry state. From Fig. 7, we conclude that the impedometer 'sees' about 200 μ (0.008 in) into the dried pulp sample. All

subsequent runs were made with sufficient pulp to make certain that Δdb data were unaffected by sample thickness.

Obviously, for the ultrasonic beam to sense the presence of the material on top of the bar, that material must adhere to the polished quartz surface. With liquids, there is no problem, because molecular contact with the surface is automatically attained; when a fibrous material is dried on to the quartz surface, however, total coverage of the surface is impossible because of the porous nature of the fibre bed. A typical contact pattern for pulp fibres is shown in Fig. 8. The measured Δdb in such a situation will be lower than that characteristic of the true shear impedance of the film. In case absolute Δdb



Fig. 8—Fibre contact area on quartz—bleached sulphite woodpulp 430 csF (dark regions are areas of optical contact × 50)

data are needed for calculation of a shear modulus, the measured Δdb must be corrected for area of contact. We found by a model experiment using creped pressure-sensitive tape (for which the contact area could be controlably varied over 15–95 per cent) that a linear area-of-contact correction to Δdb was permissible. The optical and acoustical areas of contact are therefore approximately proportional.

Determination of complete 'drying curves' (Δdb against percentage solids) was accomplished by air-drying the pulp mat to increasing solids contents as measured by direct weighing. The drying process could be conveniently

interrupted at any point by simply applying a cover of PTFE tape to the top of the glass retaining wall. The early stages of the drying process could be speeded up by blotting off free water through a papermaking wire screen. When only the final, dry Δdb was needed, the sample was pressed to about 25 per cent solids and dried at 50°C in a draught oven. The final Δdb values were not significantly affected by this procedure.

Drying curves—The most significant feature of the ultrasonic impedometer is the ability to monitor the transition from liquid to solid continuously and non-destructively on single samples. Myers has followed the drying of paint films and coalescence of latices by this technique.^(1,2)

In the area of paper technology, we have been able to monitor the consolidation of pulp slurry from about 3 per cent solids to dryness. A typical drying curve is presented in Fig. 9. In almost all pulp drying curves that we have measured, the Δdb continues to increase through the entire solids range. Therefore, internal stresses in the dry mat are insufficient to disrupt the adhesion of the fibres to the quartz surface. This is not the case with synthetic latices dried below their minimum film-forming temperature.⁽²⁾ The first departure of Δdb from that of water alone occurs at 3–4 per cent consistency. Below this concentration, the fibres do not form a sufficiently rigid network structure to give a measurable shear impedance at the megacycle frequencies.

We attribute the slight hump in the curve at about 13 per cent solids to the initial entrance of air/water interfaces into the fibre mat. This feature of the drying curve, though minor, is consistently present in all runs. The curvature in the 50–70 per cent solids range is another consistent characteristic of pulp drying curves and may reflect the influence of the Campbell surface tension effect. The rapid rise in Δdb beyond 70 per cent solids reflects the deplasticising effect of removal of water from the fibres themselves.

The data of Fig. 9, corrected for a 40 per cent area of contact and converted to the shear modulus (assuming X = 0, valid at high solids only), are replotted in Fig. 10. The modulus changes over three orders of magnitude—which is typical of a liquid to solid transition. The behaviour at 10-20 per cent solids is more evident.

Kurath⁽¹⁵⁾ has used a double electromagnetic transducer to study the shear mechanical properties of pulp over the solids content range 10–50 per cent at frequencies up to 1 000 c/sec. The data presented in *his* Fig. 4 for an unbeaten southern pine bleached kraft pulp at 100 c/sec can be converted to shear mechanical resistance R by means of equation (10). A portion of our data (Fig. 10) is replotted in Fig. 11 as shear mechanical resistance R against concentration for comparison with the converted data from Kurath's paper. In spite of the four orders-of-magnitude difference in test frequency,

different techniques and different pulps, the results are in remarkable qualitative accord.

It is well appreciated that surface tension plays an important role in the consolidation of the wet web at various stages during drying.⁽¹⁶⁾ Fig. 12 shows the effect of an 0.1 per cent solution of an anionic surface active agent on the drying curve of moderately beaten bleached kraft softwood pulp. The concentration units and logarithmic coordinates are chosen to emphasise the low solids region. Apparently, the reduced surface tension begins to be



curve for pulp—bleached sulphite woodpulp 380 csr, f = 2.5 Mc

Fig. 10—Pulp drying curve, shear resistance—bleached sulphite wood-pulp 380 csF, f = 2.5 Mc, Δdb corrected for 40 per cent contact

influential at about 14 per cent solids concentration (6 g water/g pulp). This is in the range when air begins to enter the wet mat and to create menisci that would be susceptible to the influence of a surface active agent. The surface tension reduction ultimately leads to a reduction in interfibre bonding and fibre-to-quartz bonded area as evidenced by the reduction in Δdb throughout the drying curve.

Mechanical beating of pulp produces an increase in interfibre bonding









Fig. 12—Effect of surface tension on drying curve bleached kraft pulp 500 csr, f = 10 Mc

because of increased fibre flexibility and fibrillation. The increased fibre flexibility is manifested directly in the ability of the wet fibres to conform to a smooth surface upon drying from water. In Fig. 13, the area of contact of a dried pulp mat with the mirror smooth surface of the impedometer bar is given as a function of degree of refining. The beating engine used was a Mead laboratory refiner. Fines passing through a 100 mesh screen were removed from the whole pulp to yield the classified pulp. The area of contact was determined from geometric measurements on photographs such as Fig. 8. The replicate data on classified pulp were taken over a year after the original data and the agreement is satisfactory.

The rapid rise in contact area in the early stages of beating is a manifestation of the increase in fibre swelling or specific volume for lightly beaten pulps.^(17,18) The swollen fibre is more deformable and can conform better to the plane surface on drying. The difference in contact area between the whole and classified pulp represents the contribution of the fines to the confact area. After the initial rapid rise of contact area caused by fibre swelling, the production of fines increases and contributes a large portion to the further increases in contact area.

The high frequency shear resistance of the air-dried samples of Fig. 13 are plotted in Fig. 14 as Δdb against percentage contact area. The Δdb increases linearly with contact area and is independent of fines content for a given area. Fig. 14 shows that beating increases the Δdb of air-dried pulp only because of increased fibre-quartz contact area. The increased area of contact at the quartz surface implies an increased area of contact between fibres inside the pulp mat (that is, interfibre bonding) and it is probable that the two are directly proportional.

The straight line in Fig. 14 does not pass quite through the origin. This is most likely due to a small consistent positive error in the determination of contact area. The linearity of the plot is most significant in that it implies a direct proportionality of optical and acoustical contact area.

If the Δdb increase on beating is due solely to increased contact area, we must assume that the intrinsic high frequency shear mechanical resistance of the fibre wall material itself does not change with beating. This is reasonable, because it is well recognised that moderate beating does not change the degree of crystallinity of cellulosic fibres and, even though beating does alter the supermolecular structural organisation of the fibre, the random fibre orientation in the pulp mat would average out differences that the polarised shear wave might otherwise detect. An extrapolation of the straight line in Fig. 14 to 100 per cent contact area gives a Δdb of about 16.6, which should be characteristic of the cellulose substance. From Fig. 14, this value of Δdb corresponds to a shear modulus of about 5×10^9 dyn/cm². Assuming a Poisson ratio of 0.3, this would give a Young's modulus (in the thickness direction of the mat) of slightly greater than 10^{10} dyn/cm². This is a reasonable figure for a semicrystalline polymer.⁽³⁾

Low solids region—As mentioned earlier, the impedometer is actually a viscometer for light liquids whose relaxation frequency is far above the megacycle test frequency. In such cases, the liquid viscosity can be calculated from Δdb by using equation (23) with R given by equations (20) and (22). In



Fig. 14—Effect of beating and contact area Fig. 15—Shear mechanical impedance of on attenuation—bleached kraft pulp mercury f = 2.5-5.0 Mc

the region of viscosity below 20 poise, the Δdb is proportional to mechanical resistance R and the viscosity therefore varies with $(\Delta db)^2$. For non-relaxing liquids, the viscosity is independent of frequency, therefore R should vary with the square root of frequency.

From equation (23), we have—

where f is the frequency in c/s (equal to $\omega/2\pi$). A test of this relationship for mercury is shown in Fig. 15. The line is drawn with slope 0.5 and gives $\eta = 1.4$ centipoise, which is reasonably close to the literature value of 1.5 centipoise.

A second example of the use of the ultrasonic impedometer as a high frequency viscometer is provided by the ethanol/water system. Aqueous ethanol exhibits a marked viscosity maximum at a composition that is very close to 3:1 moles water/ethanol at room temperature.⁽¹⁹⁾ Although the impedometer was not designed for accurate measurement of low viscosities,

we had the good fortune to have one impedometer bar that gave a superb pulse echo train over 50 echoes long (over 100 individual reflections from the test surface). Using this bar, we could measure Δdb changes smaller than 0.01, corresponding to an amplitude loss per reflection of 6 parts in 10 000. The relative viscosities of ethanol-water solutions at 24°C and 14 Mc were determined using this bar and are presented in Fig. 16, along with relative viscosities of the same solutions determined with a standard capillary



Fig. 16. Viscosity of aqueous ethanol at 24°C



viscometer. (The values of Δdb involved ranged 0.12–0.20.) The correspondence of the viscosities measured by the two disparate methods is very good. The magnitude of the viscosity anomaly and the concentration at which it occurs are in perfect harmony with the literature data.⁽¹⁹⁾ This correspondence is evidence that the water-ethanol association complex has a relaxation time (or half-life) shorter than 10⁻⁷ sec, otherwise the impedance would be higher than that predicted from simple viscosity, owing to the additional contribution of a shear elasticity.

As mentioned earlier, only small structural elements are involved in the high frequency oscillations of the megacycle shear wave. Fibres or fibrils are too massive to have their centre of gravity displaced by the shear wave. In fact, even a polymer molecule in solution cannot be moved as a whole at these frequencies.^(4, 6) An excellent demonstration of this fact is to measure the high frequency shear resistance of a viscous polymer solution. For example, a 2 per cent solution of hydroxyethyl cellulose in water having a capillary viscosity 250 times that of the solvent gave an impedometry viscosity only 1.2 times that of the solvent. The high viscosity of polymer solutions is due mainly to the viscous drag resulting from rotation of the molecule in the shear field of the solvent. At megacycle frequencies, there is no rotation or translation of the molecule as a whole and the contribution of the polymer to the impedometry viscosity is limited by the small volume fraction of polymer present in the solution. Local interaction of polymer segments with solvent molecules, such as exhibited in the ethanol-water system, could lead to a high frequency viscosity contribution by the polymer somewhat in excess of that due to its mere volume concentration.

The surface of beaten cellulose fibres in water suspension is not well defined. Fibre fragments, fibrils and microfibrils partly attached to the main body of the fibre extend into the neighbouring free water. Hemicelluloses, which are present in high concentration at the surface of kraft pulps,⁽²⁰⁾ are in a state of partial solution characteristic of absorbed long chain molecules. The cellulose itself is in a highly swollen state. We might expect, therefore, some sort of polyol-water interaction to be found in dilute pulp slurries analogous to the viscosity behaviour of the ethanol-water system. Ordinary flow viscosity measurements cannot be used to detect this type of interaction in a pulp/water system, because of the overriding influence of the fibres themselves. Translation and rotation of the fibre through the surrounding water is eliminated at ultrasonic frequencies and subtle interactions of fibre with water—or of two fibre surfaces—might be detectable.

A sample of bleached softwood kraft pulp was beaten to 500 CSF and the fines removed. The pulp was separated into several portions, which were then solvent-exchanged. The final solvents were formamide, dimethyl-sulphoxide (DMSO), water, methanol and benzene. The first two solvents are very active hydrogen bonding liquids, which swell cellulose at least as much as water. The latter two solvents have much less effect on cellulose than does water. Each of these pulp slurries was examined by ultrasonic impedometry in the low solids regions. We were particularly interested in the behaviour as a function of concentration below that corresponding to the initial entrance of air into the system. The resulting shear impedance behaviour is shown in Fig. 17.

The Δdb at 0 per cent solids is that corresponding to the viscosity and density of the pure solvent. The relative viscosities calculated from these

intercepts are in good agreement with the ordinary capillary viscosities. Air could be detected at the test surface (by visual inspection through the bottom face of the impedometer bar) at 11 per cent solids in the formamide and DMSO runs and at 15 per cent solids when water was the liquid phase. There was a significant decrease in the rate of gain Δdb for the formamide and DMSO runs at about 11 per cent solids as can be seen in Fig. 17. Air began to enter the methanol and benzene mats at very low solids contents.



Fig. 17—Shear behaviour of pulp systems at low solids—bleached kraft pulp response of polyvinyl alcohol film at 24°C, 500 CSF, f = 15 Mc f = 5 Mc

The significant aspect of Fig. 17 is the small but reproducible step increase of Δdb at 3–4 per cent solids in the water/pulp system. A similar (but not as marked) change occurs in the formamide and DMSO systems in the 5–10 per cent solids range. We believe that this change represents an interaction between the polyhydric polymers at the fibre surface and the surrounding liquid phase completely analogous to the structural complex of water and ethanol discussed above. In the pulp system, with further increase in the concentration of the alcohol component (the fibres), the attenuation continues to increase, instead of passing through a maximum as in the simpler ethanolwater system. The reason for this is obviously the formation of a coherent structure (the wet web) that possesses shear rigidity.

High solids region—As discussed earlier, the attenuation of the dried film (paper, latex, paint) depends on the shear modulus of the material, as well as the area of contact, if this is not 100 per cent. The presence of small amounts

of solvent or plasticiser in such a film would be expected to reduce the shear rigidity—at least, this is the case at the low test rates typical of traditional mechanical test methods—but we have found some very unusual effects at the megacycle frequencies of the ultrasonic impedometer where the effective time of the experiment is 10^{-7} sec.

Our first observation of a surprising shear modulus behaviour in a polymerdiluent system occurred during routine removal of a dried polyvinylalcohol (PVA) film from an impedometer bar after completion of an experiment. The experimenter decided to watch the progress of film dissolution upon addition of solvent (water) by following the growth of pulse echo amplitudes displayed on the oscilloscope. To his surprise, the pulse heights decreased markedly to a minimum and only after several seconds began to rise. In other words, the film attenuation *increased* upon adding water, implying an increased shear stiffness of the system. The initial behaviour upon addition of solvent was exactly opposite to that expected.

An obvious initial explanation is that the dry polymer film was not in complete contact with the quartz surface and the softening of the film by the solvent permitted more complete contact, which resulted in an increase of Δdb greater than the loss due to the softening effect itself. This may be a partial explanation, but does not account for all the facts.

There was no visual evidence of lack of adhesion of the film to the bar, although, admittedly, the ultrasonic waves may detect loss (or gain) of adhesion before visual evidence of such loss.^(1,2) Another valid criticism is that wetting the polymer film from one side with solvent will result in a solvent gradient in the film that will probably persist until total solution occurs. A better check of the PVA/water phenomenon would be to equilibrate a dried film at various relative humidities. For this purpose, a solution of PVA was dried on the impedometer bar to form a film that was sufficiently thick (0.2 mm) to insure no dependence of Δdb on thickness (refer to discussion of Fig. 7). The film was dried over phosphorus pentoxide for one week, then conditioned successively at relative humidities of 50, 65, 75, 85 and 93 per cent. Equilibrium was reached after two days at each humidity as judged from rate of uptake of water. Impedometry data were taken during the conditioning steps (Fig. 18). The attenuation at equilibrium increases with relative humidity until, in the region between 85 and 95 per cent rh, the normal solvent behaviour comes into play to cause a reduction in Δdb . During each approach to equilibrium (dashed line), the Δdb passes through a maximum, indicating that the mere presence of a moisture gradient in the film causes an increase in Δdb . In summary, PVA films at low moisture contents (below 85 per cent rh) exhibit a shear impedance anomaly.

A possible explanation of the phenomenon at the molecular level is as

follows. Let us assume that the high frequency shear stiffness of a polymer is largely a measure of the mobility of segments of the polymer chain.^(4, 5) This mobility depends on two factors—the type and arrangement of atoms in the polymer chain itself and the forces acting between chains in the bulk polymer. We envisage water molecules, acting individually or in small clusters, serving as molecular cross-links, through hydrogen bonding. between adjacent polymer molecules or neighbouring chain segments. If the lifetime of these cross-links is longer than 10^{-7} sec, they would increase the measured Δdb of the polymer film. Although, say, 10^{-4} sec is long compared with the experimental time scale in ultrasonic impedometry, it is a fleeting instant compared with the time scale involved in traditional mechanical testing. What may look very rigid at 10⁷ c/sec may appear quite pliable in a torsion pendulum or tensile tester. Thus, it is conceivable that the 'static' modulus would be reduced through plasticisation, even while the high frequency modulus increases over a limited moisture range. Recent work in other hydrophilic polymer systems (collagen, gelatine) has revealed a density maximum upon addition of water that is attributed to single water molecule cross-links between polymer chains.⁽²¹⁾ Thermodynamic interpretation of sorption isotherms indicate that polymer/water molecular contacts are favoured over water/water contacts in several hydrophilic polymers (including cellulose) up to relative humidities of 80 per cent and over. (22)

If the water induces a molecular ordering in the polymer film, the effect should be detectable also by X-ray diffraction techniques. PVA films were prepared on glass slides that were conditioned at 0, 30 and 85 per cent rh. Tracings of the X-ray diffractograms are presented in Fig. 19. At 0 per cent rh, only a broad 'amorphous' band is present. At 30 per cent rh, a peak at $2\theta = 19.3^{\circ}$ appears; at 85 per cent rh, a second peak at $2\theta = 22.2^{\circ}$ is barely evident. These peaks are characteristic of the PVA crystalline phase.⁽²³⁾ The intensity of the amorphous phase diffraction halo decreases with increasing relative humidity. Recent work on another polymer system indicates that this 'amorphous' diffraction in reality represents the contribution by crystalline regions too small to be detected by X-ray diffraction as truly crystalline regions.⁽²⁴⁾ It appears, therefore, that water induces the aggregation of small crystallites into groups large enough to be detected by X-ray as truly crystalline. Thus, the effect of moisture in increasing the attenuation of PVA films correlates with structural changes in the polymer viewed by X-ray techniques.

Cellulose is a hydrophilic polymer and might be expected to show anomalous shear impedance behaviour upon humidification. A bleached sulphite pulp was lightly beaten (600 CSF) and well-beaten (250 CSF): samples were air-dried on the impedometer bar. Attenuation measurements were made during humidification to about 25 per cent moisture content. The shear data (expressed on a relative basis to correct for the contact area difference between the samples) are presented in Fig. 20. There was no increase in Δdb upon addition of water to the pulp. The percentage reduction in shear stiffness by the water was identical for both pulps as shown by close agreement of the two sets of data. This is in harmony with the demonstration that the dry Δdb is not a function of interfibre bonding as discussed earlier. In other words,



bleached sulphite woodpulp, f = 5 Mc

bleached sulphite woodpulp 250 CSF classified, f = 5 Mc

although the test material is a bonded fibre assemblage, the impedometer views the system simply as a polymeric material being plasticised by water. The fibrous state of the polymer merely changes the absolute value of attenuation because of incomplete contact with the bar.

Considering the dry pulp pad as a partly crystalline, hydrogen-bonded resin, we next examined the effect of other liquids on the high frequency shear behaviour of the pulp. In the following series of experiments, the liquids were applied in the form of a very fine spray to pulps that had been dried from water on to the impedometer bar. Sufficient time was allowed for the liquid to redistribute itself in the pulp pad before attenuation measurements were taken. A few side experiments confirmed that the equilibrium Δdb was the same as it would have been had the solvent been introduced solely from the vapour phase.

Fig. 21 shows the effect of several liquids on the measured Δdb at 5 Mc of a beaten bleached sulphite pulp. The liquids were chosen to represent a broad spectrum of hydrogen bonding capacity. All the liquids (except octane) cause a reduction in Δdb at low levels of additions.

The increase in Δdb at higher levels of addition of all liquids but water and formamide has nothing to do with the properties of the cellulose. The increase begins when the cellulose has been saturated by the liquid and any further increments of liquid addition serve only as an acoustical impedance match between bar and fibre surfaces not truly in contact. This secondary effect occurs in a system as inert as glass fibre and benzene. The curves are dashed in this region so that attention can be drawn to the significant part of the rewetting curves below fibre saturation.

The most remarkable aspect of Fig. 21 is that the more strongly hydrogen bonding the liquid, the less effective is a given amount of that liquid (mole or weight basis) in reducing the Δdb . Thus, the order of decreasing reduction in Δdb (at sorption levels below saturation) is—ethanol, methanol, water, formamide—just the opposite of what would be expected on the basis of the recognised hydrogen bonding capacity of these liquids.

The pulp had been air-dried before addition of the organic solvents and therefore contained about 5 per cent water at the start of each wetting curve as indicated in Fig. 21. In the absence of this water (desiccated pulp), the differences in the solvents' effects are even greater as seen in Fig. 22. Furthermore, the same observations were found for other pulps (bleached and unbleached kraft, rag) and at a higher frequency (25 Mc). To extend the perspective, the effects of three other liquids—tertiary butyl alcohol, dimethylsulphoxide (DMSO) and 2-ethoxy-ethanol—are shown in Fig. 23.

DMSO, a remarkable solvent in many respects, shows the most anomalous behaviour of any other liquid tested. As seen in Fig. 23, up to 15 per cent DMSO added to a dry sulphite pulp reduced the Δdb by only about 3 per cent in spite of this liquid being a powerful carbohydrate solvent.

Although the cellulose fibre systems do not produce an increase in Δdb upon addition of a plasticising liquid as is the case in the PVA/water system, the above comparison of the effectiveness of the various liquids indicates that there is some anti-plasticisation phenomenon taking place. A molecular cross-linking by hydrogen bonding is a possible explanation here as in the

PVA/water system. The same considerations with regard to lifetime of the cross-links and time scale of the experiment should apply.



Fig. 22—Effect of alcohols on ultrasonic shear response of dry pulp bleached sulphite woodpulp 250 csF classified, f = 5 Mc

Fig. 23—Effect of liquids on ultrasonic shear response of dry pulp bleached sulphite woodpulp 250 CSF classified, f = 5 Mc

Conclusions

THE physical events constituting the consolidation of the paper web from 3 per cent consistency to dryness can be continuously monitored on single laboratory samples by the technique of ultrasonic impedometry. In the low solids region, fibre/water interactions at the fibre surface are detected before the attainment of significant network structure. In the high solids region, an anomalous effect of water and other plasticising liquids on the high frequency shear rigidity of pulp is interpreted as evidence of short-lived cross-links formed by the penetrating liquids.

31—с.р.w. і

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Appendix—Visco-elasticity and dynamic moduli

FUNDAMENTALLY, there are only two types of mechanical stress to which materials can be subjected-tensile (or compression) stresses and shear stresses. Under stress, an object distorts and the magnitude of the distortion is the strain. Because of the three natural dimensions of space, any stress pattern may be analysed into six stress components-one shear and one tensile stress for each coordinate. Similarly, there are six components of strain. In general, any stress can produce any strain as, for example, a pure tensile stress causes lateral contraction in the directions perpendicular to the stress direction for materials that 'neck down'. For perfectly elastic materials (deformation energy completely recoverable), the ratio of a given stress to a given component of strain is called an elastic modulus. For a completely anisotropic elastic material, 36 moduli would be required to describe fully its mechanical properties-one for each stress/ strain combination. For a completely isotropic elastic material, the symmetries are such that only two independent constants are needed-the two Lamé constants λ and μ . The more familiar parameters such as Young's modulus, bulk modulus or compressibility and Poisson's ratio are merely special combinations of λ and μ .

The constant μ is identical with the shear modulus G, which describes the elastic resistance of a material to deformation in the shear mode. A light liquid such as water, when subjected to ordinary rates of strain, exhibits no shear elasticity and would give G = 0. The modulus λ is the bulk compressibility of liquids. In ultrasonic impedometry, the shear mechanical behaviour of materials is measured.

Many materials of commercial interest such as plastics, paints, greases, elastomers and paper do not behave as perfectly elastic bodies, but exhibit a time-dependent strain response to imposed stresses. The term *visco-elastic* applied to such materials suggests the combined properties of liquids and solids that they possess. The mechanical behaviour of visco-elastic materials can be established in creep or stress relaxation experiments, but cyclic or 'dynamic' stress experiments can in most cases produce equivalent information.⁽³⁾

In a dynamic mechanical experiment, the test material is usually subjected to a stress or strain varying sinusoidally with time. A perfectly elastic material responds immediately to a varying stress, consequently the response varies sinusoidally and is in phase with the stress. The sinusoidal strain response of a perfect fluid (no shear elasticity) lags the driving force by 90°. In visco-elastic materials, the strain lags the stress by some phase angle δ lying between 0 and 90°. In the visco-elastic case, a shear stress can be analysed into components in phase and out of phase with the strain and divided by the peak strain to yield the real and imaginary (elastic and viscous) components of a complex shear modulus G^* . Thus—

$$G^* = G' + iG''$$
 (A-1)

$$\tan \delta = G''/G'$$
 (A-2)

and

where G' and G'' are the elastic and viscous components and tan δ is the familiar loss tangent, which is a measure of the ratio of energy lost to energy stored per stress cycle.

The quantity G'' is often expressed in terms of a dynamic viscosity η' —

$$\eta' = G''/\omega$$
 . . . (A-3)

where ω is the angular frequency in radians/sec. As ω approaches zero, the dynamic viscosity approaches the ordinary steady flow viscosity.

For a light liquid such as water, the dynamic viscosity at frequencies up to at least 10^{11} is equal to the capillary viscosity and G' remains zero; but, at sufficiently high frequencies, any liquid will begin to exhibit shear elasticity and ultimately behave as an elastic solid. The reason for this is simply that the molecular motions involved in shear flow require a finite length of time and cannot take place during the brief stress cycle of a sufficiently high frequency disturbance. At such frequencies, the rigidity of the instantaneous liquid lattice structure is the sole contributor to G^* . At room temperature, a highly associated viscous liquid such as glycerol just begins to show solid-like behaviour (G' different from zero) at about 10^7 c/sec.

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.

Ultrasonic impedometric studies

'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