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CONFORMABILITY OF WET PULP FIBRES AT SMALL LENGTH SCALES

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ABSTRACT

The conformability of wet pulp fibres has long been recognized as a key factor in the papermaking process. In order for fibres to bond in the sheet, their surfaces must be brought into contact. The conformability of wet pulp fibre surfaces at extremely low forces (nN) and displacements (nm) was investigated by micro-indentation measurements with a standard AFM tip and cantilever. Force-distance curves were measured as the tip impacted wet sulphate softwood fibre surfaces. The surface stiffness showed a large variability, even at different locations on the same fibre surface. Rough estimates of the local apparent elastic modulus of the wet fibres gave low values in the 0.01 GPa range.

INTRODUCTION

The conformability of wet pulp fibres has long been recognized as a key factor in the papermaking process. In order for fibres to bond in the sheet, they must be brought into contact by flow and capillary forces during sheet drainage and by external pressure in the press section. The more flexible the fibres, the denser and more highly bonded the sheet. The flexibility of pulp fibres is one, but only one, of the contributing factors in traditional measurements of pulp properties such as pulp freeness and water retention. Many ways to measure fibre flexibility have been proposed; these have been assigned into four main classes (classification methods, conformability

methods, network methods and bending beam methods) by Kuhn et al. [1].

Measurement of the flexibility of *individual* pulp fibres is not trivial, especially when the fibres are wet. A number of ingenious methods have been proposed. Mohlin [2] measured the relative flexibility of a drying fibre from its ability to bend across a thin glass fibre. Steadman and Luner [3] used a very low density sheet dried over fine parallel stainless steel wires on a glass slide. Kerekes and Tam Doo [4] and Kuhn et al. [1] measured fibre flexibility from the deformation of fibres in a defined hydrodynamic flow field. The morphological factors that influence wet fibre flexibility and collapse have been reviewed by Paavilainen [5].

Interpretation of the flexibility considered in much of the experimental work ignores details of the fibre structure, and treats the fibre as a long uniform beam with a fixed cross-section and modulus. The flexibility of such a beam is a measure of the curvature induced by application of a bending moment to the beam [6]. Wet fibre flexibility, F_{WF} ($N^{-1}m^{-2}$), and its inverse, wet fibre stiffness, S_{WF} (Nm^2), are usually defined as

$$F_{WF} = 1/S_{WF} = 1/EI \tag{1}$$

where E(Pa) is the modulus of elasticity and I is the moment of inertia of the fibre cross-section.

Atomic force microscopy has proven useful for imaging and characterizing wood and pulp fibres [7]. The deflection of the AFM cantilever also has been employed to measure force-distance curves as the tip approaches and contacts pulp fibres in water [8,9]. The slope of the force-distance curves as the tip contacted the water-swollen fibre surface showed that beaten pulps were more readily compressed than unbeaten fibres [8]. The AFM force-distance curves for an AFM tip in contact with a plane surface can be related to the local surface compliance [10]. In essence, the AFM tip is used to perform a micro-indentation experiment on a relatively soft material, in which the indentation force is of the order of nanoNewtons and the deformation is in the nanometre range. In the AFM micro-indentation method, the force applied by tip depends on cantilever deflection and cantilever spring constant; the indentation distance is the displacement of the sample less the deflection of the cantilever (Figure 1). The instrumental curves of tip displacement against piezo z displacement (Δz_d vs Δz_p) must be converted to force-indentation curves (P vs Δz_I), using k_c values for the cantilever measured against a non-deformable surface. The slope of the force/distance curve may then be related to the micromechanical properties of the fibre surface.

For bodies in contact under a load P, the surface stiffness, S_{MS} (N/m), has a very simple form for a surprisingly wide range of configurations [10]. For a

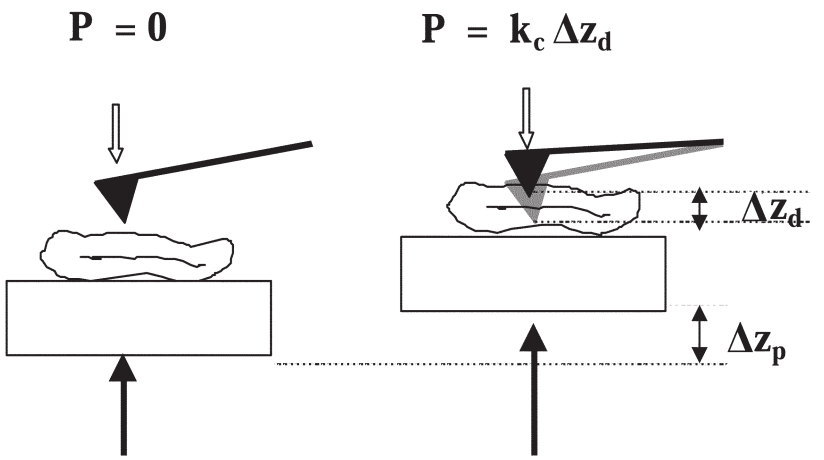

Figure 1 Schematic of tip-sample deformation. P is the applied force, k_c is the cantilever spring constant, Δz_p is the piezo actuator displacement, Δz_d is the cantilever tip displacement and Δz_i ($= \Delta z_p - \Delta z_d$) the indentation displacement.

hard spherical tip in contact with a much softer plane, where the force is applied along a direction z normal to the plane,

$$S_{MS} = \delta P/\delta z = 2Ea/(1 - v^2) \tag{2}$$

where E and v are the Young's modulus and Poisson's ratio for the surface material, respectively. Despite the quite different stress distributions for different detailed tip geometries, the surface stiffness in all cases is simply proportional to contact radius, *a*, and the elastic modulus, E. For most of the likely tip-flat configurations, $S_{MS} = k.\ aE$ is a fairly good general expression, where *k* is a number between 1.9 and 2.4 and E is the substrate modulus when the deformability of the tip can be neglected. Even the introduction of surface forces does not significantly change this simple behaviour [10]. Thus, the experimental measurement of S_{MS} from AFM force-distance curves as the tip is pressed into a wet fibre surface can be used to estimate an apparent local modulus of elasticity of the fibre near the fibre-tip contact area from the relation

$$S_{MS} \sim 2.1\ a\ E_{MS} \tag{3}$$

where the deformation of the tip is neglected relative to that of the fibre. Note that the stiffness, S_{MS}, refers to the deformation of a microscopic area of the surface close to the tip. The units of S_{MS} are N/m, and it is thus quite distinct from the macroscopic bending stiffness, S_{WF}, in Equation 1, which has the units of Nm^2. Of course, the concept of a modulus for the wood fibre wall is a gross simplification, in that the fibre wall is a complex structure, rather than a uniform material. In Equation 3, E_{MS} (Pa) should be viewed as an apparent compressive modulus of the fibre wall.

EXPERIMENTAL

The fibre source was a series of sulphate pulps, laboratory cooked from a mix of pine and spruce, (Pinus Sylvestris and Picea Abies 50:50). Three of the samples were Kraft pulps cooked to kappa numbers 61, 88 and 110. A TCF pulp was cooked to kappa number 25 in a simulation of ITC cooking with liquid exchange, then bleached in a OQ(OP)(ZQ)(OP) sequence to kappa 2.7. All pulps were defibrated after cooking, but were not beaten.

The AFM measurements were made with a Nanoscope IIIa Controller (Digital Instruments), a J scanner with standard DI cantilever and tip was used for both imaging and indentation measurements. Fibres were attached to clean glass cover slips by drying from dilute suspensions in water. The cover slips were attached to the AFM piezo with pressure sensitive adhesive. Images of the dry fibre surfaces were aquired in contact or phase contrast modes. To measure the force required to indent the wet fibre surfaces, a dry fibre attached to a cover glass was immersed in a drop of water. A thin ring cut from paraffin wax film was used to contain the drop. The tip displacement was measured as a function of the piezo displacement as the sample was raised towards the tip. This data was converted to force-distance curves as described above (Figure 1). The data reported here are for the initial scan. The cantilever spring constant was measured from the force-distance slope on the glass cover slip. The stiffness, S_{MS}, was estimated from the slope of the corrected force-distance curves, which were often approximately linear for forces in the 5–40 nN force range.

RESULTS AND DISCUSSION

An AFM amplitude image of the surface of an unbeaten softwood fibre, kraft pulped to kappa 88, is shown in Figure 2. It is important to note the obvious heterogeneity of the surface. When considering the indentation data

below, it must be remembered that the AFM tip that generates images such as this is also the object that is causing the surface deformation, so that the area deformed is a fraction of the width of the scale bar on Figure 2. It is not surprising that the force-distance results are variable; this reflects the differences in material properties at different locations on the surface. Three images of a similar fibre surface at a higher magnification are shown in Figure 3. In addition to the usual AFM height and amplitude images, a phase contrast image of the identical area is shown. Initially we had hoped to quantify the stiffness of the hard and soft regions of the fibre surface by the phase contrast technique, but while the images were striking, the relationship between phase shift and stiffness depended on the instrumental parameters and on surface topology, so that interpretation of phase contrast images is unclear.

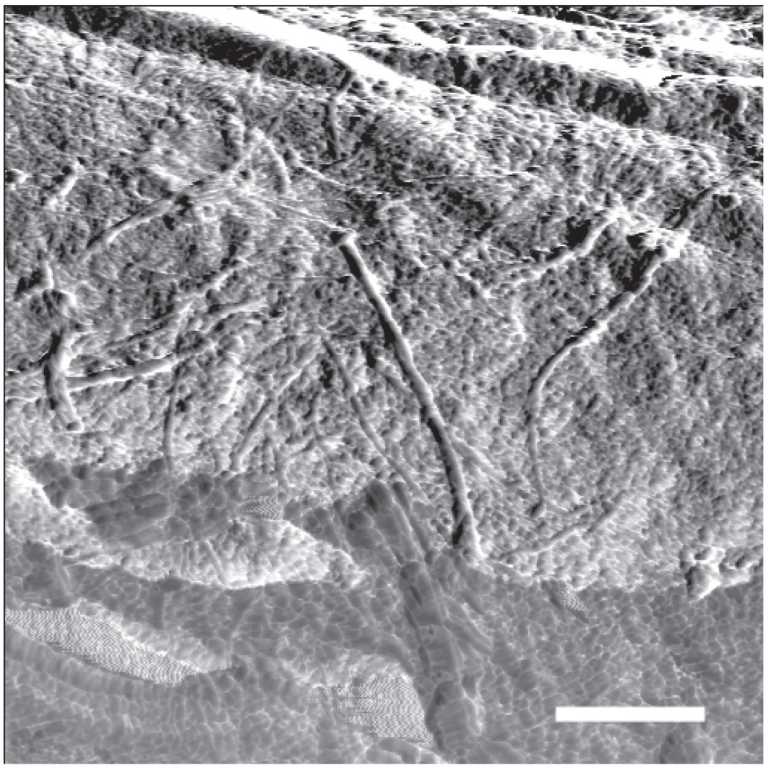

Figure 2 AFM image of the surface of an unbeaten softwood fibre, kappa 88. Scale bar, 5 μm.

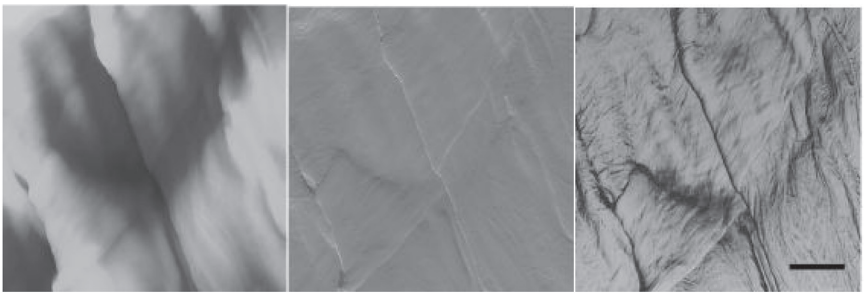

Figure 3 AFM images of the same area of a spruce kraft fibre (kappa 88) surface, generated by three different techniques. From left; height image, amplitude image and phase contrast image. Scale bar, 1μm.

In previous work [8,9], force distance curves were measured for a standard Si_3N_4 AFM tip approaching the surface of pulp fibres. Here, we attempt a rough interpretation of the results in the contact region. For unbeaten or lightly beaten low-yield sulphite fibres, the force-distance curves remained relatively flat, then rose steeply on contacting the fibre surfaces. The curves were linear for the initial contact repulsive forces in the range 1 to 10 nN. These slopes, which correspond to the local stiffness, S_{MS}, of the fibre measured normal to the surface, are tabulated under fibres (A) and (B) in Table 1, assuming the spring constant of the cantilever was the nominal 0.58 N/m specified by the manufacturers.

Table 1 Force-distance slope data for pulp fibres in aqueous media [8,9]

Fibre	Medium	S_{MS} (N/m)	Reference
A) Dissolving grade sulphite, unbeaten	Deionized water	3.5	8, fig.1
B) Dissolving grade sulphite, 5,000 PFI	Deionized water	1.3	8, fig.1
C) Dissolving grade sulphite, 20,000 PFI	0.1 M NaCl	0.57	8, fig.2
D) Bleached Kraft, Beaten 15,000 PFI	0.1 M NaCl	0.15	9, fig.6

Increased beating leads to surface fibrillation, which in turn generates a repulsive force at significant distances from the fibre surface. There is thus no sharp linear increase in repulsive force as the tip contacts the surface. However, by adding salt and thus collapsing the microfibrils onto the surface, a

reasonably linear region was detected, both on highly beaten sulphite (Table 1, fibre C) and kraft (fibre D) surfaces. The surface stiffness clearly decreased with beating. The measurement and interpretation of the stiffness, S_{MS}, depends on the tip dimensions, cantilever spring constant and deformation geometry. Ignoring the detailed structure of the pulp fibre, the elastic modulus may be estimated from Equation 3. The nominal tip radius is in the range 20–60 nm . Taking *a* as 40nm, then from Equation 3, E = S/*a*k = S/(2.2 x 40 x 10^{-9}) or

$$E\ (Pa) = S(N/m) \times 11 \times 10^6\ (m^{-1}). \quad (4)$$

Thus, from Equation 4 and the data in Table 1, the apparent elastic modulus of the pulp fibres ranges from 38 Mpa for a low-yield unbeaten sulphite fibre down to 1.6 MPa for a beaten kraft fibre, give or take an order of magnitude due to the uncertainty in tip radius and geometry, and in the cantilever spring constant. It is also clear that surface properties such as degree of fibrillation (9) vary markedly from place to place on the surface of a single fibre, so a large variation in microscopic stiffness across the surface is also expected.

Calibration with silicone rubber

In order to lower the uncertainty in the above measurements, an attempt was made to calibrate the procedure, and repeat measurements on a series of unbeaten chemical pulps over a range of lignin contents, using the same cantilever and tip. Silicone rubber hemispherical caps were used to calibrate the indentation measurements. The Young's modulus of the caps, 1.57 MPa, was measured independently by observing the macroscopic deformation of the silicone rubber hemispheres in contact with a flat glass plate and applying the JKR theory [11].

Repeat force-distance curves for a regular Nanoscope Si_3N_4 tip contacting a silicone rubber cap are shown in Figure 4. The curves were seldom this reproducible. A relatively linear force-distance slope of 0.47 N/m (average of five advancing curves) was found with the same cantilever and tip for forces in the range 10–40 nN. However, the selection of the linear portion is rather arbitrary, and reproducibility between cantilevers and caps is not good; for a different cap and cantilever, a slope of 0.82 ± 0.06 was found.

For the tip and cantilever used below on wet pulp fibre samples, taking S = 0.47 N/m for a silicone rubber of modulus 1.57 MPa, the calibration method thus gives:

$$E = 1.57 = 0.47/a\text{k}\ ;\ E\ (MPa) = 3.3\ S\ (N/m) \quad (4)$$

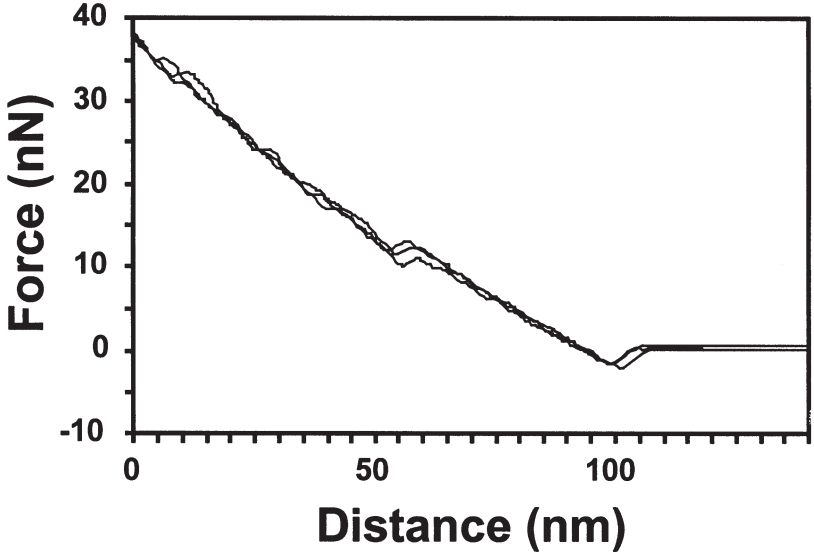

Figure 4 Force-distance curves for AFM tip indenting silicone rubber cap in air.

Thus the calibration of this tip/cantilever with the silicone cap gives about one third the value for E for a given surface stiffness, compared to the estimate based on nominal cantilever spring constant and tip geometry in Equation 3.

Measurements on softwood pulp fibres

From AFM force-distance indentation curves on individual pulp fibres, measurements of surface stiffness, S_{MS}, were attempted on a series of softwood kraft pulps with a range of Kappa numbers, and on a chlorine free (TCF) bleached sample. The shape of the force-distance curves was very variable, even at different locations on the same fibre (Figure 5), even though efforts were made to avoid morphological features such as pit borders. Results for S_{MS} were consequently very scattered (Table 2). The mean value appears to increase with lignin content. Thus, even at a microscopic scale, removal of lignin decreases the stiffness and increases the local surface deformability.

A similar trend is of course observed for the macroscopic deformation of pulp fibres (see Table 3 and references cited therein). However, the number of

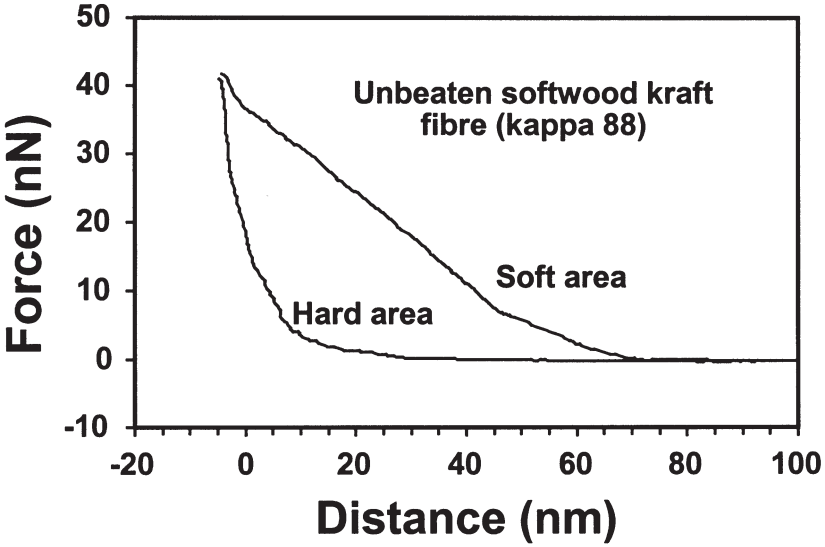

Figure 5 Force-distance curves for AFM tip indenting two positions on the surface of a wet softwood kraft fibre.

Table 2 Local stiffness and modulus of fibres estimated from AFM data

Fibre	S_{MS} (N/m) Mean value	S_{MS} (N/m) Range of values	E_{MS} (MPa)
TCF bleached, unbeaten (2 fibres)	2.1	1.6–2.8	7
Kraft kappa = 61 (3 fibres)	3.8	2.5–5.3	13
Kraft kappa = 88 (7 places on 3 fibres)	4.3	0.6–9.0	14
Kraft kappa = 110 (3 places on 2 fibres)	4.5	2.5–8.1	15

Table 3 Some examples of apparent moduli for spruce pulp fibres

Fibre	Deformation	Modulus	Reference
Crystalline cellulose I	Wet and dry axial tensile	128 GPa	Sakurada et al. [15]
Spruce holocellulose and low-yield kraft, dry	Calculated modulus in the fibril direction	77 GPa	Page et al. [13]
Spruce holocellulose and low-yield kraft, dry	Calculated modulus transverse to the fibril direction	8.8 GPa	Page et al. [13]
Spruce holocellulose dry	Axial tensile	26.7 GPa	Ernrooth and Kolseth [14]
Spruce holocellulose wet	Axial tensile	9.2 GPa	Ernrooth and Kolseth [14]
Spruce kraft pulp, unbeaten, wet	Hydrodynamic bending, (calculated from wet stiffness, with $I = 1 \times 10^{-21}$ m^4)	5.5 GPa	Kuhn et al. [1]
Spruce kraft pulp, beaten, wet	Hydrodynamic bending, (calculated from wet stiffness, with $I = 1 \times 10^{-21}$ m^4)	3.4 GPa	Kuhn et al. [1]
Spruce kraft pulp, kappa 42, earlywood, unbeaten, dry	Transverse compressibility	0.9 GPa	Hartler and Nyren [16]
Spruce kraft pulp, kappa 42, earlywood, unbeaten, wet	Transverse compressibility	0.56 GPa	Hartler and Nyren [16]
Spruce kraft pulp, kappa 42, earlywood, beaten, wet	Transverse compressibility	0.44 GPa	Hartler and Nyren [16]
Low-yield spruce kraft, rewetted, unbeaten, wet	Osmotic swelling	0.004 GPa	Scallan and Tigerstrom [17]
Spruce kraft kappa 61, unbeaten, wet	AFM transverse microcompressibility	0.013 GPa	This work
TCF bleached softwood kraft, unbeaten, wet	AFM transverse microcompressibility	0.007 GPa	This work

fibres sampled here is small, and the range of values is very large. The surface stiffness probed by AFM is obviously very variable, even on a given fibre. While much more work is necessary to characterize the reasons for this variability, it might be expected that regions of microcompressions on these unbeaten fibres would be much more swollen and deformable than regions of undeformed cell wall. This heterogeneity in surface deformability mirrors the heterogeneity in fibrillation observed by AFM on individual highly beaten fibres [9].

Taking the simple Herzian model for local deformability [10], and calibrating the cantilever by comparison with results on a silicone rubber samples (Equation 4), modulus values in Table 2 were estimated from the measured S_{MS} values. Again, confidence in these values is low, due to scatter in S_{MS} and uncertainty regarding the tip/substrate geometry. Nevertheless, the method probes the mechanics of the wet fibre surface at extremely low deformations, and thus may relate to the conformability necessary for fibre-fibre bonding.

Deformation and elastic moduli; comparison with literature

Care is necessary in interpretation of modulus for pulp fibres. Essentially, any description of the elastic response of a structure as complex as wood or a wood fibre requires a deformation matrix rather than a single modulus [12], and wet fibres are unlikely to be purely elastic for any but the smallest strains. Nevertheless, some comparisons of apparent elastic moduli from the literature is worth while.

Pure cellulose microfibrils show a very high tensile modulus that is the same both wet and dry (Table 3). The tensile strength of wood fibres depends on fibril angle and is reduced by microcompressions and other defects [13]. Pulp fibres are stiffest along the predominant microfibril direction, but show a marked decrease in strength on wetting, presumably because of swelling and hydrogen bond breakage between wood polymers. For spruce holocellulose fibres, the wet modulus is reported as 9.2 GPa [14], about one third of the dry value.

An estimate of the tensile modulus may also be derived from bending stiffness measurements (Equation 1). The bending stiffness of individual pulp fibres has been measured in hydrodynamic flow fields [1,4]. The order of magnitude of I for northern softwood kraft fibres is around 1×10^{21} m^4, based on the distribution of moments of inertia measured by Yang et al. [16] in a kraft sheet. The moment of inertia varies approximately as the third power of the fibre thickness, depending on the cross-sectional geometry, so that values for I cover a very broad range for a given pulp sample. The

modulus of wet kraft fibres is thus of the order of 5.5×10^9 Nm^{-2}, using S_{WF} for unbeaten kraft and I for dry kraft fibres in Equation 1.

Less work has been reported on the transverse mechanical properties of pulp fibres. Hartler and Nyrén [17] measured the transverse compressibility of kraft and sulphite spruce pulp fibre samples by compressing a number of fibres between optically flat glass plates, after sufficient force to collapse the fibres had been applied to the sample. They showed that the moduli decreased with decreasing yield, and with beating, with latewood fibres being stiffer than earlywood fibres. The magnitude of the wet transverse modulus (measured on collapsed fibres) was about half the dry value, and was more than an order of magnitude less than the axial modulus. For an unbeaten earlywood spruce sample, the wet transverse modulus was 0.5 GPa [16].

In a novel approach to measuring the modulus of wet wood fibre walls, Scallan and Tigerström [18] noted that an increase in swelling results from the osmotic pressure generated within the fibre wall when the counter-ions of the acidic groups are exchanged from hydrogen to sodium form. They used this stress-strain phenomenon as the basis of a method to obtain a bulk elastic modulus of the water-swollen cell wall. The modulus of never-dried kraft pulps was found to decrease from 10 to 2 MPa as the yield was lowered from 100% to 65% and thereafter the modulus was almost constant. Drying-and-rewetting caused no change in the modulus of the high yield pulps but it did increase the modulus of the lowest yield pulps from 2 to 4 MPa. Beating a dried-and-rewetted bleached low-yield kraft pulp lowered its elastic modulus from 4 MPa down to 1 MPa. These moduli are orders of magnitude lower than more conventionally measured moduli (Table 3), but the stress is generated by osmotic pressure and the strain is a volume change, predominantly due to changes in the cell wall thickness and measured by a size exclusion method [17].

The AFM measurements also probe deformations in the thickness of the cell wall, but on a much smaller scale. The variability in suface stiffness with position is very high, as mentioned above. Nevertheless, the rough magnitude of the AFM measurements on bleached spruce fibres (~12 MPa) is of the same order of magnitude as that for the osmotic measurements, but significantly lower than estimates based on the transverse compressibility of a number of fibres between flat plates (Table 3). However, the high value was measured after the forced collapse of many fibres, and for much larger stresses and strains.

CONCLUDING REMARKS

The AFM can be used to measure the resistance of wet pulp fibres to microindentation in the nanoNewton/nanometer range. Improved methods for determining and interpreting microindentation force-distance curves on uniform elastic materials are being developed [19,20], but the wide variability of results on pulp fibres suggests that the simplified interpretation taken above is adequate. Pulp fibre surfaces show a wide range of resistance to microindentation, even at different locations on the same fibre. The modulus for fibre compression is ill-defined because of the anistropic structure of the fibre and the unknown and variable area of contact between fibre and tip. Nevertheless, the apparent modulus is low, and the results may relate to a swollen, easily deformed surface layer involved in fibre-fibre bonding. In essence, the conformability measured by AFM relates not to the macroscopic bending of fibres to achieve contact in the sheet-forming process, but to the microconformability needed to achieve intimate contact between the fibre surfaces that form strong interfibre bonds.

ACKNOWLEDGEMENTS

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Transcription of Discussion

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PLEASE NOTE THAT IN THIS PAPER THERE ARE TWO EQUATIONS LABELLED FIGURE 4

Vincent Craig Australian National University

I have a suggestion as to where some of your variability may come from. The roughness of your surfaces is of the same order of your indentation and roughness is known to be important on all of these adhesion type measurements. My suggestion would be, as a lot of us do, is to place a sphere on the end of your tip which means of course that you go to a slightly larger surface area, but you can characterise that area much more effectively and that may improve your reproducibility.

Derek Gray

I agree. I am sure that it would improve our reproducibility.

Kari Ebeling UPM-Kymmene Corporation

How much was the kappa number for the TCF pulp, it was not indicated?

Derek Gray

The kappa number for the laboratory-refined TCF pulp kappa = 2.7.

Discussion

Jean-Claude Roux EFPG

How can you relate these nano mechanical properties to the scale of the millimeter or to the micro scale. Have you some ideas to make this correspondence, because I have fears about these kinds of measurements, it is interesting but I have trouble relating it to the real world.

Derek Gray

We hope there is a connection between our nano-world and the real world! For example, Prof. Peter Wild and his students at Queen's University, Kingston have built an apparatus that can make multiple cyclic compression on single pulp fibres. They have measured force/compression curves for the same pulps used in our work, and their refining results for the compressive modulus of collapsed fibres were surprisingly close to our values, which were measured at forces and deformations that were orders of magnitude smaller, as shown in Table 3, Hartler and Nyren measured much high compressive modulus.

Lars Wågberg

I support everything you are saying. The point that I would like to make is rather serious though because what we are doing is to measure global entities and interpret them on a molecular level, which is the wrong way around. What this is all about is to measure fundamental properties and to use the collected data to calculate how the fibres will deform in the fibre/fibre crossings. We are doing that at the moment, and by doing so you can really interpret from the molecular level the effect you would get on the fibre level, which is a new approach.

Peter Wrist Consultant

I am wondering whether the different moduli reported by Hartler and by yourself came about because you were each looking at different phases in the consolidation of the sheet. In Hartler's method he was considering the surface tension forces bending the fibres in the sheet to pull them into close proximity where they crossed on another in the early stages of consolidation . You were measuring the moduli of the surface structure, particularly where micro fibrils may be extending from the surface and which are in a much looser structure than the fibrils of the fibre walls. These are the micro fibrils which are capable of extending across the micro gaps between the two surfaces of contacting fibres and most likely contributes to bond formation

between the fibres. Then the distribution of soft and hard regions you measure on the fibre surface may reflect the potential of the different regions for contributing to bond formation and hence to the bond strength of the fibre structure.

Derek Page Institute of Paper Science & Technology

I very strongly believe that what you are doing here is right, and your results showing the very low transverse modulus of the cell wall. My reason is because first of all I believed in Tony Scallon's work where he found that the transverse modulus of the cell wall when it was wet was extremely low. Secondly I believe in Cousins work, I don't know if you are familiar with his work, but Cousins did work on the measurement of the elastic modulus of hemicellulose gels over a range of moisture contents from zero to completely saturated and found three orders of magnitude difference between them. Cousins used a micro indentation procedure and used your equations to get the elastic modulus out of a micro indentation. The micro indentation procedure has been around in material science for some time. Yours is a nano procedure, but I think that it is giving the same results. Cousin's values for wet hemicellose gels were exactly the same as your results here, so I think that it is alright. The problem came when Hartler and Nyren did their experiments and got very high values for the elastic modulus, I think that is explained by the fact that their values were obtained at very high pressure after the gel had been squashed until the fibrils were in contact with one another. In other words elastic modulus is an enormous function of moisture content, and I think you are getting correct values for the modules of the completely saturated cell wall.

John Parker Consultant

I would like to know how k is derived because it must have some connection to the width of the fibres, or is this not so?

Derek Gray

No, it should be independent of fibre dimensions, and depend only on fibre mechanical properties and the geometry of the indenting tip.

John Parker

You are talking of the indentation of the flat surface of a collapsed fibre?

Discussion

Derek Gray

Yes, exactly. Either we used the estimates for k from reference (IO) or from force indentation measurements on a silicone rubber substrate of known modulus according to Equation 4 on bottom of Page 217 (which should be labelled Equation 5). One of the critical things is some sort of linear dimension related to the tip, we tried to avoid that, it comes out much the same if you take the literature values for a radius of the tip, assume it is a hemisphere, there is lots of literature as Derek said on hemisphere pushing its way into a gel, and it comes out more or less right if you take that dimension and the spring constant that the manufacturer gave for the AFM tip but we eventually used the calibration procedure on the silicone gel, which turns out to have roughly the same compressive modulus as the range we were looking at by luck, so if you want, if you believe the sphere penetrating an infinite plate so that sort of number or the calibration, they both come out more or less the same order of magnitude.

Pekka Mauranen KCL

Derek Gray mentioned the influence of the salt content on the closeness of fibrils, and Derek Page mentioned also the importance of the moisture content on the modulus, so could you elaborate a little bit further on the influence of the physical chemical conditions on the conformability and the state of the fibres.

Derek Gray

This is a very good question, as I missed emphasizing one key point. In order to mount the fibres, they have to be dried down onto a glass surface. So although the initial pulps were in some cases never dried, the corresponding moduli are for once-dried fibres. Also, the fibres that we used for the compression measurements reported in Table 2 were not di-ionized.

Dick Kerekes University of British Columbia

I have been working on making some calculations about the forces acting on fibres in refining. For some time, I have been puzzled as to why these are so much lower than the force coursing fibre collapse formed by Hartler I too then Wilde's recent results from Queens. His levels which as I recall were up to two orders of magnitude lower, accord with the levels of forces of like compression that I have estimated in refining. So, from the refining point of view, things seem to be coming together.