Preferred citation: B. Duncker, N. Hartler and L.G. Samuelsson. Effect of drying on the mechanical properties of pulp fibres. In **Consolidation of the Paper Web**, *Trans. of the IIIrd Fund. Res. Symp. Cambridge, 1965*, (F. Bolam, ed.), pp 529–537, FRC, Manchester, 2018. DOI: 10.15376/frc.1965.1.529.

EFFECT OF DRYING ON THE MECHANICAL PROPERTIES OF PULP FIBRES

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Synopsis—Changes in the axial dimension of chemical pulp fibres were studied, using various combinations of drying and wetting. It was found that the commonly experienced elongation, brought about as a result of wetting, was exchanged for a shrinkage when the applied load before wetting was considerably lower than that applied before the preceding drying. Dimensional stabilisation was found for certain combinations of drying and wetting loads.

In addition, fibre stiffness was studied. During drying, the stiffness increased sharply within a dry solids content range of 15–35 per cent. Upon further drying, the stiffness of the late wood fibres did not change, whereas that of the early wood fibres was decreased. The former effect is most likely associated with an increased modulus of elasticity, whereas the latter is probably a result of changes in the fibre cross-section involving collapse.

Introduction

IN the papermaking process, the fibrous paper sheet is consolidated during drying, implying that water is removed from the space between the fibres and within the fibre material. The anisotropic nature of the fibre wall and the phenomenon of hydrogen bond formation suggest that important dimensional changes should be brought about as a result of drying from water through evaporation.

Relevant investigations reported in the literature mainly concern the paper properties, but a few studies have also been carried out on the effect on the individual fibres. In a wet fibre, elements of some sort are positioned at a distance from each other. On drying, this separation becomes less pronounced[1] and, as a result, the fibre shrinks considerably in its transverse

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direction.[2] The dry density of the cell wall varies for fibres of different origin and this can probably be explained on the basis of varying proximity between fibrils.[3,4] The result of drying is not only increased packing in the wall, but also a collapse that is more radical, the thinner the wall and the larger the diameter. This means that the alteration brought about by drying is much more drastic for early wood fibres than for late wood fibres as outlined originally by Emerton[5] and later, in more detail, by Jayme & Hunger.[6]

Upon drying, the modulus of elasticity increases for textile fibres,[7] but no information is available for woodpulp fibres. When dried under axial tensile load, wood fibres have a higher modulus of elasticity as well as breaking strength compared with fibres dried without restraint.[8]

Changes in fibre cross-sections, which also means moment of inertia, as well as in the modulus of elasticity are both important when considering the flexibility of the fibres. Measurements of the change in fibre flexibility caused by drying have been carried out by observing fibres in the shear zone of a Couette viscometer[9] and the results show that their flexibility is decreased.

In the present investigation, some properties of individual fibres have been measured and, in particular, the changes brought about by varying the moisture content of the fibre. Individual fibres were loaded to predetermined levels and changes in the stress measured. The observed effects could easily be evaluated as dimensional changes in length. Secondly, fibre stiffness was measured: factors affecting it are fibre dimension in the transverse direction, fibre collapse and modulus of elasticity.

Experimental

Preparation and sampling of fibres—The pulps studied in this investigation were prepared from spruce wood (*Picea excelsa*) from the south of Sweden. The wood density was 0.41 g/cm^3 (dry weight and dry volume). The width of the growth rings was approximately 5 mm. The procedures used in preparing the chips and in cooking have been described in earlier publications.[10,11] The chips were cut by hand so that the early wood and late wood pulps could be easily separated from each other after the cook.

Measurements of changes in stress in loaded fibres—For the stress measurements, unbleached sulphate late wood fibres were used. They were taken by tweezers from a suspension containing a comparatively large number of fibres and were fixed during the measurement at their ends by two clamps, one of which was connected to a strain gauge giving to a recorder a signal proportional to the force: the other was connected to a micrometer screw.

The paper in the recorder was driven at a constant speed of 12 mm/min. The moisture content of the fibres was changed by blowing nitrogen gas of different relative humidity on to the erected fibres. This gas was taken from a cylinder and 100 per cent rh obtained by passing it through a series of wash bottles containing water. To obtain 30 per cent rh, the nitrogen from the cylinder was passed through a cooling bath at $-40°C$ to decrease the relative humidity to the desired level. In both cases, the temperature of the conditioned gas was $20 \pm 0.5°C$.

External stresses in the length of the fibre were applied by increasing the gap between the micrometer screw, thus loading the fibre. The load was applied as fast as possible—that is, under 5 sec. Although only qualitative indications were aimed at, 10–15 replicates were made.

Measurements of the bending stiffness of fibres—For the stiffness measurements, unbleached sulphite and sulphate fibres were used. As fibres of a given moisture content should be used, thin sheets were formed from diluted fibre suspensions and these were dried in a desiccator, the temperature being about 20°C and the relative humidity about 20 per cent. By varying the drying time, fibres with different moisture contents were prepared. The moisture was determined by drying samples at 105°C. Samples for stiffness measurements were prepared by agitating the fibres with a propeller in silicone fluid with a viscosity of 1 cSt. When rewetted fibres were used for stiffness measurements, these were prepared by suspending the dried fibres in water.

Stiffness measurements were performed according to a technique described in an earlier publication.[12] Individual fibres were erected as cantilevers and bent by the force from a flowing liquid, directed at rightangles to the fibre axes. From the flow velocity, the deflexion of the fibre end and the suspended fibre length, the fibre stiffness was calculated. For the measurements of the stiffness of dry fibres, the liquid used in the testing apparatus was a silicone fluid with a viscosity of 20 cSt and, for the measurements on wet fibres, the liquid used was water.

The fibres were sampled by dilution of the suspension to a very low fibre concentration and taking out a volume containing about 50 fibres. Approximately 50 per cent of these fibres could be measured in the testing apparatus. The quoted values are the average of the medians of six independent determinations. The confidence limits at the 95 per cent probability level are about ± 10 per cent of the average stiffness value. The stiffness values are given relative to the stiffness of glass fibres, which has been determined by stress/strain measurements of the modulus of elasticity and by microscopic determinations of the diameter. The obtained value is 1.3×10^{-11} Nm^2 (Newton $\times$ square metre).

Results

THE changes in stress as developed in the fibre subsequent to application of a given load are shown in Fig. 1*a*. In the wet condition, a stress decrease was always observed subsequent to an application of a load to a given predetermined level. The stress decrease should be a result of elongation. After 5–10 min, this relaxation ceased and an apparent steady state followed. When the relative humidity was lowered to 30 per cent, an increased stress was observed as the drying gradually proceeded to a moisture content of approximately 5 per cent. This was interpreted as a shrinkage, which amounted to approximately 0.3 per cent.

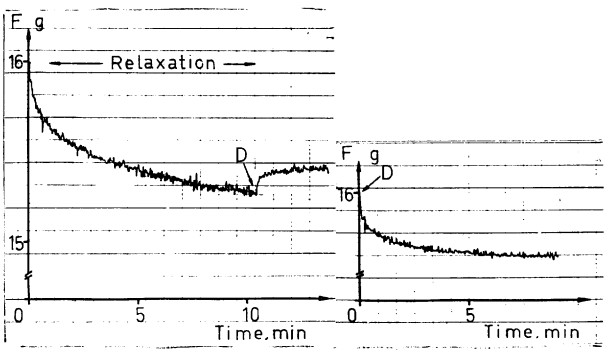

Fig. 1—Stress in a loaded fibre during the relaxation following application of the load and subsequent drying
(*a*) Ample time allowed for relaxation before drying
(*b*) No wet relaxation—that is, drying following immediately after the load application

When the drying followed immediately upon the load application, a smaller decrease in stress was observed as evidenced in Fig. 1*b*, being a net effect of two processes—relaxation of the applied load and shrinkage effected by drying. Depending upon the time between the load application and beginning of drying, any stress behaviour between the two extremes given in Fig. 1 could be experienced.

When the measurement of the developed stress started, the never-dried fibre was in equilibrium with nitrogen of 100 per cent rh. Similar measurements were made, but with the exception that the fibres throughout the period of mounting were exposed to a water fog. By doing so, the lumens of the virgin fibres were never emptied. After having reached an apparent steady

state in the stress, the water fog was exchanged for nitrogen of 100 per cent rh. A small steady increase in the stress was experienced and this was interpreted as being connected with cooling effects in the mounting device because of water evaporation. Any sudden change in stress, particularly when simultaneous with the emptying of lumen (which occasionally occurred), was never experienced.

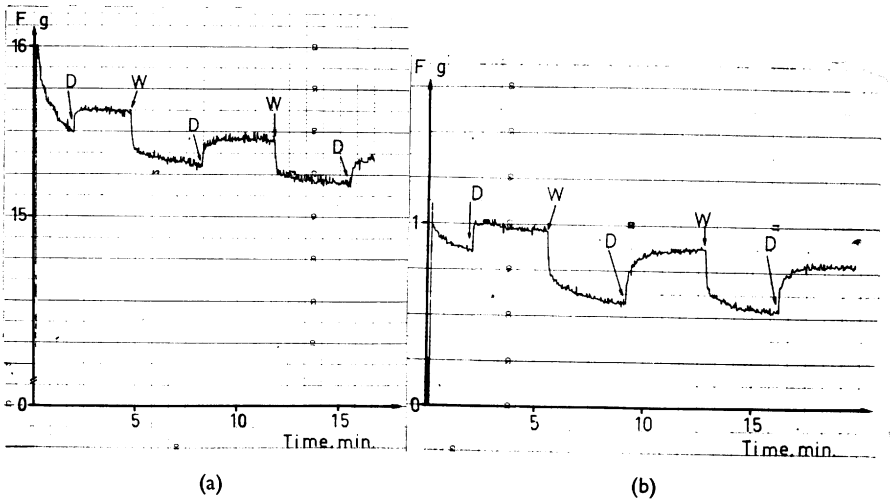

Fig. 2—Stress in a loaded fibre as a function of time with successive drying and wetting (D = drying, W = wetting)—
(*a*) Externally applied load of 16 g before drying as well as to wetting
(*b*) Externally applied load of 1 g before drying as well as to wetting

After drying, the fibre was wetted in nitrogen of 100 per cent rh. If no external change in load was made from drying to wetting (Fig. 2), the stress decreased—that is, elongation occurred. When the load externally applied before wetting was larger than that applied before drying (Fig. 3), the stress also decreased, but was more pronounced in this case than in that corresponding to data presented in Fig. 2.

When the load applied before wetting was decreased below that applied before drying, the stress decrease became less and less pronounced and finally turned into an increase—that is, shrinkage. Such conditions are shown in Fig. 4, in which case the load before drying was adjusted to 16 g and before wetting to 1 g. At a given intermediate load, the fibres could be wetted without

any resultant dimensional change in length. This can be seen from Fig. 5, where mutually connected loads are found as intercepts on the abscissa. Experiments were performed at wetting loads of 1, 8 and 16 g. The fitted curves in Fig. 5 are based upon averages having a confidence limit at the 95 per cent probability level of ± 0.07 g.

There seem to be two different effects operating during wetting—liberation of the shrinkage potential and elongation caused by applied load. Shrinkage potential and wetting elongation counteract each other and it is understandable that the net effect can be an elongation (Fig. 2 and 3), a shrinkage (Fig. 4) or a dimensional stabilisation (Fig. 5).

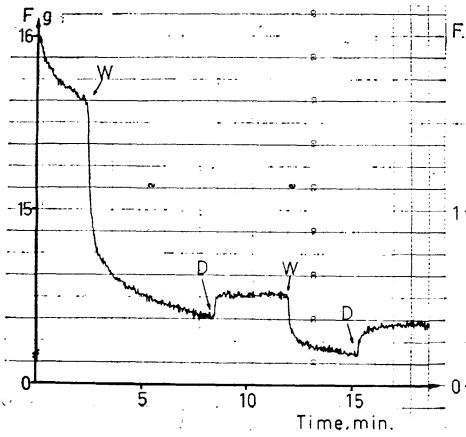

Fig. 3—Stress in a loaded fibre as a function of time with successive wetting and drying: applied load before the first period of drying was 1 g followed by an externally applied load of 16 g before the subsequent operations

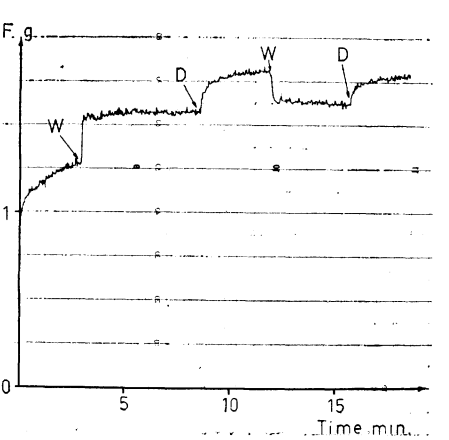

Fig. 4—Stress in a loaded fibre as a function of time with successive wetting and drying: applied load before the first period of drying was 16 g followed by an externally applied load of 1 g before the subsequent operations

After the first cycle of drying and wetting, the fibre was subjected to additional similar cycles. Throughout, the drying resulted in shrinkage and wetting in elongation provided that, as in all the experiments reported, the externally applied wetting load was not too low compared with that applied before drying.

The average course of the stress throughout all the cycles was found to be a relaxation in those cases corresponding to Fig. 2 and 3. The net curve has the initial wet relaxation as a basis, with superimposed contributions from each drying/wetting cycle. On the other hand, a recovery is experienced when the

load externally applied before wetting is considerably lower than that applied before drying (Fig. 4). In this case, the dry recovery curve forms the basis, with superimposed contributions from each drying/wetting cycle. These contributions correspond to incremental liberations of potential shrinkage (dried-in stresses).

In Fig. 6, it can be seen that the stiffness of the fibres was increased by drying up to about 35 per cent solids content. On further drying, the stiffness levelled out for late wood fibres, but decreased to a lower level for early wood fibres. Wetting of the fibres seemed to bring back the stiffness to a level

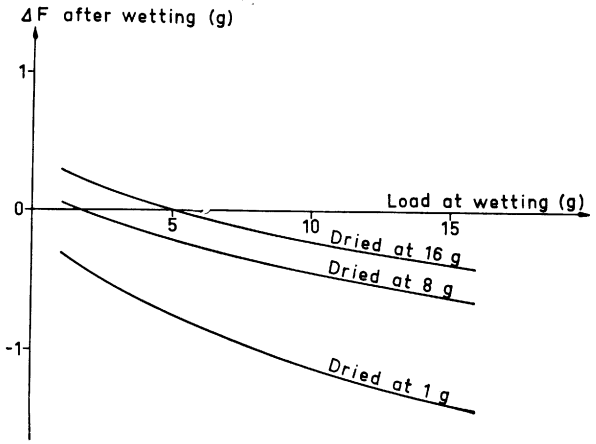

Fig. 5—Change in stress (ΔF) in a loaded dry fibre as a result of wetting plotted against load before wetting with load applied before the preceding drying as parameter

in the order of the original stiffness value. The scattering in the results does not permit any conclusions to be drawn about the differences between sulphate and sulphite fibres. The fact that the stiffness decreased for early wood fibres, but not for late wood fibres, can be explained qualitatively by considering the change in cross-section—thus, moment of inertia—for the two types of fibre. The tendency for early wood fibres to collapse is much more pronounced than for the late wood fibres and this should cause a more pronounced fall in the moment of inertia for the former than in that for the latter on drying.

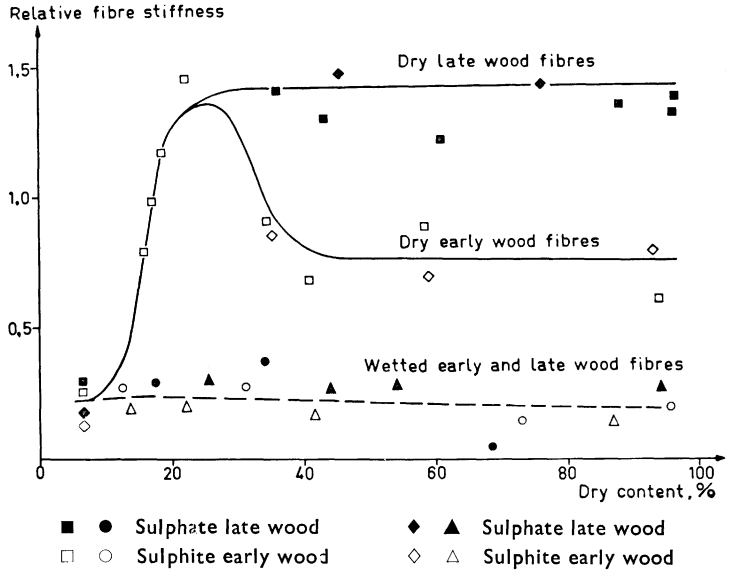

Fig. 6—Relationship between relative stiffness and solids content of the fibre—The two upper curves represent dried fibres measured in silicone fluid and the lower curve wetted fibres measured in water

Discussion

On drying from water by means of evaporation, a fibre inherently shrinks. The more this is impeded through application of a load before drying, the greater the potential for shrinkage under low loads upon subsequent wetting. Ordinarily, the fibre changes its axial dimension upon wetting, but the externally applied load before wetting can be adjusted to counterbalance the two opposing effects and so prevent any axial dimensional movement in connection with wetting. Those drying and wetting loads found experimentally to be mutually connected are 16–5 g and 8–2 g, respectively.

For the dimensional stability of paper, changes in the transverse dimension of the fibre are far more important than those in the axial dimension. In spite of this fact, qualitatively similar results were obtained for paper by Fahey and Chilson.[13] They found that the dimensional stability of a paper is improved by restraining it from shrinkage during drying.

More important for the consolidation of the paper web are the results of changes in stiffness during the gradually proceeding drying. At a very early stage in drying, between solids contents of 15–35 per cent, the stiffness increases most markedly for early wood as well as for late wood fibres. This

increase is most likely a result of an increase in the modulus of elasticity. It is not known during which phase of the drying this increase takes place, but the data in Fig. 6 suggest the above explanation. Nor is it known during which phase of the drying dimensional changes in the transverse direction and subsequent collapse take place. This collapse, which can be expected to bring about a much more pronounced effect for the early wood fibres than for the late wood fibres, seems to be particularly responsible for the decrease in stiffness observed for the early wood fibres at moisture contents between 35 and 50 per cent. This difference between the two types of fibre, brought about by rather far-reaching drying, is probably most important for the conformability of the fibre when the bonds are to be finally established.

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Discussion

Chairman—Van den Akker and his co-workers have shown a considerable change to occur in the property of the fibres when they are alkali-extracted, which they attribute to decrease in hemicellulose content. If you treat a fibre with 8 per cent potassium hydroxide, is not a considerable proportion of the native cellulose converted to cellulose II? Could not the onset of mercerisation be more responsible for the effect than that portions of hemicellulose are extracted?

Dr J. A. Van den Akker—Spiegelberg observed that the 002 diffraction peak was not disturbed by treatment with 8 per cent potash solution, thus showing that the cellulose remained cellulose I. He was very concerned, of course, with both this and the problem of degradation, which he handled as described in the paper.

It is difficult to resolve the differences between the data of Duncker, Hartler & Samuelsson and ours (as someone has asked), because the bases were different. In the Swedish work, the fibre was quickly extended a fixed distance, whereas in our laboratory the fibre was subjected to a fixed load and so permitted to extend. When a fibre of helical structure is dried under constant load and is free to extend, the structure after drying is different from that of a fibre dried under fixed strain and would have different properties. Without a doubt, a complete resolution of the two sets of results must await more information on the visco-elastic properties of wet and dry fibres.

Chairman—Indeed, the trouble is that we do not understand the background of visco-elastic properties of any material, whatever it is, so the problem is really of quite a magnitude.

Dr B. Leopold—Van den Akker referred to the work that McIntosh and I have done as being along the same lines as his own. What I have to say refers to the Chairman's question on the effect of alkali extraction. Our results show that the most drastic effect of extraction on fibre strength occurs at the lower end of the concentration range; in other words, long before cellulose II has

a chance to appear. We observe no change once the concentration range is reached when mercerisation is likely to occur, which I think supports what Van den Akker said. We have been bolder than he in trying to attribute the changes to specific fractions of the hemicellulose and think that the removal of xylan is mainly responsible for the fall in fibre strength.

Dr C. A. Jentzen—Referring first to the Chairman's question, after extracting cotton fibres with the same treatments used for the pulps, an increase in the modulus occurred, whereas extraction of the pulp caused a decrease in modulus. Then, additional experiments were run to confirm the results of sudden extension at the start of drying. Measurements taken at several span lengths gave the same percentage elongation, which indicated no fibre slippage in the clamping jaws. The exact time of extension and its amount were predictable and reproducible.

Prof. H. W. Giertz—We have to keep in mind that the hemicellulose, which is supposed to be located between the microfibrils, is plastic when wet, but stiff when dried. Thus, the dried fibre is composed of two solid phases—the anisotropic microfibrils (which are extremely strong in their length direction) and the more or less isotropic hemicellulose. When the fibre is loaded, the microcompressed areas will elongate and the hemicellulose in these parts will be broken down. This flow elongation will proceed until the microfibrils are straightened. With this approach, the flow properties of paper should be referred to the irreversible microcracking of the interfibrillar hemicellulose material.

Mr D. H. Page—Had Giertz not commented as he did a few minutes ago, I would probably have said exactly the same thing, except that I would have left out the word hemicellulose.

I would like to refer to Fig. 4C of the paper on load elongation properties of fibres by Kallmes & Perez and to the comment on it in the text—'Quite frequently, fibres picked from handsheets underwent a small plastic deformation somewhere in the middle of the curve (Fig. 4C). This may have been caused by a removal of microcompressions or straightening of the fibres . . .' Now, if we have a fibre with a microcompression in it and it gives under test a stress/strain curve like that of Fig. 4C, this implies that the stress/strain curve of the microcompressed region of the fibre would be quite similar to the curve for paper, having an initial elastic region followed by an appreciable plastic region. There would seem to be a case for the view that we expressed at Oxford that the whole stress/strain curve of a paper containing appreciable

microcompressions can be explained by the stress/strain curve of microcompressed fibres and that the random structure of paper merely acts to produce an averaging effect.

Mr J. A. S. Newman—In the investigation of the stress/strain characteristics of fibres, we appear to be at the same point we were ten years ago in the investigation of the stress/strain characteristics of paper. The explanation of paper strength properties is not being validly based on the statistical geometry of the fibre network. Equally, I believe that the theory of the strength properties of fibres should be based on the concept of the statistical geometry of a network of fibres or of microfibrils inside the fibre itself, which are cross-linked or bonded together at discrete points.

Mr P. A. Tydeman—I do not want to appear ungracious after the extensive reference to microcompression made by Kallmes & Perez, but I have one comment to make on the cross-direction or transverse modulus of fibres, which has obvious importance. I think that there is an anomaly. The argument is that, by bonding other fibres at random to your tensile test fibre, its modulus is doubled. The implication that at least as much fibrous material again is bonded to the test fibre seems unlikely upon consideration of your method. Can this apparent anomaly be explained?

Prof. B. G. Rånby—May I first refer to the question of visco-elasticity. I am not as pessimistic as the Chairman about the state of knowledge of visco-elasticity in polymer systems: I think the theory is in good shape for amorphous polymers. For partly crystalline polymers, the interpretation is more difficult. For papermaking fibres, the problems are even more difficult, because the virgin wet fibres are thixotropic.

I would like to make one remark about the properties of papermaking fibres by referring to the *Summing up* at the Oxford symposium in 1961—published, but not much observed. There is accumulating evidence that the hemicelluloses are fairly well ordered, in the native fibres, although they are *not* X-ray crystalline. It can be shown that the hemicelluloses carry part of the load when the pulp fibres from wood are stretched or dried under tension. There are close relationships between the cellulose microfibrils and the hemicelluloses—for example, well-ordered hydrogen bonds. Our recent NMR data gives support to this concept and they will be published elsewhere.

Dr O. J. Kallmes—First Tydeman's comments. The measurements consisted of taking a small section out of a thin sheet, then one fibre from the

sheet, with numerous fibres bonded to it, was strained to a point below failure and relaxed. All the fibres were carefully pulled off and its stress/strain curve measured. The fibre was not completely bonded, but there were several fibres almost parallel to that being strained. This showed whether or not this technique would be sensitive to fibres bonded to it.

In reply to Hudson's comment, fibre properties varied throughout the sheet to a far greater extent than is generally realised. This is what I was referring to.

The curves referred to by Page are purely speculative so far as curves in paper go. We have never measured stress/strain curves of fibres in paper, though we have developed a technique of measuring the size of strains in paper and found the variation of strain along a fibre to be very marked. Some stretch tremendously, some parts do not stretch at all, so it is from this idea that I drew this curve. There are many ways you could draw the curve and Fig. 4C was purely speculative. These are the only two that have been measured and they were measured on fibres in air.

It is going rather far to say that microcompression explains the stress/strain behaviour of paper. This picture does not take into account, for example, bond failure, nor does it take into account the parts of the fibre that are stiff and straight. In other words, in a sheet dried under tension in this direction, fibres lying in this direction did not shrink and there are no microcompressions.

Chairman—It is easy to speculate. May I remind you that, about 15 years ago, Eyring and a few others were working on stress/strain properties of different fibres. Some types of wool exhibited unusual kinks in their stress/strain curves. Within half a year, Eyring & Halsey produced a beautiful absolute reaction kinetic theory that explained this new feature. It was found that the diameter of this specific form of wool fibre was not uniform.

We are dealing with natural fibres, which are very complicated in their build-up; when we measure stress and strain on single fibres, we are dealing with something that is rather poorly defined material geometrically. It is probably easier to make theories than to make observations. We have many new observations today and I think the future will bring more.

Mr L. G. Samuelsson—In preparing our specimens for fibre stiffness measurements, thin, wet paper sheets were dried in a desiccator to different solids contents by varying the time. It is important to remember this, because no conditioning of the specimens occurs under these circumstances. The drying conditions could rather be compared with those present on the paper-machine. Since we cannot expect an even moisture content in the fibre material, the outer fibre surface, which is most efficiently exposed to the drying

medium, can very well have a high solids content, even if the inner parts of the fibre are still wet. We believe, therefore, that the increase in fibre stiffness during drying can occur within the range 15–35 per cent solids content, since it is the outer layer of the fibre that most probably determines the stiffness of the fibre.