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The Mechanical Properties of Single Wood Pulp Fibers. III. The Effect of Drying Stress on Strength

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Synopsis

An experimental study has been made of the effect of drying tension on the tensile strength of single fibers from several wood species pulped in various ways. Some pulps are strengthened by drying stress, whereas others show no response. These apparently contradictory results are explained in terms of the effect of drying stress on the morphologic features responsible for strength. In part I of this series, it was shown that fiber strength is controlled by the fibril angle of the S_2 layer and the extent and severity of defects. These defects are mostly the local disturbances of fibril alignment termed "dislocations," "slip-planes," or "microcompressions." It appears that drying stress strengthens fibers both by reducing the fibril angle and by aligning the fibrils in the dislocated regions. This is only possible, however, if the matrix between the fibrils can flow in shear under the applied stress. Thus, strengthening is possible for fibers of high hemicellulose content, the matrix of which flows readily in the water swollen state. Strengthening does not occur, however, for predried kraft fibers or alkali-extracted holocellulose, for which the matrix is well bonded and insufficiently swollen.

INTRODUCTION

In the papermaking process, tensile stresses applied to the drying web by the machine draws enhance the tensile strength of the dry sheet. The mechanism of enhancement is uncertain, but it has been argued that the strength of fibers is increased by the axial stresses they experience during drying. Early work with textile fibers[1-4] showed that their strength could be appreciably increased by drying stresses, and four research workers, Kallmes and Perez,[5] Jentzen,[6] and Spiegelberg,[7] have sought the same effect for wood pulp fibers. Kallmes and Perez, working with a commercial, never-dried, unbleached kraft pulp from pine and spruce, found that fiber strength increased with increasing drying stress, but the scatter in their data was large and the increase was not statistically significant. Jentzen used a holocellulose sample, carefully prepared from the 23rd growth ring of a 31-year-old tree of longleaf pine, and found that drying stress increased strength considerably. Spiegelberg obtained similar results on holocellulose fibers, alkali extracted to various degrees, from the 27th and 28th growth rings of a 49-year-old tree of longleaf pine. A plot of Jentzen's and Spiegelberg's data for unextracted holocellulose is shown in Figure 1. The slightest drying stress caused a large strength increase, but further stress increments only caused modest strength increases. Jentzen found that the highest

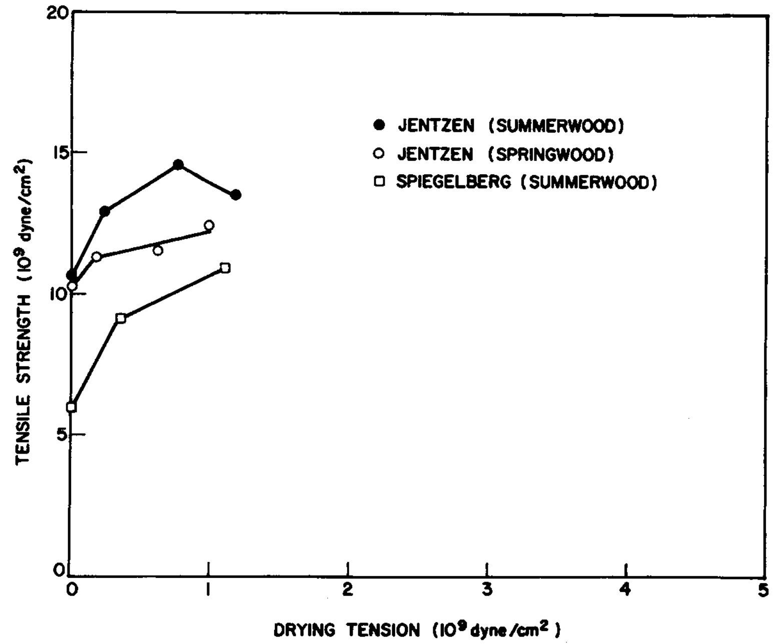


Fig. 1. Effect of drying tension on tensile strength of holocellulose fibers. Data of Jentzen and Spiegelberg. Each point is the mean of 30–70 fibers.

drying stresses caused a loss of strength, but this was not confirmed by Spiegelberg.

The mechanism of strength increase is not clear. Both authors hypothesize that improved orientation of the crystallites and improved stress distribution between the fibrils are responsible, but these concepts were not developed further in morphologic terms and the evidence presented was indirect. In a recent paper from this laboratory,[8] it was shown that the tensile strength of fibers can be related to morphologic features. Two factors seem to be in control:

1. The fibril angle of the S_2 layer. This layer contains by far the larger part of the cell wall material and consists of cellulosic fibrils helically wound at an angle, termed the fibril angle, to the fiber axis. The fibrils are held together by an amorphous matrix of hemicellulose and lignin, so that the structure is analogous to a fiber-reinforced resin. As expected from this analogy, the strongest fibers are those with a fibril angle of zero, the strength gradually falling off with increasing fibril angle.

2. The extent and severity of defects. Substantially, these consist of features variously termed dislocations,[9] slip-planes,[10] and microcompressions,[11,12] that are induced by bending and compressive stresses during chipping, pulping, defibering, refining, and drying. They are local disturbances in the direction of the fibrils and are thus easily seen in the polarizing microscope as illustrated in Figure 2a. The changes in fibril direction that the micrograph implies are shown in Figure 2b. These dislocations weaken the fiber probably by setting up stress concentrations in an otherwise evenly stressed structure.

It is reasonable that drying stress could increase fiber strength because of a possible effect on fibril angle and defect structure. Firstly, by shearing the water-swollen interfibrillar matrix, it could reduce the fibril angle of the S_2 layer.

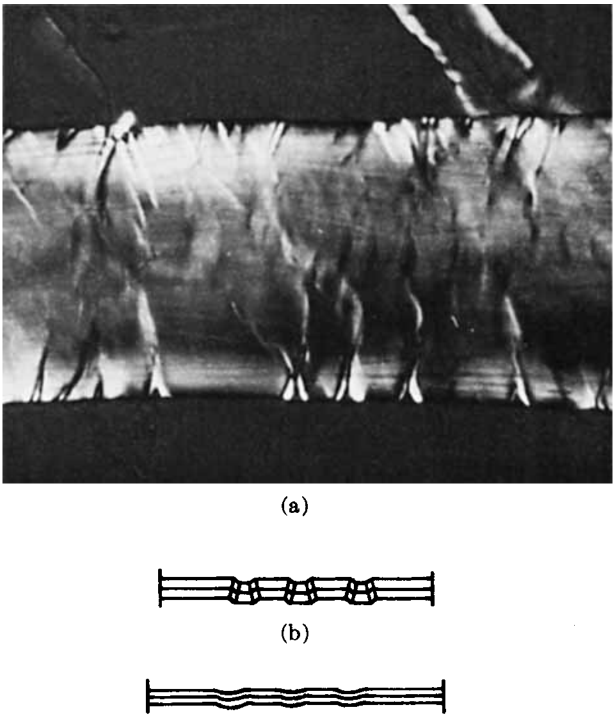


Fig. 2. (a) Polarized light micrograph of pulp fiber with dislocations at lower edge. (b) Schematic diagram showing the changes in fibril direction at the lower edge of the fiber of Fig. 2a. (c) Proposed change in fibrillar alignment when fiber is dried under load.

Secondly, also by shearing the matrix, it could restore the fibrils in the dislocations to a more straightened form as in Figure 2c and thereby relieve the stress concentration. The work described here attempts to determine whether strength improvement can be explained by these effects.

EXPERIMENTAL

The pulp samples used were prepared largely from individual growth rings to ensure similarity of fibril angle within a sample. Seven pulps were made from black spruce, white pine, white spruce, and loblolly pine. Details of the samples, species, and pulping processes are given in Table I.

The procedures for fiber preparation and apparatus for measuring the tensile properties are complex and will be described fully elsewhere. The essential details follow.

Each pulp sample was permitted to dry in air as a loose mat which was then impregnated under vacuum with mercury for subsequent measurement of fibril angle using the method of Page.[13] The pulp mat was reslurried using gentle agitation.

Single fibers were transferred from the slurry to a drop of water on a microscope slide that had been made water repellent by treatment with dichlorodimethylsilane. A small sliver of coverslip, about 0.75×4 mm, was laid across each fiber

TABLE I

Sample	Species	Origin	Pulping process	Fibril angle, degrees		Predrying treatment
				Mean	S.D.	
A	Black spruce	80th growth ring of 106-year-old tree	chlorite holocellulose	5.0 (estimated)	—	dried in loose mat but not impregnated
B	Black spruce	80th growth ring of 106-year-old tree	chlorite holocellulose	3.54	2.64	dried in loose mat and impregnated with mercury
C	Black spruce	55th growth ring of 106-year-old tree	chlorite holocellulose extracted with 9% KOH	7.39	3.18	dried in loose mat and impregnated with mercury
D	Black spruce	80th growth ring of 106-year-old tree	kraft, 60% yield	3.52	2.85	dried in loose mat and impregnated with mercury
E	White pine	71st growth ring of 73-year-old tree	chlorite holocellulose	21.96	1.83	dried in loose mat and impregnated with mercury
F	White pine	71st growth ring of 73-year-old tree	kraft, 60% yield	13.25	2.73	dried in loose mat and impregnated with mercury
G	White spruce	representative sample of whole tree, 84 years old	kraft, 60% yield	23.00	2.40	dried in loose mat and impregnated with mercury
H	Loblolly pine	12th growth ring of 23-year-old tree	chlorite holocellulose	43.00	5.32	dried in loose mat and impregnated with mercury

and held down under light pressure until dry. The fiber was thus prevented from twisting along the pressed length and was conveniently flattened for microscopic observation. At this stage, the fibril angle was measured using the mercury reflection technique.[13] The coverslip was lifted using a micromanipulator. The fiber tends to adhere to it rather than to the hydrophobic slide, so that the slide could be removed and replaced by a prepared mount consisting of two glass tabs separated by a constant gap and held in place by two stiff cards glued between the tabs. The coverslip with its adhering fiber was laid across the gap, the protruding fiber ends were glued, and the cover slip was removed. The glue, an epoxy resin, was brought to the edge of the tabs. In this way, the fiber was never stressed during mounting since it was never handled in an unsupported state. The glass tabs were mounted in the jaws of the tensile tester, and the supporting cards were burned through with a hot wire leaving the fiber as the only link between the two jaws.

The tensile tester is an Instron table model heavily modified for improved stability and precision. It is fitted with a Zeiss research polarizing microscope to permit observation of the fiber during mounting and testing, and a ciné camera to provide a permanent record of the observation.

The test span was maintained at 0.35 mm for all samples, and the straining rate was 0.02 cm per minute. The relative humidity of the test room was maintained at 50 ± 1% and the temperature, at 71 ± 1°F.

Following testing, a part of the fiber was cut away for measurement of cross-sectional area according to Hardacker's method[14] modified in this laboratory. In this method, the fiber is compacted between two glass slides, the compacted thickness is determined by interference microscopy, and the compacted width, by using a microscope fitted with a measuring eyepiece.

The following procedure was used for drying fibers under load. After mounting the fiber in the test apparatus, it was wetted by a drop of water from a syringe. The fiber was strained until the prescribed load was reached. The fiber was permitted to dry while the load was maintained by manual adjustment of strain. The loss of water from the lumen could be clearly observed in the microscope, and drying was judged complete 15 min later. The stress was then brought to zero, and a further 15 min was allowed to elapse before the fiber was tested to failure.

The fibers were dried using a much wider range of drying tensions than that used by previous authors, from 0 to 5×10^9 dynes/cm^2.

RESULTS

The data for the seven pulps examined are presented in the graphs of Figures 3, 4, and 6 to 11. Each point is the result of a single test. The points on the ordinate refer to fibers that have been dried in the usual way beneath a cover glass but have not been rewetted and dried. They will be referred to as "untensioned" fibers.

DISCUSSION

The most remarkable feature of this work is the general absence of the so-called Jentzen effect. For only three of the seven pulps examined is there any effect of drying tension on strength. As we will see, however, the results fit a consistent

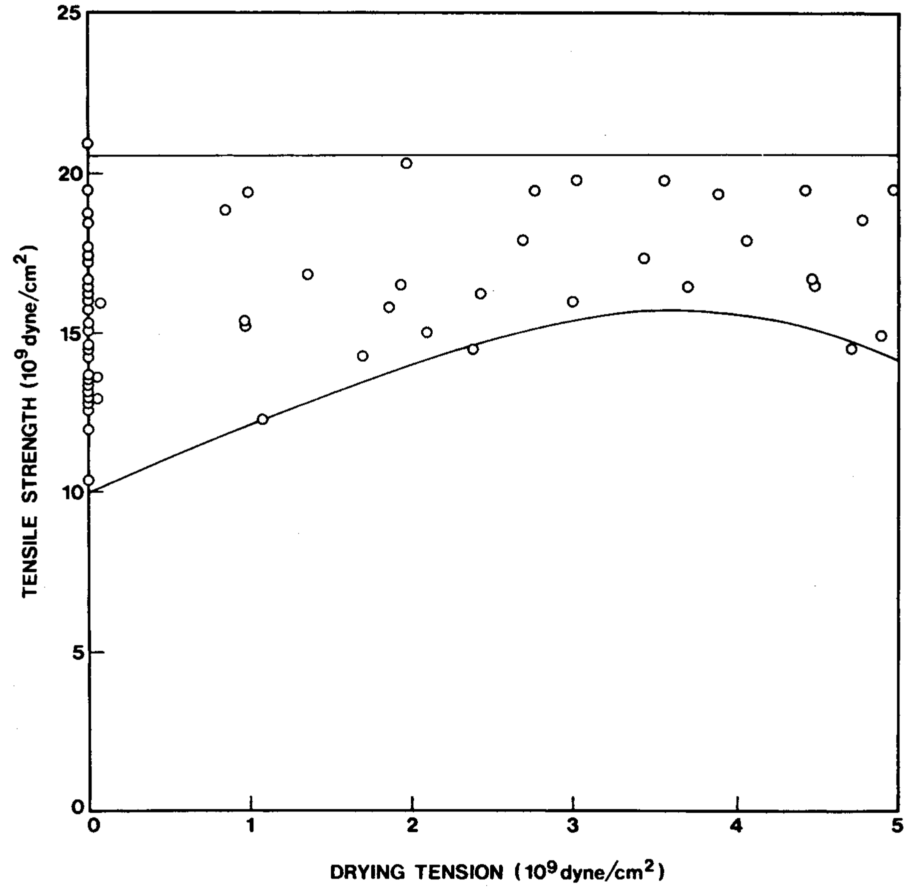


Fig. 3. Effect of drying tension on tensile strength of black spruce holocellulose fibers, air dried. Sample A.

pattern that not only gives meaning to this study but provides a deeper understanding of the earlier work of Kallmes and Perez, Jentzen, and Spiegelberg. The results will be discussed under two headings.

Fibers of Low Fibril Angle—the Effect of Drying Tension

The fibril angle of the S_2 layer and the presence of defects control fiber strength as reported in the introduction.[8] In order to test whether drying tension affects strength through these two factors, fibril angle was first eliminated as a variable by selecting fibers with fibril angles less than 10°, a range within which strength is independent of fibril angle.

Figure 3 gives data for black spruce holocellulose fibers, air dried and not impregnated with mercury. The strength of the untensioned fibers ranges from 10 to 21 dynes/cm^2. On drying under load, this wide range is reduced, the mean is increased, while the upper limit of strength remains constant. It seems that the weakest fibers are strengthened by drying tension while the strongest are unaffected. Strength improves gradually with increasing drying tension, although there is some indication that at the highest stress a slight loss in strength occurs.

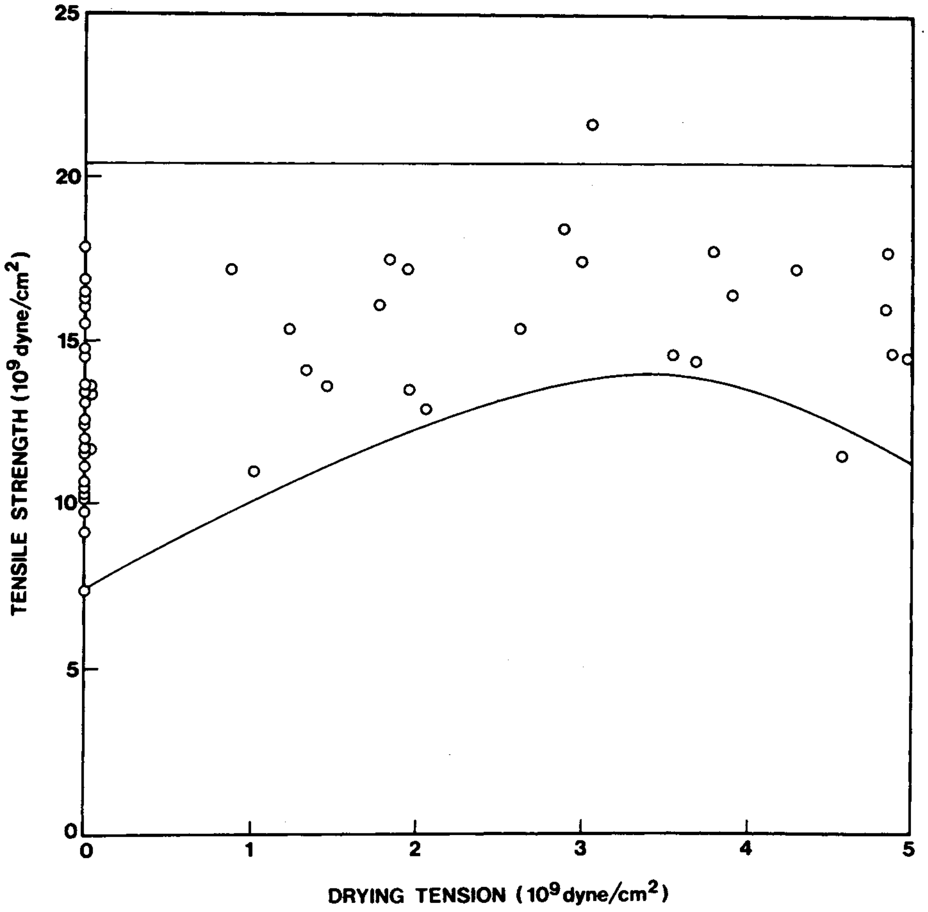


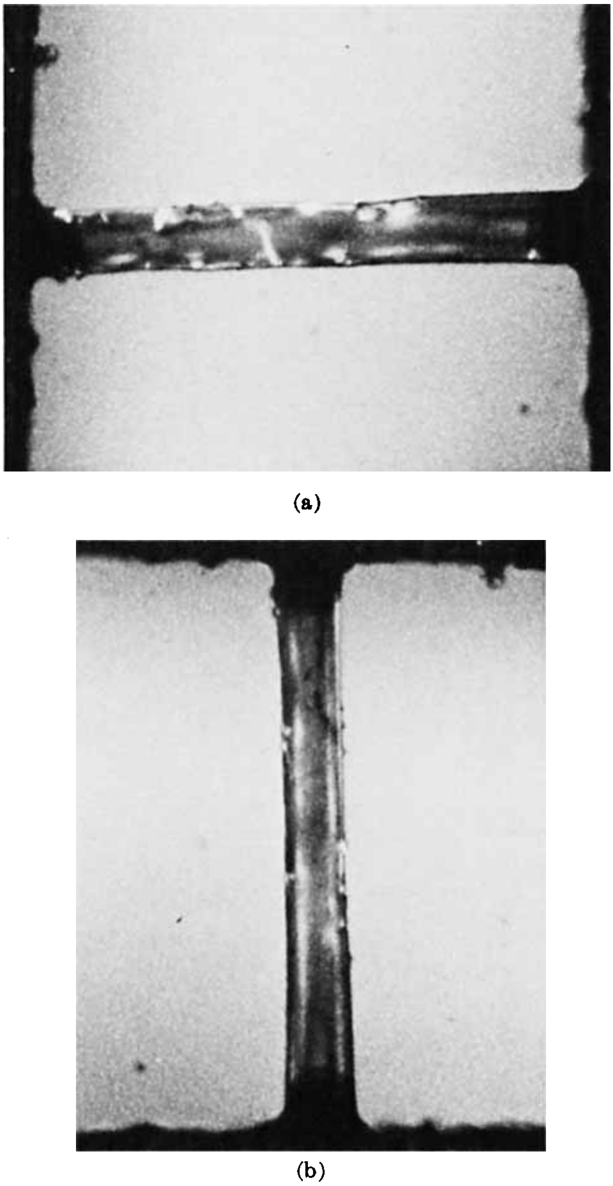
Fig. 4. Effect of drying tension on tensile strength of black spruce holocellulose fibers, dried and mercury impregnated. Sample B.

These results were confirmed in a further experiment using the same pulp mercury impregnated (Fig. 4). Although the overall strength of the fibers is slightly reduced, probably by the vacuum drying that precedes mercury impregnation, the general pattern is identical.

As proposed in the introduction, these results may be explained by the response of dislocations to drying tension. Dislocations may be removed by subjecting the water-swollen fiber to axial stress; this is clearly revealed by microscopic observation as demonstrated by Figure 5. Drying tension thus strengthens the weakest fibers by pulling out dislocations but cannot strengthen the strongest which are free from dislocations.

Apparently contradictory results were obtained for two other pulps prepared from the same black spruce tree. Figures 6 and 7 give data for holocellulose extracted by alkali and 60% yield kraft, respectively. As with holocellulose, the strengths of the untensioned fibers covers a wide range, but *drying tension has no effect at all* either on the mean strength or its distribution.

These results may be explained by resorting to a further postulate. It is suggested that dislocations can only be removed by drying tension if the inter-



(a)

(b)

Fig. 5. Ciné stills of a wet fiber (a) before straining and (b) under load of 0.5×10^9 dynes/cm^2.

fibrillar matrix is sufficiently swollen in water to allow it to flow. Holocellulose fibers even after drying and rewetting are highly swollen, and the matrix should easily flow under stress. Alkali-extracted holocellulose and kraft fibers are less swollen when rewetted, and the more rigid matrix could resist removal of dislocations.

Fibers of High Fibril Angle—the Effect of Drying Tension

The behavior of holocellulose fibers of white pine and loblolly pine is shown in Figures 8 and 9. For both samples, fiber strength increases with drying tension.

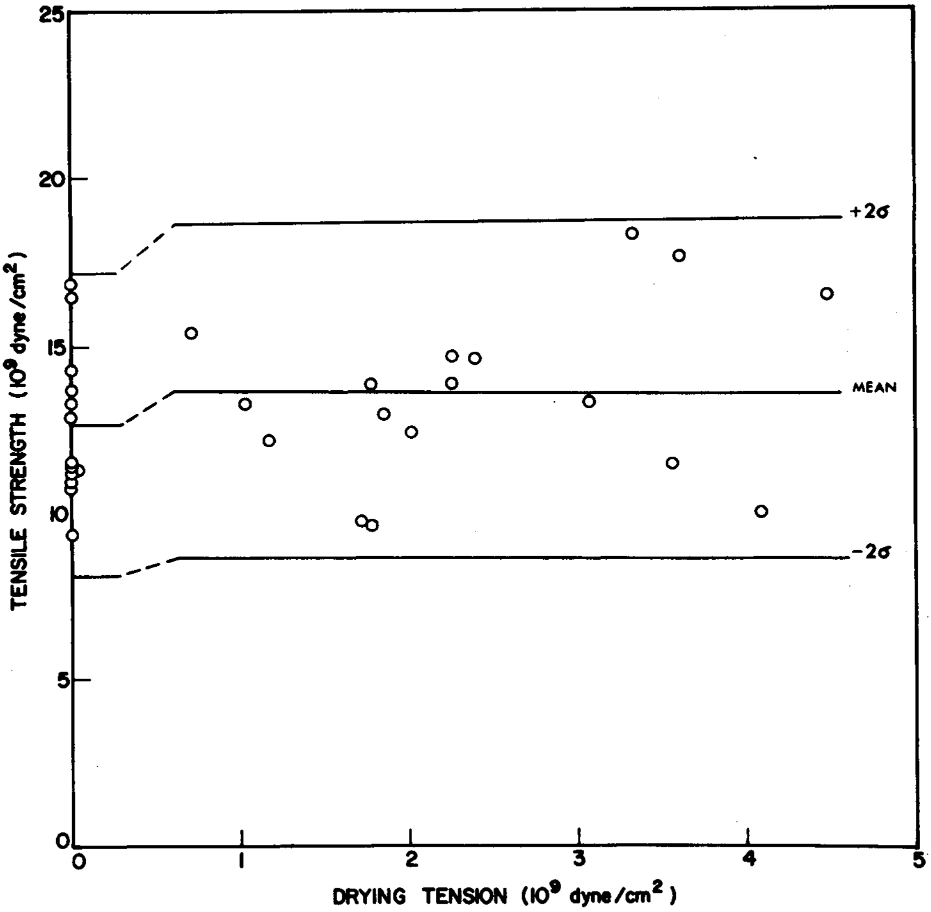


Fig. 6. Effect of drying tension on tensile strength of black spruce holocellulose fibers extracted with 9% KOH solution, dried and mercury impregnated. Sample C. In this figure and also Figs. 7, 10, and 11, the means and 2σ limits of both the untensioned and tensioned fiber strengths are indicated.

The manner of increase is quite different from that of low fibril-angle fibers. It occurs over the whole range of drying tensions; it is not caused apparently by a strengthening of the weakest fibers only, thus increasing the mean and reducing the standard deviation, but by a general increase in the strength of all the fibers. These results are explained by a reduction in fibril angle caused by the drying stress. In earlier unpublished work,[15] it was shown that when wet holocellulose fibers are strained, the fibril angle is reduced by shear between the fibrils. The reduction in angle can be quite large, from, say, 25° to 10°; this would be expected to cause an increase in strength of about 50%[8] which is of the order observed.

Predried kraft fibers behave differently. No increase in strength occurs on drying under load (Figs. 10 and 11). The explanation may be similar to that given earlier for the absence of strength increase for kraft fibers of low fibril angle. Bonding takes place in the matrix between the fibrils during the first drying; but because the kraft fibers do not swell highly in water, these bonds are

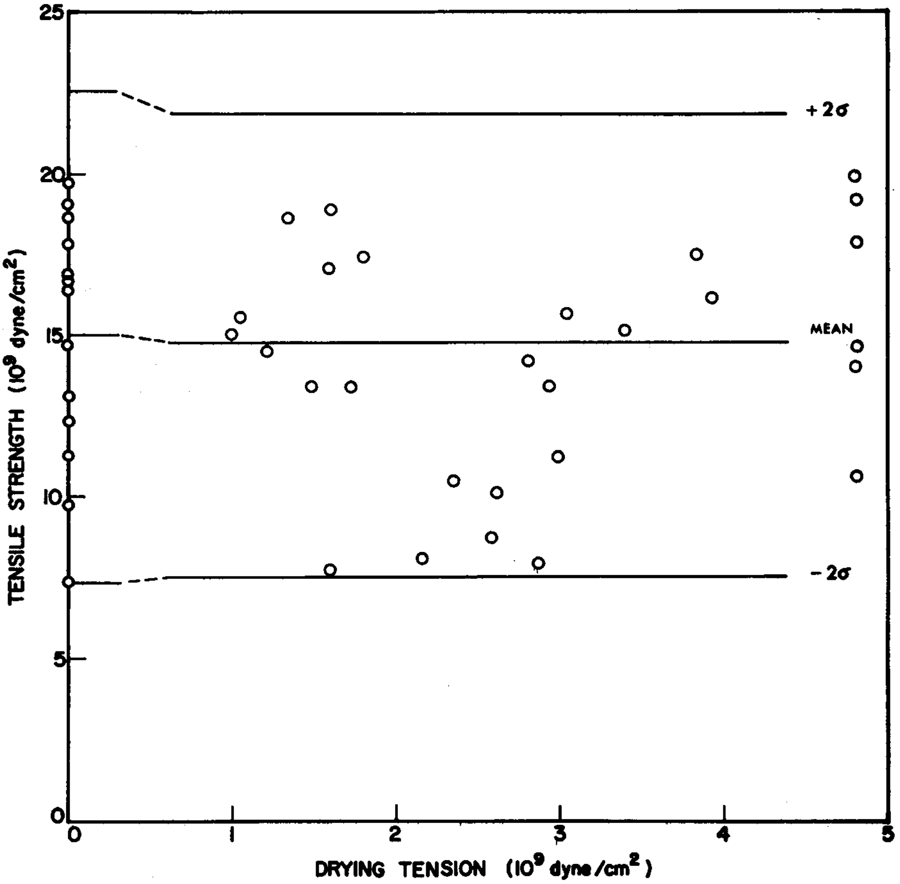


Fig. 7. Effect of drying tension on tensile strength of black spruce 60% yield kraft fibers, dried and impregnated. Sample D.

not broken and the shear in the cell wall necessary to allow a fibril angle change cannot occur. The hypothesis is supported from the stress–strain curves of Figure 12 for wet kraft and holocellulose fibers of high fibril angle. For holocellulose, a point is reached on the stress–strain curve where the structure yields, presumably in shear, but this point is never reached for kraft.

CONCLUSIONS

The work on the effect of drying tension on strength now forms a complete picture. There are two mechanisms. Dislocations formed during defibering, refining, and other mechanical treatments act as stress raisers and lower fiber strength. In some circumstances, the dislocations can be pulled out under tension and the strength of the fibers is restored. This is the only mechanism for fibers of low fibril angle. Fibers of high fibril angle can be strengthened by the reduction in fibril angle that drying stresses produce. Both mechanisms only operate, however, if the matrix between the fibrils can be sheared in the wet state. For holocellulose pulps, the fibers are sufficiently swollen that shear is permitted and strengthening occurs by either or both mechanisms. In once-

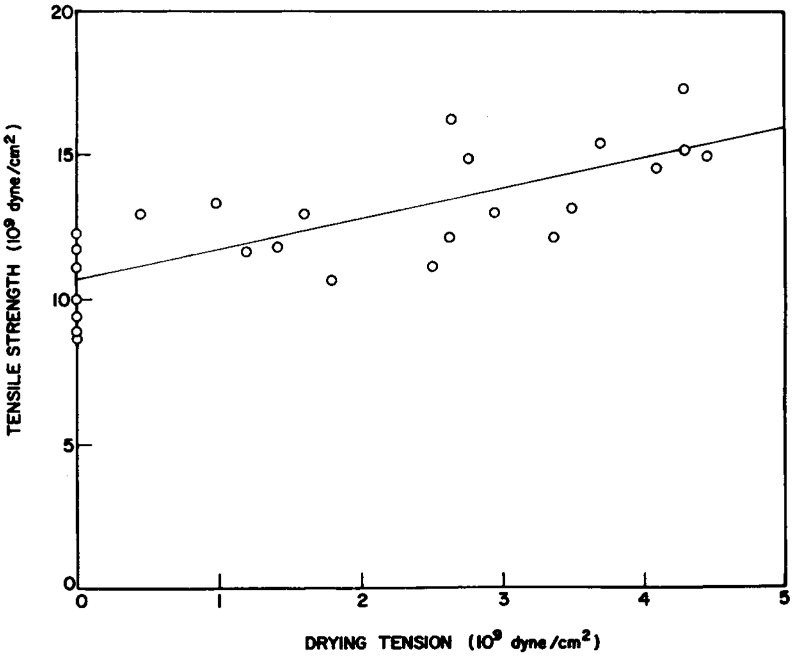


Fig. 8. Effect of drying tension on tensile strength of white pine holocellulose fibers, dried and mercury impregnated. Sample E. Regression equation: tensile strength = 10.62 + 1.06 × drying tension; $r^2 = 0.58$.

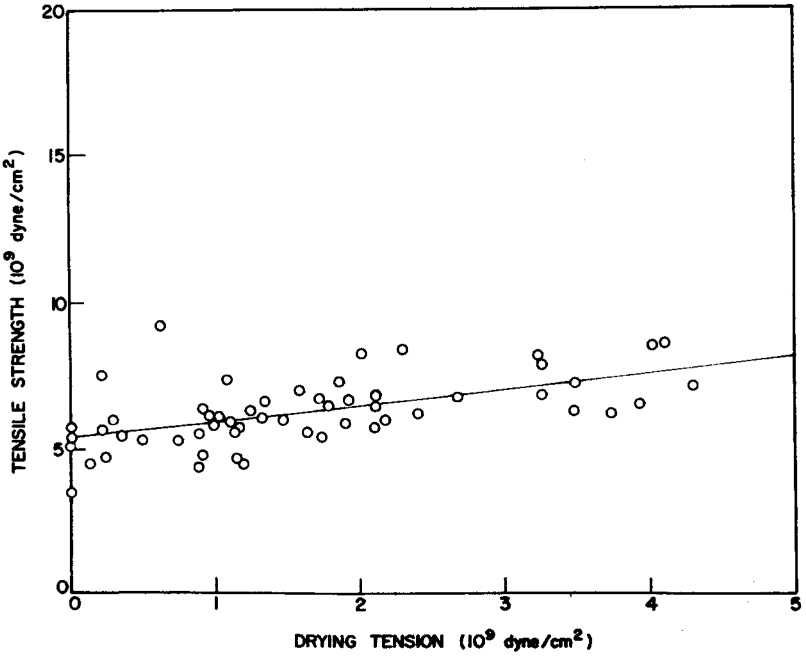


Fig. 9. Effect of drying tension on tensile strength of loblolly pine holocellulose fiber, dried and mercury impregnated. Sample H. Regression equation: tensile strength = 5.38 + 0.55 × drying tension; $r^2 = 0.29$.

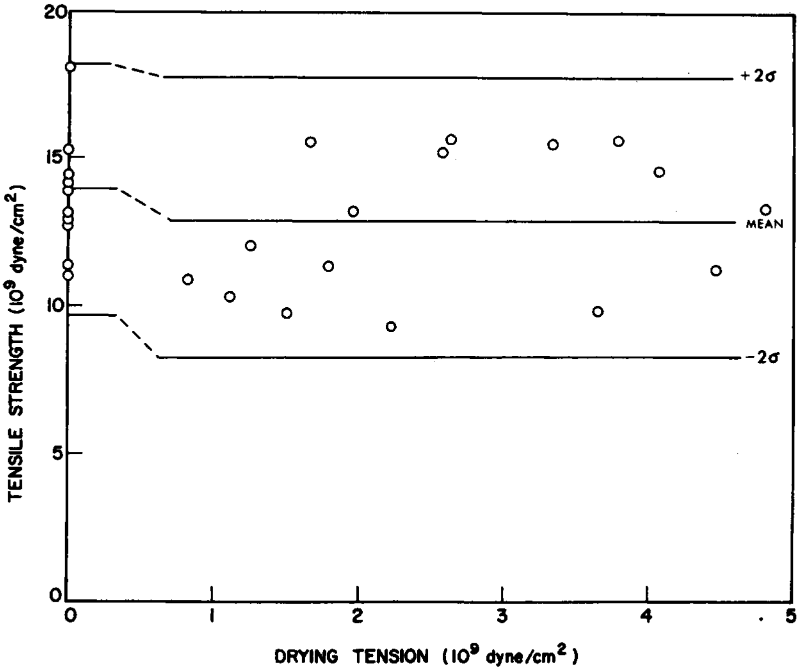


Fig. 10. Effect of drying tension on tensile strength of white pine 60% yield kraft fibers, dried and mercury impregnated. Sample F.

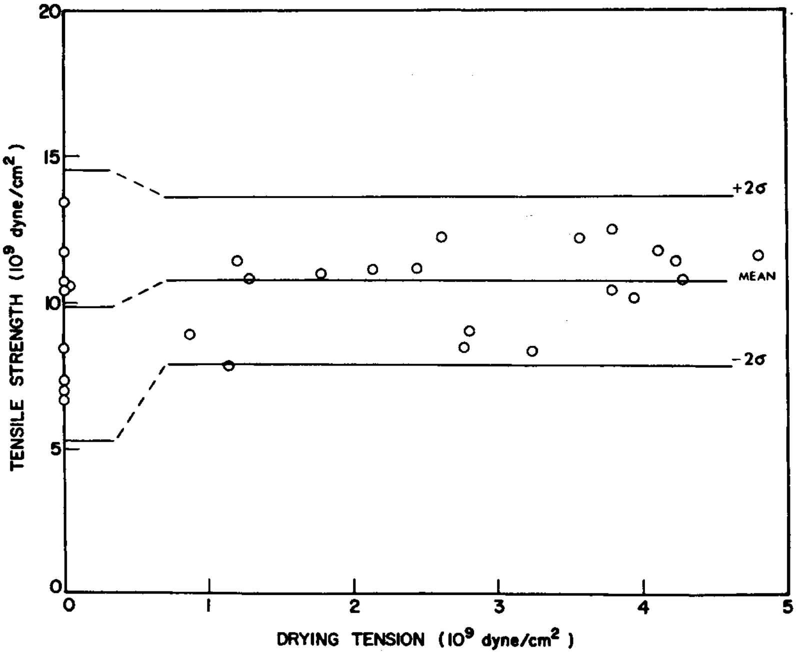


Fig. 11. Effect of drying tension on tensile strength of white spruce 60% yield kraft fibers, dried and mercury impregnated. Sample G.

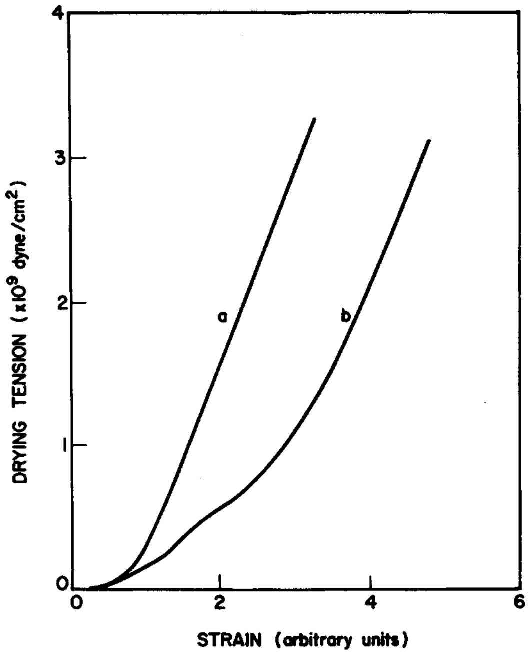


Fig. 12. Stress–strain curves of wet fibers: (a) white pine 60% yield kraft fiber of fibril angle 19.5°; (b) white pine holocellulose fiber of fibril angle 20.0°.

dried kraft fibers or once-dried holocellulose fibers from which the hemicelluloses have been extracted by alkali, the fibrils cannot shear in the wet state and no strength increase is observed.

The model can be used to interpret earlier work and to speculate on the behavior of other pulps. Both Jentzen and Spiegelberg observed a large increase in strength by the smallest drying stress and a further modest increase with increasing stress. It seems that the initial increase should be interpreted as removal of dislocations while the later increase may also include a change of fibril angle. Kallmes and Perez found no effect of drying tension on strength. The reason is now clear. These authors worked with a kraft pulp predried on Teflon. Such a pulp does not increase in strength because the matrix between the fibrils cannot shear in the predried and rewetted state.

If we generalize from these findings, we conclude that any never-dried fiber that is weak, either because of its high fibril angle or presence of dislocations, will be strengthened by these mechanisms when it is dried under tension but that a predried fiber will only be strengthened if the matrix structure is such that it becomes highly swollen in water. It is likely that a predried fiber, upon beating, will be restored to the condition of a never-dried fiber and may be strengthened under tension. Strengthening never develops beyond a value of about 20×10^9 dynes/cm^2, and it seems that this must be the ultimate strength of an unflawed fiber of zero fibril angle.

The results have papermaking significance. They imply that under some circumstances very considerable increases in paper strength can be obtained by the application of drying stresses, for example, with a never-dried pulp weakened by a high fibril angle and many dislocations. For other pulps, such as a dried pulp lightly beaten and little swollen, the strength improvement might be disappointingly low.

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