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# Theory of Mechanical Properties of Fibrillar Structures

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## Introduction

In an earlier paper[1] a theory of the deformation of plant fibers with a regular spiral arrangement of fibrils was worked out and shown to conform reasonably well with experimental results. A structure of this type is only possible where some specific biological mechanism is involved in the formation of the fiber. If crystallization of polymers in oriented man-made structures, such as synthetic and regenerated fibers, occurs in fibrillar form, it would be expected to give a somewhat irregular arrangement such as is illustrated in Figure 1. The likelihood of such a structure's actually occurring has been discussed in other papers.[2,3] The present paper is concerned with working out an approximate theoretical treatment of the deformation of such a structure, and a comparison of its predictions with experimental results.

## Modulus of an Irregularly Oriented Fibrillar Structure

### *The Theoretical Model*

In a partially crystalline, partially oriented, fibrillar structure (and in the absence of any special organization such as the spiral structure of plant fibers) it may be assumed that the fibrils follow a rather irregular path, the whole collection of fibrils being fitted together into an interlocked assembly, such as is illustrated in Figure 1. Between the imperfectly crystalline fibrils there will be the noncrystalline regions. To predict fiber behavior, it would be very useful to know the extent of curving and intertwining of the fibrils; these effects are probably exaggerated in Figure 1.

When a tension along the line of the fiber axis is applied to such a structure, extension can occur as a result of two mechanisms. First, the fibrils, together with the interfibrillar material, may stretch. Second, the fibrils may bend (or unbend) so that they follow a straighter path, until at the limit they are all pulled out so as to lie parallel to the fiber axis. Accompanying the straightening of the fibrils, there will be some deformation of the noncrystalline regions as the fibrils are pulled closer together in some places and separated farther from one another in other places.


Fig. 1. Roughly oriented fibrillar structure.

Unfortunately, the model shown in Figure 1 would not be easy to analyze theoretically, and drastic simplification is needed in order to make any progress. The deformation of any one fibril, together with the closely associated noncrystalline regions, may be viewed as taking place against a steady background of the rest of the structure—provided that it is assumed that there is no correlation between the paths of adjacent fibrils—so that the neighboring fibrils are as likely to move toward the fibril under consideration as away from it. Further simplification comes if the curve in the fibril is regarded as being in a single plane containing the fibril axis: this reduces the problem to two dimensions. Finally, the shape of the curve is idealized into a regular zigzag, and the model structure shown in Figure 2 is obtained.

This model may be characterized by the following parameters:

Angle of orientation (between fibril and fiber axis) $= \theta$

Thickness of fibril $= t$

Length of fibril in one repeat of zigzag $= 2a$

Volume of crystalline material per total fiber volume $= \gamma$

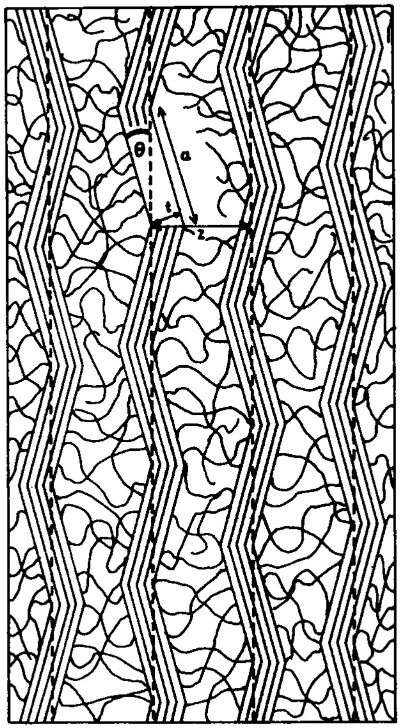


Fig. 2. Idealized model structure.

The thickness of the element perpendicular to the plane of the paper is put equal to $b$. (As the problem has been reduced to two dimensions, this could be put equal to unity without further loss of generality, but the symbol $b$ is retained in order to facilitate dimensional checking.)

If $z$ is the average distance between the center lines of fibrils, taken perpendicular to the fiber axis, we shall have:

$$\gamma = t \sec \theta / z \tag{1}$$

*Extension of Fibrils*

Figure 3 represents the extension of one half-repeat of the fibrillar zigzag, the volume of the structure being kept constant. If $x$ is the length of the half-repeat parallel to the fiber axis, and $dx$ the increase in $x$, then:

$$\text{Fiber strain} = \epsilon = dx/x$$

$$\text{Volume of element} = x(a^2 - x^2)^{1/2}b$$

Since the volume remains constant during the deformation, it follows that:

$$[(a^2 - x^2)^{1/2}b - x^2(a^2 - x^2)^{-1/2}b]dx + xa(a^2 - x^2)^{-1/2}bda = 0$$

$$da/dx = [x^2(a^2 - x^2)^{-1/2} - (a^2 - x^2)^{1/2}]/[xa(a^2 - x^2)^{-1/2}] = (2x/a) - (a/x) \tag{2}$$

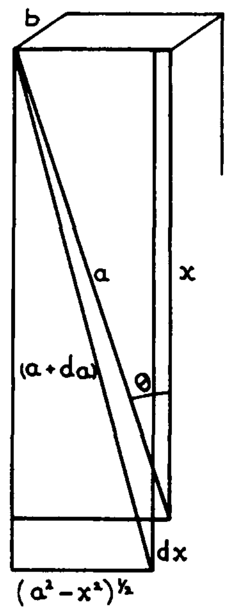


Fig. 3.

Strain in fibril is:

$$\begin{aligned} da/a &= (x/a)(da/dx)(dx/x) \\ &= (x/a)[(2x/a) - (a/x)]\ (dx/x) \\ &= \epsilon(2\cos^2\theta - 1) \\ &= \epsilon\cos 2\theta \end{aligned} \tag{3}$$

Therefore the stress in fibril is:

$$E_{c,\|}\epsilon\cos 2\theta \tag{4}$$

where $E_{c,\|}$ = crystalline fibril modulus, parallel to fibril axis.
Thus:

$$\text{tension in fibril} = E_{c,\|}tb\epsilon\cos 2\theta \tag{5}$$

and:

$$\text{Component of tension parallel to fiber axis} = E_{c,\|}tb\epsilon\cos 2\theta\cos\theta \tag{6}$$

As we are considering an element of fibril and associated region, of total width $z$, the part of the overall fiber stress due to fibrillar extension is:

$$E_{c,\|}tb\epsilon\cos 2\theta\cos\theta/bz = \gamma E_{c,\|}\epsilon\cos 2\theta\cos^2\theta \tag{7}$$

from eq. (1).

There will also be some contribution from the noncrystalline regions, and this may be roughly allowed for by adding in a term, $(1 - \gamma)E_{n,\|}\epsilon$ cos

$2\theta \cos^2 \theta$, where $E_{n,\parallel}$ is the modulus of the noncrystalline regions parallel to the fibril axis. This then gives the fiber modulus (for this mechanism):

$$[\gamma E_{c,\parallel} + (1 - \gamma)E_{n,\parallel}] \cos 2\theta \cos^2 \theta = E_1 \cos 2\theta \cos^2 \theta \tag{8}$$

where $E_1 = \gamma E_{c,\parallel} + (1 - \gamma)E_{n,\parallel}$.

Strictly, a contribution for the transverse deformation of the fibrils should also be included, but this deformation will not be important when $\theta$ is small (i.e., under the conditions for which this mechanism is found to predominate), and so it has been neglected.

*Deformation by Bending of Zigzag and Accompanying Strain*

**Actual Extension of the Zigzag.** Let AOB in Figure 4 represent one half-repeat of a fibril which, under a tension $F$ acting parallel to the fiber axis and along the center line of the fibrillar path, deforms by bending to

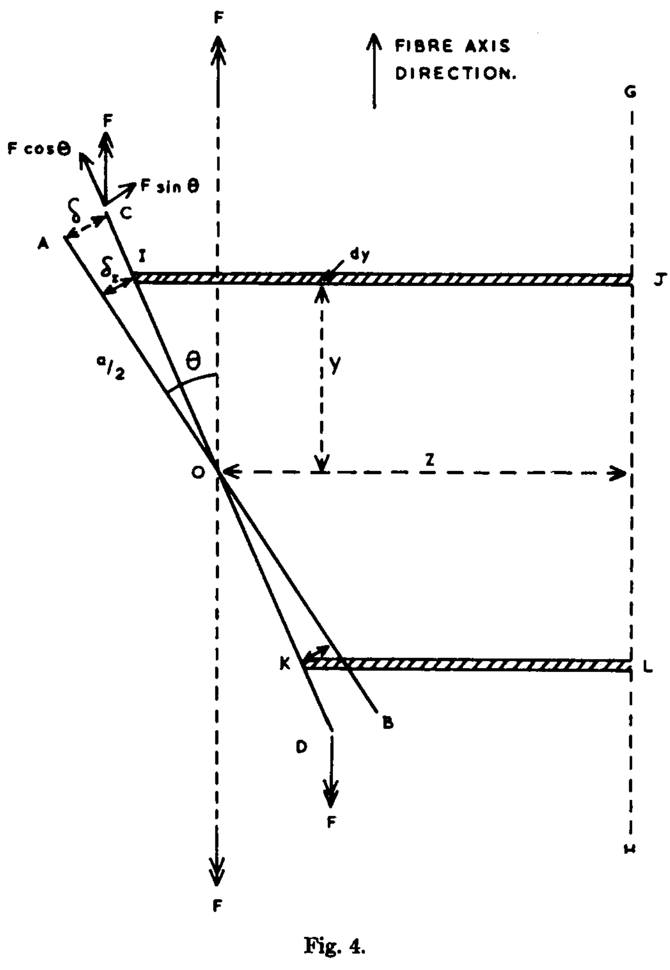


Fig. 4.

the line COD without changing in length. The problem is that of the bending of a beam AO of length $a/2$ with a force $F \sin\theta$ applied perpendicular to the end of the beam. Applying the usual equation for the deformation of a cantilever,[4] we have the displacement AC, perpendicular to the end of the fibril:

$$\begin{aligned}\delta &= [4F \sin\theta(a/2)^3]/E_{c,\|}bt^3 \\ &= Fa^3 \sin\theta/2E_{c,\|}bt^3 \qquad (9)\end{aligned}$$

The displacement of C, end of fibril, parallel to the fiber axis is $\delta \sin\theta$, and thus the corresponding fiber strain is:

$$\epsilon = \delta \sin\theta/[(a/2)\cos\theta] \qquad (10)$$

$$= Fa^2 \sin^2\theta/E_{c,\|}bt^3 \cos\theta \qquad (11)$$

The contribution to modulus from this cause is:

$$\begin{aligned}(F/zb)(1/\epsilon) &= E_{c,\|}(t^3/a^2z)(\cos\theta/\sin^2\theta) \\ &= \gamma E_{c,\|}(t/a)^2 \cot^2\theta \qquad (12)\end{aligned}$$

from eq. (1).

**Strain parallel to Fiber Axis.** Accompanying the extension of the zigzag there will be an extension of the noncrystalline regions parallel to the fiber axis. This will give contribution to the modulus $= (1 - \gamma)E_{n,\|}$.

**Strain Perpendicular to Fiber Axis.** As a result of the bending of AOB, some parts of the fibril, such as the element at I in Figure 4, will be pushed nearer to the neighboring fibril whose center line is GH, while others, such as the element at K, will be pulled farther away. Consequently, some parts of the material lying between fibrils will be compressed while other parts will be extended. This deformation will provide a resistance to the bending.

The neighboring fibril, represented by its center line GH, will also be bending, but assuming that there is no correlation between the relative positions of neighboring fibrils, any movement of an element of this fibril is as likely to be away from as to be toward the fibril AB. We may therefore consider the deformation induced by the bending of AB as being relative to the straight line GH. We must, however, count in the deformation in the region to the left of AB, arising from the bending of AB. It may be noted that the deformation in these regions resulting from the bending of GH, and the comparable fibril to the left of AB, are not counted in.

Consider an element IJ of thickness $dy$ at a distance $y$ from a line through O perpendicular to the fiber axis. From the cantilever theory,[4] it follows that the displacement $\delta_I$ of I perpendicular to AO is given by:

$$\begin{aligned}\delta_I &= 3\delta[2(y \sec\theta/a)^2 - {}^4/_3(y \sec\theta/a)^3] \\ &= a\epsilon \cot\theta(3p^2 - 2p^3) \qquad (14)\end{aligned}$$

from eq. (10), where $p = y \sec \theta / a$.

$$\text{Displacement of I perpendicular to fibril axis} = \delta_I \cos \theta$$

This change in length will be shared between a length $t \sec \theta$ of crystalline region and a length $(z - t \sec \theta)$ of noncrystalline region, in which strains of $\epsilon_c$ and $\epsilon_n$, respectively, occur. But for the equality of stresses we must have:

$$\epsilon_c E_{c,\perp} = \epsilon_n E_{n,\perp} \tag{15}$$

where $E_{c,\perp}$ and $E_{n,\perp}$ are the moduli of crystalline and noncrystalline regions, respectively, perpendicular to the fiber axis. Therefore:

$$\begin{aligned} \delta_I \cos \theta &= \epsilon_c t \sec \theta + \epsilon_n (z - t \sec \theta) \\ &= \epsilon_n [z - t \sec \theta + (E_{n,\perp}/E_{c,\perp}) t \sec \theta] \\ &= \epsilon_n z [1 - \gamma + \gamma E_{n,\perp}/E_{c,\perp}] \end{aligned} \tag{16}$$

from eq. (1).

$$\epsilon_n = \delta_I \cos \theta / 2(1 - \gamma + \alpha\gamma) \tag{17}$$

where $\alpha = E_{n,\perp}/E_{c,\perp}$.

The energy change resulting from this deformation of IJ is given by:

$$\begin{aligned} &[{}^1/_2 E_{c,\perp} \epsilon_c^2 t \sec \theta b dy + {}^1/_2 E_{n,\perp} \epsilon_n^2 (z - t \sec \theta) b dy] \\ &= {}^1/_2 \epsilon_n^2 [(E_{n\perp}^2/E_{c,\perp}) t \sec \theta + E_{n,\perp}(z - t \sec \theta)] b dy \\ &= (b \delta_I^2 \cos^2 \theta / 2z) [E_{n,\perp}(\alpha\gamma + 1 - \gamma)/(1 - \gamma + \alpha\gamma)^2]\, dy \\ &= [b \delta_I^2 \cos^2 \theta E_{n,\perp}(\alpha\gamma + 1 - \gamma)/2z(1 - \gamma + \alpha\gamma)] dy \\ &= [b E_{n,\perp} \epsilon^2 a^3 / 2z(1 - \gamma + z)] \cos^3 \theta \cot^2 \theta (3p^2 - 2p^3)^2 dp \end{aligned} \tag{18}$$

from eq. (1).

Since $p = {}^1/_2$ when $y = (a/2) \cos \theta$, the total energy for deformation to the right of AO is:

$$[b E_{n,\perp} \epsilon^2 a^3 / 2z(1 - \gamma + \alpha\gamma)] \cos^3 \theta \cot^2 \theta \int_0^{1/2} (3p^2 - 2p^3)^2 dp \tag{19}$$

But:

$$\begin{aligned} \int_0^{1/2} (3p^2 - 2p^3)^2 dp &= \int_0^{1/2} (9p^4 - 12p^5 + 4p^6) dp \\ &= [(9p^5/5) - (12p^6/6) + (4p^7/7)]_0^{1/2} \\ &= (9/5.2^5) - (1/2^5) + (1/7.2^5) \\ &= 33/32.35 \end{aligned}$$

Thus, the energy of deformation to the right of AO is:

$$(33/64.35)[E_{n,\perp} a^3 / z(1 - \gamma + \alpha\gamma)] \cos^3 \theta \cot^2 \theta\, b \epsilon^2 \tag{20}$$

This energy must be supplied by the force extending the fiber, but we have:

$$\text{Energy supplied} = {}^1/_2 E' \epsilon^2 z b (a/2) \cos \theta \tag{21}$$

where $E'$ is the contribution to the modulus from this cause. Taking account of energy of deformation to both right and left of AO, as mentioned earlier, we get:

$$^1/_2 E' \epsilon^2 zb(a/2) \cos \theta = (33/32.35)[E_{n,\perp} a^3/z(1 - \gamma + \alpha\gamma)] \cos^3 \theta \cot^2 \theta b \epsilon^2 \quad (22)$$

$$E' = (33/280)(a^2/z^2)[1/(1 - \gamma + \alpha\gamma)] \cos^2 \theta \cot^2 \theta \, E_{n,\perp}$$
$$= (33/280)(a^2/t^2)[\gamma^2/(1 - \gamma + \alpha\gamma)] \cos^4 \theta \cot^2 \theta \, E_{n,\perp} \quad (23)$$

**Summation of Contributions to Modulus.** The total fiber modulus when deformation occurs as a result of bending of the zigzag will be given by adding together the three terms calculated above. This gives:

$$\text{Fiber modulus} = \gamma E_{c,\parallel} (t/a)^2 \cot^2 \theta + (1 - \gamma) E_{n,\parallel} + E_{n,\perp}(33/280)(a/t)^2[\gamma^2/(1 - \gamma + \alpha\gamma)] \cos^4 \theta \cot^2 \theta \quad (24)$$

from eqs. (12), (13), and (23).

It is to be expected that $(t/a) \ll 1$; i.e., the thickness of the fibril is much less than $a$, which corresponds in the real material to the average distance between points of inflexion in the curved path followed by a fibril. Because $(a/t)^2 \gg 1$, it will be possible to neglect the first two terms in the above expression, and we thus see that the effective resistance to deformation by bending of the zigzag comes from the lateral deformation of regions between the fibrils. Furthermore if $E_{n,\perp} \ll E_{c,\perp}$ as would be expected, $\alpha \ll 1$, and the term in $\alpha\gamma$ can be dropped. We thus have the fiber modulus due to this mechanism:

$$E_{n,\perp}[33\gamma^2/280(1 - \gamma)](a/t)^2 \cos^4 \theta \cot^2 \theta = E_2 \cos^4 \theta \cot^2 \theta \quad (25)$$

where $E_2 = \{33\gamma^2/[280(1 - \gamma)]\}(a/t)^2 E_{n,\perp}$.

### *Combined Effect of the Two Mechanisms*

The resistances to extension in the mechanisms, arising respectively from extension and bending of the fibrils, have been worked out. These two mechanisms of extensions are alternatives; in other words, any deformation occurring as a result of fibrillar extension reduces the amount of bending needed to give the required fiber extension, and vice versa. If the resistance to deformation by one mechanism is much less than the resistance by the other, then the latter may be neglected. The curves plotted in Figure 5 show that for highly oriented fibers, when $\theta$ is small, the extension mechanism, with $E = E_1 \cos 2\theta \cos^2 \theta$, is dominant; in fact, the resistance for the bending mechanism, given by $E_2 \cos^4 \theta \cot^2 \theta$, is infinite when $\theta = 0$. However, this latter function decreases more rapidly with $\theta$, and the bending mechanism may be expected to predominate when $\theta$ is large.

For intermediate values of $\theta$, the deformation will be due partly to extension of the fibrils and partly to bending. The exact form of the

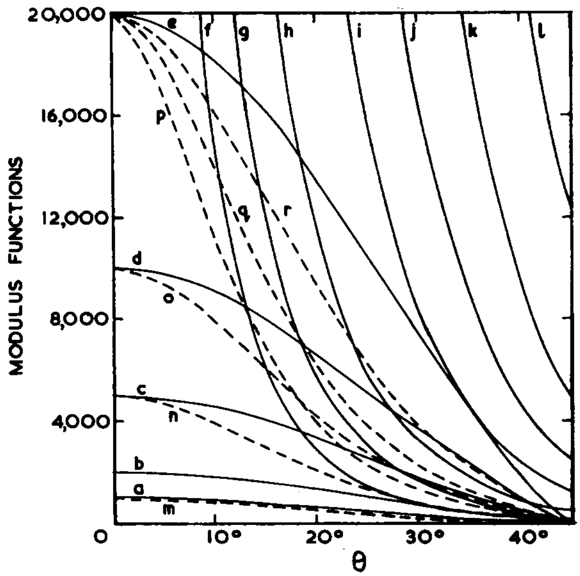


Fig. 5. Curves of modulus functions against orientation angle $\theta$: (a − e) $E_1 \cos 2\theta \cos^2\theta$ for $E_1 = 2000$ (a), 1000 (b), 5000 (d), 10,000 (c), 20,000 (e); (f − l) $E_2 \cos^4\theta \cot^2\theta$ for $E_2 = 500$ (f), 1000 (g), 2000 (h), 5000 (i), 10,000 (j), 20,000 (k), 50,000 (l); (m − r) $E_1E_2 \cos 2\theta \cos^4\theta \cot^2\theta / E_1 \cos 2\theta + E_2 \cos^2\theta \cot^2\theta$ for $E_1 = 1000$ and $E_2 = 500$ (m), $E_1 = 5000$ and $E_2 = 1000$ (n), $E_1 = 10{,}000$ and $E_2 = 2000$ (o), $E_1 = 20{,}000$ and $E_2 = 1000$ (p), $E_1 = 20{,}000$ and $E_2 = 2000$ (q), $E_1 = 20{,}000$ and $E_2 = 5000$ (r).

equation combining the two functions may be complex. However, the arrangement is generally similar to two springs in series (where the extension of one spring reduces the extension of the other) and the same combination equation may be used as an approximation. This gives the fiber modulus:

$$E = E_1 \cos 2\theta \cos^2\theta\, E_2 \cos^4\theta \cot^2\theta / (E_1 \cos 2\theta \cos^2\theta + E_2 \cos^4\theta \cot^2\theta) \quad (26)$$

$$= E_1E_2 \cos 2\theta \cos^4\theta \cot^2\theta / (E_1 \cos 2\theta + E_2 \cos^2\theta \cot^2\theta)$$

The value of $E_1$ from eq. (8) will be of the order of magnitude of the modulus of extension of the crystalline fibrils, for which values have been calculated for some materials.[5] The value of $E_2$ from eq. (25) will be of the order of magnitude of 0.1 $(a/t)^2 E_{n,\perp}$. This is very difficult to estimate since little is known about the curvature of the fibrils or the modulus of the noncrystalline regions. The parameter $a/t$ will be large, but $E_{n,\perp}$ is likely to be appreciably less than $E_{c,\parallel}$ .

## Comparison of Theory and Experiment

Unfortunately, it is difficult to find adequate experimental results on man-made fibers with which to test the theoretical equation (26). Furthermore, in addition to the approximations of the model, there is the difficulty of calculating a value of $\theta$ in fibers: effective orientation angles can be calculated from birefringence measurements, but only if a particular model for the structure is chosen. Using the equation given by Hermans and Platzek[6] to relate orientation to birefringence, values of modulus have been plotted against $\theta$ for nylon, ordinary rayon, and high-modulus rayon, with the use of data from British Nylon Spinners,[7] de Vries,[8] and Courtaulds.[9] An attempt to fit eq. (26) to experimental results for nylon and ordinary rayon at angles $\theta$ of up to 15° led to negative values of $E_2$, and this indicates poor agreement between experiment and theory for these materials.

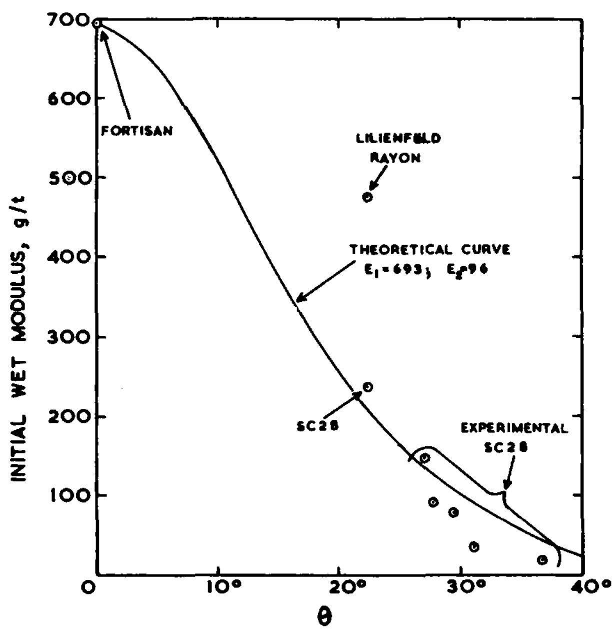


Fig. 6. Variation of modulus of high-modulus rayons with orientation angle; Comparison of experiment and theory (data from Courtaulds[9]).

The results for high-modulus rayon are shown in Fig. 6. The modulus figures were obtained in the wet state, and the data include results for Fortisan (effectively perfect orientation), a Lilienfeld rayon, normal S.C.28 high-modulus rayon, and an experimental series of S.C.28 fibers with varying stretch. A theoretical curve with $E_1$ = 693 g./tex and $E_2$ = 96 g./tex fits the experimental results quite well. The value of $E_1$ is equivalent to 1000 kg./mm.$^2$ which is of the right order of magnitude, and it is reasonable that the value of $E_2$ should be much lower. These results therefore show that the modulus of high-modulus (polynosic) rayons is compatible with a fibrillar structure.

The effect of moisture on the mechanical properties of rayon fibers is also interesting. The polynosic fibers show a high dry modulus (rather greater than that of cotton) which is reduced to a limited extent on wetting, as shown in Figure 7. This is entirely compatible with a fibrillar structure and the comparatively small change on wetting shows that the continuous crystalline fibrillar network does have an important effect on the mechanical properties.

By contrast, the ordinary and high-tenacity rayons show a lower dry modulus, and this is reduced enormously on wetting. In fact, the initial steep part of the stress-strain curve disappears completely in the wet fiber, as shown in Figure 7. This sort of behavior is what would be expected for

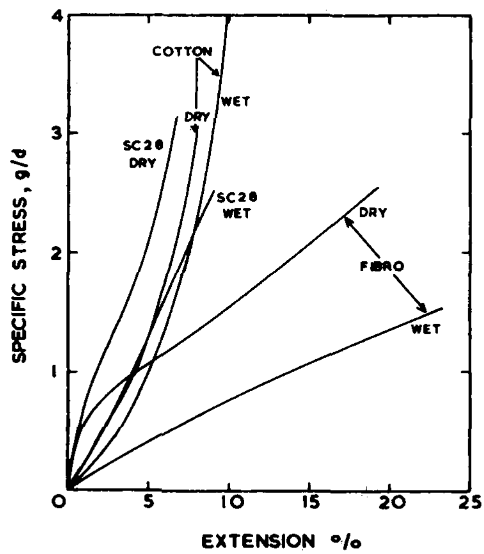


Fig. 7. Load–extension curves for rayon (after Griffiths[11]).

a fringed micelle structure, in which the deformation is essentially that of noncrystalline material restricted in only a limited way by the presence of occasional blocks of crystalline material. On plasticizing the structure with water, the modulus would be expected to fall drastically, as a result of the breaking of all crosslinking between the molecules in the noncrystalline regions. The theory of deformation in these materials should therefore be worked out by a development of the methods used on a fringed micelle structure by Cumberbirch and Mack,[10] who have developed a theory of the strength of rayon fibers which shows good agreement with experimental results.

## Conclusion

An approximate theory of the deformation of fibers containing an irregular, roughly oriented, fibrillar structure has been worked out. The theoretical equation does not fit experimental results for nylon and ordinary rayon fibers, but in view of the crudities of the analysis and the simplifications of the model this cannot be taken as conclusive evidence against a fibrillar structure, particularly as the experimental values were limited to values of $\theta$ less than 15°. This evidence does add support to a view that crystallization in these fibers may be dominated by nucleation and thus may not lead to a fibrillar structure.

On the other hand, the theory does fit the experimental results for high-modulus (polynosic) rayons which are formed by the regeneration and crystallization of cellulose as a result of a chemical reaction in an intermediate oriented solid fiber of a cellulose derivative. This particular mode of formation may be expected to lead to a fibrillar structure.

The mechanical behavior of polynosic rayons differs from that of ordinary rayons, notably in the greater stiffness and in the influence of water, and this illustrates the importance of understanding the relation between structure and mechanical properties of fibers. Changes in physical fiber structure may prove to be a very useful means of modifying fiber properties.

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## Synopsis

A theory of the extension of a roughly oriented fibrillar structure is worked out. Two mechanisms are involved: an extension of the fibrils, and a bending of the fibrils with accompanying deformation of noncrystalline material lying between them. The combined equation for both mechanisms does not fit experimental results for nylon and ordinary rayon, but does fit results for high modulus (polynosic) rayons.

## Résumé

On a élaboré une théorie de l'extension d'une structure fibrillaire partiellement orientée. Celle-ci comprend 2 mécanismes: une extension des fibrilles et une tension des fibrilles accompagnée de la déformation du matériau noncristallin situé entre elles. L'équation combinée pour les 2 mécanismes ne correspond pas aux résultats expérimentaux dans le cas du nylon et de la rayonne ordinaire, mais s'accorde bien aux résultats pour des rayonnes à module élevé (polynosique).

## Zusammenfassung

Eine Theorie für die Dehnung einer mässig orientierten Fibrillenstruktur wird ausgearbeitet. Zwei Mechanismen werden berücksichtigt: eine Dehnung der Fibrillen und eine Biegung der Fibrillen mit gleichzeitiger Deformation des dazwischen befindlichen nichtkristallinen Materials. Die kombinierte, beide Mechanismen berücksichtigende Gleichung entspricht nicht den Versuchsergebnissen an Nylon und gewöhnlichem Rayon, wohl aber denjenigen an hochelastischen (polynosischen) Rayons.

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