Elastic Stiffness of Crystalline Cellulose in the Folded-Chain Solid State*

P. P. GILLIS, R. E. MARK, R-C. TANG
University of Kentucky, Lexington, Kentucky, USA

In previous papers the axial stiffness of crystalline native cellulose has been calculated for two proposed configurations of the cellulose chains within the elementary fibrils: an extended chain configuration, and a configuration in which the chains are folded to form a ribbon which in turn is helically wound into a rather open, spring-like structure. In the present paper two additional folded-chain configurations are treated: a more tightly wound helical configuration in which axial secondary bonds are formed between adjacent turns of the helix; and a configuration in which the chains are folded rather infrequently and remain in a fully-dense close-packed arrangement. It is shown that this last configuration is mechanically equivalent to the extended chain configuration so far as axial stiffness is concerned, and that either helical configuration has a substantially lower axial stiffness than that of the extended chain.

1. Introduction

In previous papers [1-4] elastic constants for crystalline native cellulose have been calculated, via consideration of the interatomic bending and stretching force constants applicable to the solid state, for one major extended-chain model and one widely-discussed folded-chain model. These models are shown schematically in figs. 1a and b respectively. A third major type of model, exemplified by the proposal of Marx-Figini and Schulz, [5] appears in fig. 1c. It may be described as a fully-dense folded-chain solid state model. Its mechanical behaviour will be investigated in this paper, as well as the case closely related to it shown in fig. 1d, which is a folded-chain helical coil wound so tightly that the folds in adjacent turns of the helix come into sufficiently close proximity to permit hydrogen bonding between turns. A structure such as that shown in fig. 1d thus becomes a tube.

The extended-chain configuration used in our earlier work [1, 4] was the classical crystallographic model of Meyer and Misch [6] as modified by Frey-Wyssling [7]. In this model the cellulose chains are aligned in the [010] crystallographic direction (b-axis). Interchain hydrogen bonds seem to provide the main mechanism for stabilising the crystal against relative displacement of the chains, since the possible stability contribution of van der Waals forces has not been quantitatively assessed. It is assumed that there are no primary cross-linking bonds joining adjacent cellulose chains.

In the folded-chain configuration considered previously [2, 3], a single chain molecule is folded repeatedly forming a ribbon-like band that is twisted into a helical configuration. This is the model of Manley [8]. The study of this folded-chain model indicated that it is grossly incompatible with the observed mechanical properties of cellulosic fibres, whereas reasonable values for the elastic stiffness of the extended-chain model were obtained when the contributions of interchain hydrogen bonds to axial modulus of elasticity were accounted for [4].

In references [2] and [3], we considered the case as illustrated in Manley's original paper, wherein the spacing between adjacent turns of the coil is too large to permit hydrogen bonds to form between turns, but in which there are

a   b
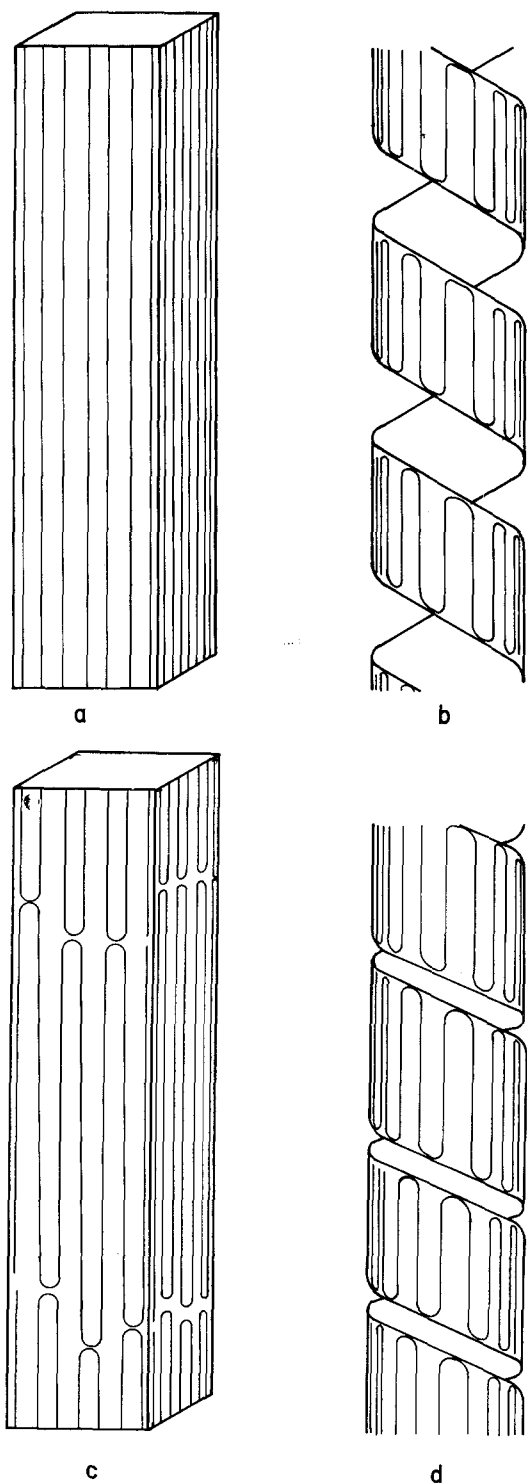
c   d

Figure 1 Proposed models for crystalline native cellulose. (a) Extended-chain. (b) Folded-chain model of Manley. (c) Folded-chain model of Marx-Figini and Schulz. (d) Tightly-coiled modification of Manley model.

1004

hydrogen bonds between adjacent folded-chain segments within the ribbon. The tubular configuration of fig. 1d applies to a model that would be helical except for its failure to meet the criterion of no bonding between adjacent turns of the coil, but which does retain the 35 Å diameter and other dimensional features of the original Manley model.

Regardless of the internal polymer configuration, it is becoming increasingly accepted that the 35 Å diameter for elementary fibrils (protofibrils) proposed by Mühlethaler [9] is a dimension that reasonably represents the smallest unit of fully coherent cellulose chain aggregation in plant cell walls. According to this conception, the larger microfibril dimensions often observed (in electron micrographs, etc.) are really multiples of 35 Å and are the result of fasciation of the elementary fibrils.

The present paper considers the cases illustrated in figs. 1c and d, and shows that generally the modulus of elasticity in the direction of the fibril axis will be less than that of the extended-chain structure analysed earlier [1, 4] by only a small amount in the former case, but by a substantial factor in the latter. In this paper and previous works, several basic structural configurations have been considered. However, various refinements, such as the intrachain hydrogen bonding pattern proposed by Liang and Marchessault [10] remain to be evaluated more thoroughly.

2. Analysis

Consider first the case of a helically wound ribbon having adjacent ribbon edges sufficiently close for hydrogen bonding (or even some form of primary bonding) as shown in fig. 1d. Structurally this arrangement is equivalent to a tube. Assuming that the lateral restraint offered to axial extension – the Poisson effect – in this configuration does not differ greatly from that in the extended-chain configuration, we can calculate the tubular stiffness by comparison to the extended form.

A prismatic element from the extended-chain configuration is shown in fig. 2. It has an axial length L and contains a single chain having an associated cross-sectional area A_0 equal to one-half the area of the unit cell of cellulose I. The stiffness is defined as the ratio of load P to extension δ. Hooke's law for elastic extension of a prismatic element gives:
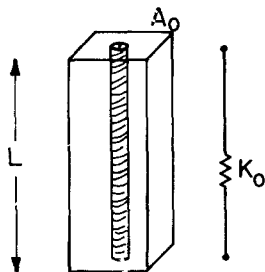
$$K_0 = P/\delta = A_0 E_0/L . \tag{1}$$

Figure 2 Prismatic element from an extended-chain segment of crystalline cellulose 1.

Here K_0 is the stiffness and E_0 is the elastic modulus in the chain direction for the extended-chain configuration.

Equation 1 shows that the stiffness, or "cumulative spring force constant" [11], for any segment of the tubular structure containing one or more primary or secondary bonds will be inversely proportional to the length of the segment. A long chain segment will have a smaller K value than that of a shorter segment containing identical repeat units and bonding.

Next consider an element from the ribbon of the tightly wound helical configuration as in fig. 3. The figure shows the ends of the element perpendicular to the protofibril axis, although they should actually be inclined at an angle corresponding to the helical pitch. However, the subsequent analysis makes it clear that so far as stiffness is concerned the helical tube is mechanically equivalent to a tube composed of alternating rings of cellulose chains (or folded-chain segments) aligned axially, and secondary bonds.
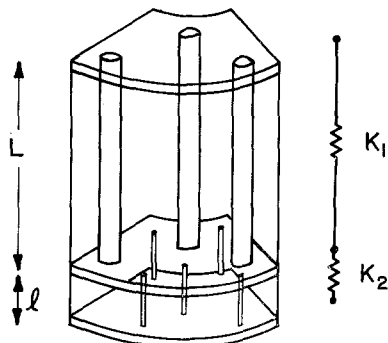

Figure 3 Element of a tightly-coiled, tubular folded-chain cellulose structure.

Denote by m the number of axially oriented chain segments in the element of fig. 3 and by n the number of secondary bonds in the element

that have formed to join the chain segments in this element to the next. Let the sum of chain length L and secondary bond length l be equal to H, the linear spacing of the layers of secondary bonds so that the element is a characteristic repeat unit along the protofibril axis. Since the upper portion of this element depends for its stiffness on the axial chains, it must have a stiffness K_1 that is m times the stiffness of a single chain of the same length, given by equation 1.

$$K_1 = m K_0 = mA_0E_0/L . \qquad (2)$$

Similarly, the lower portion of the element has a stiffness K_2 that is n times the stiffness, k, of a secondary bond.

$$K_2 = nk . \qquad (3)$$

Here the bond stiffness k is the value appropriate for combined stretching and bending of the hydrogen bonds linking adjacent chain folds, resolved in the direction of the protofibril axis. Since no detailed configurations have yet been suggested for such bonds we assume for simplicity in subsequent calculations that the bonds are aligned for direct axial stretching only. This is the stiffest possible configuration. No length term appears in equation 3 as it does in 1 since the stiffness k already implies the characteristic length of the corresponding hydrogen bond.

The two portions of this element acting in series have a combined stiffness K obtained from:

$$1/K = 1/K_1 + 1/K_2 . \qquad (4)$$

Thus the overall stiffness of the element is:

$$K = K_1/[1 + (K_1/K_2)] . \qquad (5)$$

The value K will be determined primarily by the lower of the two values, K_1, K_2. Even though the primary bonds in the chain segment are individually stiffer than the intercoil hydrogen bonds K_1 will be less than K_2 because of the greater length of primary chain (see equation 1).

In order to compare tubular and extended-chain configurations, equation 5 can best be interpreted in terms of aggregate packing densities. Each protofibril has a certain gross cross-sectional area and is threaded by a certain number of chains. Therefore, a gross area per chain, A, can be determined and the corresponding cross-sectional area supported by the element of fig. 3 is mA. The length of this element is H and thus by applying the formula of equation 1 relating the stiffness of a prismatic element to its

dimensions and elastic modulus, to equation 5 an elastic modulus, E, can be calculated for the tubular structure with the assistance of equation 3.

$$\frac{mAE}{H} = \frac{mA_0E_0}{L} \div \left\{ 1 + \frac{mA_0E_0/L}{nk} \right\}. \quad (6)$$

Thus the modulus of the tubular structure is:

$$E = E_0(A_0/A)(H/L)/[1 + (m/n)(A_0E_0/L/k)]. \quad (7)$$

Equation 7 expresses the modulus of the tubular structure in terms of that for an extended-chain structure, the ratio of chain densities in the two structures, the axial fraction occupied by chains as opposed to secondary bonds, and a factor involving the stiffness ratio of a characteristic length of cellulose chain to the interconnecting secondary bond.

Consider next the densely packed prismatic elementary fibril shown in fig. 1c. Analysis of an axial element from such a structure proceeds formally in exactly the same manner as for the element of fig. 3. Hence equation 7 also gives the axial modulus for this configuration keeping in mind that the appropriate geometrical parameters will be different in the two cases (figs. 1c and d).

3. Calculations

Manley's elementary fibril (protofibril) is 35 Å in diameter, but the constraints imposed by the coiling of a folded-chain ribbon within this dimension preclude filling of some lattice positions (see figs. 4 and 5). This effect decreases the packing density of chains, i.e. increases the cross-sectional area per chain A. If one takes the inside diameter of the helical ribbon as 19 Å the value for A_0/A becomes approximately $1 - (19/35)^2 = 0.7$ for this model. With H and L set at 40 Å and 37 Å respectively, the second ratio in equation 7 has the value 1.08 and it remains only to evaluate the denominator.

We assume that at each fold of the cellulose chain, one hydrogen bond forms, bridging the inter-ribbon gap so that the ratio of chains to hydrogen bonds, m/n, is 2. Then taking $A_0 = 32.5 \times 10^{-16}$ cm^2 for the Meyer and Misch extended-chain configuration and $E_0 = 32 \times 10^{11}$ dynes/cm^2, the maximum value computed by Gillis [4], we obtain $K_0 = A_0E_0/L \simeq 3 \times 10^4$ dynes/cm for the 37 Å segment. This value is typical of the stretching force constant for a hydrogen bond. Thus if $(A_0E_0/L)/k$ is taken as unity, the effective modulus of the bridged
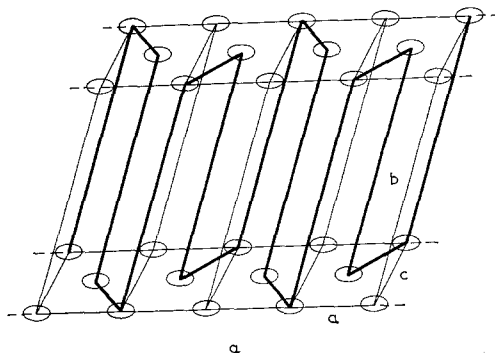
1006

Figure 4 Configuration of the folded cellulose chain molecule within the helically wound ribbon that forms the protofibril according to the concept of Manley. Note that some lattice positions are vacant if the chains are fitted to the monoclinic array generally accepted for cellulose. (Reprinted from [3] with permission.)
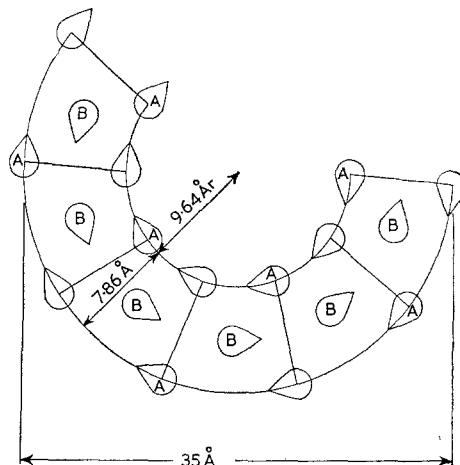

Figure 5 Cross-section of the helix formed from the folding and twisting of molecular cellulose according to the scheme shown in fig. 1b. Chain segments such as illustrated in fig. 4 would pass through positions shown by A and B, with chains absent elsewhere. Distortion of the monoclinic arrangement is introduced by the constraint of the 35 Å protofibril diameter. (Reprinted from [3] with permission.)

helical configuration is $E = E_0(0.7)(1.08)/3 = 0.25E_0$. Substitution of the calculated E_0 values yields solutions for E that are always lower than experimental determinations of natural cellulosic fibres [12, 13], thus violating the rule of mixtures [3].

On the other hand, for the densely packed model of Marx-Figini and Schulz, the fold length suggested by these authors is 800 Å. In

this case H/L and A_0/A are both virtually unity but here $A_0E_0/L = 0.13 \times 10^4$ dynes/cm. If one takes $k = 3 \times 10^4$ dynes/cm and $m/n = 2$, as in the previous case, the effective modulus given by equation 7 is $E = E_0/1.09 = 0.92E_0$.

4. Conclusion

Examination of the theoretical elastic properties of native cellulose has continued in this study of two more suggested configurations. The Manley model for native cellulose would violate the physical "rule of mixtures" even if the gaps between adjacent helical wraps were bridged by a reasonable number of hydrogen bonds. This effect is due in part to a lower net packing density of chains in the hollow protofibril, but mainly it is due to the large fraction of hydrogen bonds that would be essentially in series with the cellulose chains if the secondary bonds occurred approximately every 40 Å.

The Marx-Figini and Schulz densely-packed folded-chain model is mechanically indistinguishable from an extended-chain model since relatively few in-series hydrogen bonds occur at a spacing of 800 Å. The methods of mechanics alone are not sufficient, therefore, to accept or reject this model. However, the chemical evidence provided by Muggli [14] to show that determinations of molecular weight of carbanilated native (ramie) cellulose are consistent only with an extended-chain configuration, seems to have resolved the question by another means. High-resolution electron microscopy should provide us with a final answer on the best conformation model, perhaps in the near future.

Acknowledgement

References

1. M. A. JASWON, P. P. GILLIS, and R. E. MARK, *Proc. Roy. Soc.* **A306** (1968) 389.
2. R. E. MARK, P. N. KALONI, R. C. TANG, and P. P. GILLIS, *Science* **164** (1969) 72.
3. *Idem, Text. Res. J.* **39** (1969) 203.
4. P. P. GILLIS, *J. Polymer Sci.* **A2** 7 (1969) 783.
5. M. MARX-FIGINI and G. V. SCHULZ, *Biochim. Biophys. Acta.* **112** (1966) 81.
6. K. H. MEYER and L. MISCH, *Helv. Chim. Acta.* **20** (1937) 232.
7. A. FREY-WYSSLING, *Biochim. Biophys. Acta.* **18** (1955) 166.
8. R. S. J. MANLEY, *Nature* **204** (1964) 1155.
9. K. MÜHLETHALER, "Cellular Ultrastructure of Woody Plants", edited by W. A. Côté Jr (Syracuse University Press, 1965) pp. 191-198.
10. C. Y. LIANG and R. H. MARCHESSAULT, *J. Polymer Sci.* **37** (1959) 385.
11. R. E. MARK, "Cell wall mechanics of tracheids" (Yale University Press, 1967) p. 122.
12. K. H. MEYER and W. LOTMAR, *Helv. Chim. Acta* **19** (1936) 68.
13. I. SAKURADA, Y. NUKUSHINA, and T. ITO, *J. Polymer Sci.* **57** (1962) 651.
14. R. MUGGLI, Thesis, Eidgenössische Technische Hochschule, Zürich (1968).