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Calculation of Crystallite Modulus of Native Cellulose

Kohji Tashiro and Masamichi Kobayashi

Department of Macromolecular Science, Faculty of Science, Osaka University,
Toyonaka, Osaka, 560 Japan

Summary

A crystallite modulus of native cellulose along the chain axis has been calculated based on the X-ray analysed molecular conformation and the force constants used in the vibrational analysis. The calculated values are 172.9 GPa and 70.8 GPa for the cases with and without the intramolecular hydrogen bondings taken into account, respectively. The intramolecular hydrogen bondings have been found to play an important role on the determination of crystallite modulus and the chain deformation mechanism, based on the calculation of the strain energy distribution to the internal coordinates such as bond lengths, bond angles, and so on.

Introduction

Cellulose is a naturally occurring polymer found in all higher plants as a structural material in the cell walls. It may be useful to evaluate the limiting value of crystallite modulus of this basically important polymer. Sakurada et al. (1, 2) reported the crystallite modulus of about 127 GPa by the X-ray diffraction method. The value is comparable to those of aromatic ring polymers such as poly-p-phenylene terephthalamide (153-200 GPa), poly-m-phenylene isophthalamide (88 GPa) and so on (3). The reason why the cellulose, an aliphatic ring polymer, possesses such a fairly high crystallite modulus along the chain axis should be clarified from the molecular theoretical point of view. Although the calculation of crystallite modulus of cellulose chain has been carried out by several authors (4-8), the employed molecular models were not necessarily so realistic and the assumed potential fields were also too simplified without any consideration on the internal rotational coordinates which may play an important role on the mechanical deformation mechanism of non-planar polymer chains (3).

In this paper we will describe the calculated results of the crystallite modulus of native cellulose based on the molecular model analysed by the X-ray method and the force fields which can reproduce well the actual infrared and Raman spectral data. We will also clarify how largely the internal rotations and the intramolecular hydrogen bondings contribute to the crystallite modulus.

Parameters for the Calculation of Crystallite Modulus

The calculation of the crystallite modulus E_1 was performed according to the so-called B matrix method (3, 9), in which the Cartesian coordinates of the constituent atoms and the intramolecular force constants are needed as input data for the electronic computor.

The molecular model (Figure 1) is based on the result of the X-ray analysis by Gardner and Blackwell (10). In general the elastic modulus along the chain axis is almost determined by the skeletal conformation of the chain (3), and so the hydrogen atoms are neglected here in the first approximation. The unit cell has the dimensions of a = 16.34 Å, b = 15.72 Å, c (f.a.) = 10.38 Å, and γ = 97.0°, in which the eight chains are packed together (10). Therefore the effective cross-sectional area of a single chain is about 31.87 $Å^2$.

The intramolecular force constants of the valence-force-field type were transferred from the paper of Blackwell et al. (11) with some modification. The intramolecular hydrogen bondings are also taken into consideration as shown in Figure 1. In Table 1 are listed the numerical values of the utilized force constants.

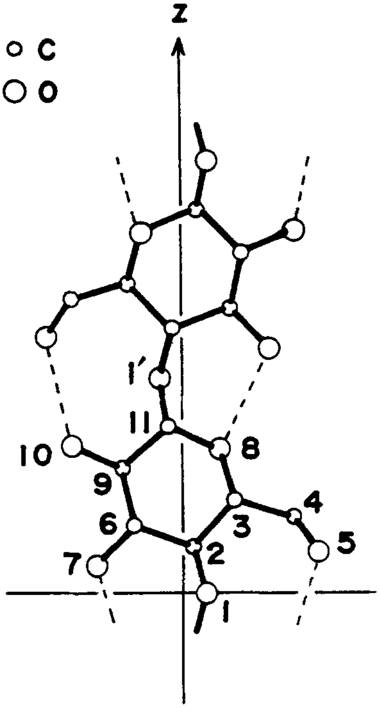

Figure 1. Molecular structure of native cellulose (11).

Results and Discussion

The calculation of E_1 has been made for the two sets of force constants; (a) with and (b) without the intramolecular hydrogen bondings taken into account. The calculated results are as follows.

(a) E_1 = 172.9 GPa with intramolecular hydrogen bonds

(b) E_1 = 70.8 GPa without intramolecular hydrogen bonds

The crystallite modulus observed by Sakurada et al. is about 127 GPa (1, 2). The actual samples may contain, more or less, some structural defects within the crystalline regions and so the experimental value is generally considered to be lower than the theoretical value as frequently observed for many crystal-

Table I

Intramolecular Force Constants for a Cellulose Chain (Valence Force Field Type)

No.	Coordinates involved	Common atoms	Values[a]
1	C-O		5.090
2	C-C		4.261
3	C-O, C-O	O	0.288
4	C-C, C-O	C	0.101
5	C-C, C-C	C	0.101
6	O-C, C-O	C	0.101
7	$\angle$COC		1.313
8	$\angle$CCO		1.182
9	$\angle$CCC		1.071
10	$\angle$OCO		1.200
11	CO, $\angle$COC	CO	0.483
12	CO, $\angle$CCO	CO	0.618
13	CC, $\angle$CCO	CC	0.403
14	CC, $\angle$CCC	CC	0.417
15	$\angle$CCO, $\angle$CCO	CO	-0.041
16	$\angle$CCO, $\angle$CCC	CC	-0.041
17	$\angle$COC, $\angle$OCC	(C)O-C(C) [g][b]	0.011
18	$\angle$COC, $\angle$OCC	(C)O-C(C) [t]	-0.011
19	$\angle$OCC, $\angle$CCO	(O)C-C(O) [g]	0.011
20	$\angle$OCC, $\angle$CCO	(O)C-C(O) [t]	-0.011
21	$\angle$CCC, $\angle$CCO	(C)C-C(O) [g]	0.011
22	$\angle$CCC, $\angle$CCO	(C)C-C(O) [t]	-0.011
23	$\angle$CCC, $\angle$CCC	(C)C-C(C) [g]	0.011
24	$\angle$CCC, $\angle$CCC	(C)C-C(C) [t]	-0.011
25	$\angle$COC, $\angle$OCO	(C)O-C(O) [g]	0.011
26	$\angle$COC, $\angle$OCO	(C)O-C(O) [t]	-0.011
27	skeletal torsion around C-O		0.026
28	skeletal torsion around C-C		0.024
29	C...O intramol hydrogen bonding		0.3
30	$\angle$CO..O intramol hydrogen bonding		0.06

[a] The stretch constants have units of mdyn/Å; the stretch-bend interactions have units of mdyn/rad; and the bending constants have units of mdynÅ/rad^2.

[b] [g] : gauche, [t] : trans.

line polymers. Therefore we should employ the calculated value 172.9 GPa of the case (a) as the theoretical crystallite modulus of the cellulose chain. A large difference in the calculated modulus between the two cases (a) and (b) suggests an importance of the effect of the intramolecular hydrogen bondings on the mechanical property along the chain direction.

When the molecular chain is stretched by some external force, the constituent atoms are displaced from their equilibrium positions by an amount proportional to the product of the strain and the Cartesian coordinates (an assumption of affine deformation). But such an external deformation is not the most stable deformation and it is assumed that the atoms further change their relative positions so as to minimize the energy increment due to the external deformation. This displacement is called the inner strain. That is to say, the overall atomic displacement is a sum of the external and inner strains (3, 9). Figure 2 shows the inner strains induced by the hypothetically large extensional strain of 10% applied

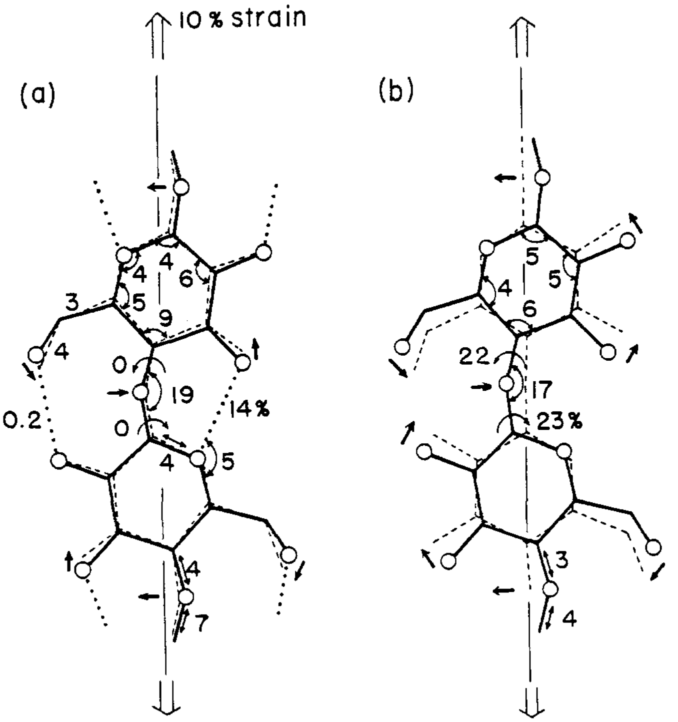

Figure 2. Atomic displacements (inner strain) and potential energy distribution (%) for the cellulose single chain deformed by hypothetically large extensional strain of 10%. (a) and (b) are for the cases with and without the intramolecular hydrogen bondings taken into consideration, respectively.

along the chain direction for the cases of (a) and (b). In Figure 3 is shown the overall atomic displacement for the case (a). As seen in Figure 2 (a) and (b), the virtual bonds of the glucose rings, which are defined as hypothetical linkages connecting the oxygen atoms 1 and 1' (Figure 1), tend to stand vertically along the draw axis as the chain is stretched. The distribution of strain energy to the stretching and bending of the ether linkages connecting the neighboring glucose rings is about 30% and commonly observed for both the (a) and (b). The distribution to the ring deformation is somewhat different between the two cases; about 40% for (a) and about 20% for (b). The larger difference between these two cases is seen in the potential energy distribution to the intramolecular hydrogen bondings and the internal rotations around the ether linkages. In the case (a), the potential energy distributes to the hydrogen bondings by about 14% and the distribution to the internal rotation of the skeletal chain is negligibly small. On the other hand, for the case (b), the internal rotations owe the main part of the potential energy added from the external field, about 45% in total. It may be reasonably considered that the intramolecular hydrogen bondings suppress the internal rotations of the glucose rings and so the skeletal chain is deformed mainly by the mechanism of the ring deformation coupled with the stretching and bending of the ether linkages.

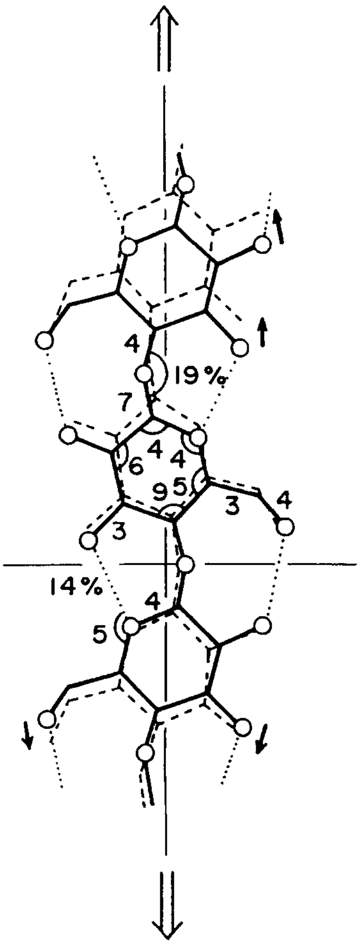

Figure 3. Overall atomic displacements and potential energy distribution (%) for the cellulose single chain stretched by extensional strain of 10% (refer to the text).

In the normal coordinates treatment of the infrared and Raman spectra of native cellulose, Blackwell et al. (11) did not take into account the force constant of the intramolecular hydrogen bondings. But the importance of this interaction is now clear from the above discussion. We have found that these intramolecular hydrogen bondings shift up the normal mode frequencies by 0 - 50 cm^{-1} in the region below 500 cm^{-1}. The low-frequency region intimately relates to the vibrational modes of the skeletal deformation and the external lattice vibrational modes, which directly reflect on the mechanical property of the crystal. Therefore, in order to estimate the crystallite modulus more reasonably, including the anisotropy in the mechanical properties, it may be necessary to carry out the more detailed vibrational analysis particularly in the low-frequency region by taking into account the intermolecular interactions as well as the intramolecular hydrogen bondings.

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