Crystalline Form of Native Celluloses

The report by Atalla and VanderHart (1), in which solid-state nuclear magnetic resonance was used to study the structure of native cellulose, proposes an interesting concept, that native cellulose is "a composite of two distinct crystalline forms" (1, p. 283). These authors claim that their observation provides a basis for reassessing current interpretations of data pertaining to the structures of native celluloses. In their discussion, they imply that those data derived by diffraction techniques are suspect because such techniques lack the sensitivity to resolve the composite. Although this may or may not be true for x-ray diffraction studies in which few reflections are evident in cellulose patterns, it is not the case for electron diffraction techniques. The interaction of electrons with atoms is much stronger, by a factor of roughly 1000, than the interaction of x-rays. Diffracted beams of intensity comparable with that of the incident beam can be given by less than 10 nm of crystalline material (2). Moreover, because of the short wavelengths of electrons, electron interference maxima appear at very small diffraction angles. Thus electron patterns contain many more reflections than x-ray patterns (3).

It was for these reasons that we turned to electron diffraction techniques in our study (4) of the exact same cellulose structures that Atalla and VanderHart investigated. Our results, electron diffraction patterns containing many strong reflections, clearly revealed the existence of two distinctly crystalline unit cells. Furthermore, the diffraction patterns of each structure could be completely resolved according to either one or the other unit cell. The *Acetobacter xylinum* and *Valonia ventricosa* structures fit the cell proposed by Nieduszynski and Atkins (5) and Honjo and Watanabe (6), whereas the cotton and ramie fit that of Wellard (7), which agrees quite well with the classical Meyer-Misch cell (8).

The super lattice assignment to *Valonia* was verified by the x-ray and electron diffraction analysis of Sarko and Muggli (9) and the x-ray work of Gardner and Blackwell (10). In a subsequent study involving computer modeling based upon x-ray diffraction data from an investigation of ramie, French concluded (11) that the two celluloses may differ in chain conformation as well as unit cell. No evidence of a composite of the two cells could be found in any of our electron diffraction patterns of cellulose.

All samples representing the four polymorphic forms could be assigned to one or the other crystalline unit cell according to the presence or absence of certain reflections. Therefore, the postulation of mixed types coexisting as a composite is seriously questioned.

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Hebert questions our conclusion that native celluloses are composites. Points similar to those he raises were considered in our analyses, although they were not discussed in our report.

We agree with Hebert that electron diffraction, because of the stronger interactions involved, is a more sensitive probe of structure than x-ray diffraction. Thus the observation by Hebert and Muller (1) of odd-order 0k0 reflections (2) for both types of cellulose clearly supports the view that the space group is not $P2_1$. Their study cannot address the possibility of composites, however, for a number of reasons. As they indicate in their report (1), the Nieduszynski and Atkins (3) unit cell has *a* and *c* axes equal to twice those of the Wellard (4) unit cell, whereas the *b* axis is the same in both unit cells. As a consequence, the plane spacings and hence the reflections of the Wellard unit cell are a subset of those for the Nieduszynski and Atkins unit cell. Thus the presence of a minor component with the Wellard unit cell in a cellulose sample dominated by the Nieduszynski and Atkins unit cell cannot be detected on the basis of indexing the reflections. Without careful intensity analyses, which Hebert and Muller did not attempt and which remain the subject of controversy, the presence of a minor component cannot be excluded. The reverse possibility of a minor component with the Nieduszynski and Atkins unit cell in a cellulose sample dominated by the Wellard unit cell is, in principle, subject to testing by indexing. The difficulties, however, are experimental ones associated with exposure time. As Hebert has noted, because the diffraction angles are small, the number of reflections observed with electron diffraction is much higher than is possible with x-ray diffraction. The disadvantage is that the reflections are so closely spaced that strong reflections can mask weaker ones. Exposure times sufficient to detect a minor component correspond to overexposure for the major component, thus masking the weaker reflections of the minor component.

It is well established that minor components in polymeric systems are frequently difficult to characterize by diffraction methods (5). The problem is compounded when electron diffraction techniques are applied to cellulose because the lifetime of the sample in the high-voltage beam is very limited. The effect of the beam is to decrystallize and eventually to decompose the sample.

The analyses by Gardner and Blackwell (6) and by Sarko and Muggli (7) incorporate the assumption that $P2_1$ is the space group, and their findings are in question (8).

We would emphasize that, although we have addressed the comments of Hebert and the implications of the findings of Hebert and Muller (1) concerning the possibility of a composite structure for cellulose, we did not in our report identify the components we detected with either of the unit cells referred to by Hebert and Muller. The nature of the composite components we have proposed remains the subject of active investigation.

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References and Notes

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