DIFFRACTION FROM MODEL CRYSTALS

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Abstract

Although calculating X-ray diffraction patterns from atomic coordinates of a crystal structure is a widely available capability, calculation from non-periodic arrays of atoms has not been widely applied to cellulose. Non-periodic arrays result from modeling studies that, even though started with atomic coordinates in periodic arrays, degenerate into a coordinate set that does not retain exact crystallinity. Being able to calculate the diffraction patterns from such models enables comparison with the observed patterns from practical samples such as cotton fibers to attempt to understand the true nature of the cellulose in that environment.

Introduction

X-ray diffraction has been applied to cellulosic materials for almost 100 years, with many different purposes. These studies have led to the understanding of polymers in general, the identification of numerous different crystal forms, as well as the arrangements of the cellulose molecules in several of those different forms. Another use of diffraction has been the characterization of cotton fibers in terms of their degree of crystallinity, a phrase that covers both the size of the crystals and the extent of deviation from absolutely regular repetition in a crystal lattice. Less crystalline fibers are usually weaker but may have a greater ability to stretch before breaking, and they are usually more reactive to dyes and other chemicals. Some 50 years ago, it gave considerable comfort to chemists to know the crystallinity of their samples which could be quickly measured on a chart recorder (Segal et al., 1959). Similarly, the width of the diffraction peaks on the chart could be translated into the crystallite size. The crystallinity, with values of about 80%, was used to evaluate different native cottons as well as to measure the degree of change brought about by various physical and chemical treatments.

Typical samples of cotton for diffraction studies consist of fiber bundles or fibers chopped up in a Wiley mill to give either a partly oriented fiber pattern or a powder pattern, respectively. The crystallites of cotton are thought to have dimensions of some 7 nm (70 Å) in cross-section and a one or two hundred nm length. Such crystallites are much smaller than are typically studied for accurate determinations of structures of small molecules such as mono- and disaccharides. One consequence of the small size is that many more molecules are on the surface. A crystallite of 7 nm cross-section could contain 81 molecules, of which 32 would be on the surface. That corresponds to nearly 40 %, while the ideal-size crystal might have 6.6×10^{11} molecules, leaving only 0.0016% on the surface. These surface molecules would not be expected to have all of the same structural details as a molecule in the crystallite interior, but would be expected to be very important for the cotton crystallite and negligible for the 'full size' crystal.

Another situation arises when making computer models of the cellulose structure in cotton. It is within current capability to readily construct model crystallites that are as large as the currently estimated sizes. Such models initially based on the published crystal structure of cellulose Iβ (Nishiyama, Langan and Chanzy, 2002) can then be subjected to energy minimization or molecular dynamics methods to alter the crystal surfaces to more realistically show how the molecules on the crystallite surfaces might differ from those in the interior. In the process of applying minimization or dynamics, the other properties of the crystal will also vary (French and Johnson, 2008, Matthews et al., 2006). Although diffraction patterns can be routinely calculated from atomic coordinates, those calculations are based on the assumption that the atoms are in periodic arrays. This is clearly not the case for the computer models. Therefore, specialized software was needed for this task.

Materials and Methods

Samples of cotton fabric were Wiley milled to 20 mesh and treated with 2.5 N HCl for 40 minutes at reflux and stored for about 25 years. X-ray diffraction with Cu Kα radiation was carried out on a Philips powder

diffractometer. Models of the crystals studied were prepared with various software based on the cellulose Ib crystal structure and subjected to energy minimization or molecular dynamics with AMBER (Case et al., 2006), using the GLYCAM04 (Basma et al., 2001; Kirschner and Woods, 2001, 2001a;) force field for carbohydrates. Diffraction patterns were calculated with the Debyer program (Wojdyr, 2009) or with new software written by one of the authors (YN).

Results and Discussion

Crystal have been built ranging in size from seven cellooctaose molecules to 49 chains, each with 20 glucose residues,. Diffraction patterns of one type or another were calculated both before and after energy minimization or molecular dynamics. As an illustration, a model with 37 cellooctaose chains (French and Johnson, 2007) that was minimized is shown in Figure 1.
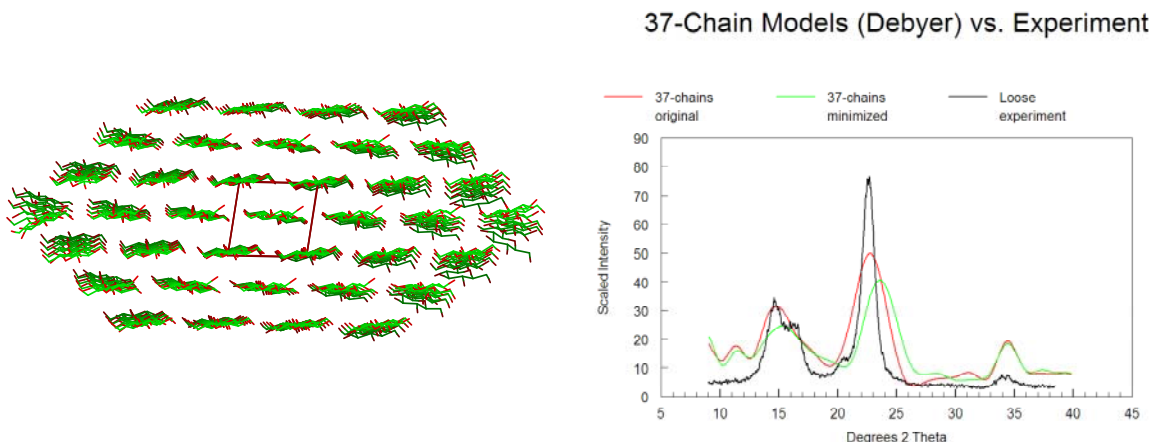

Figure 1. A cluster, or minicrystal, of cellooctaose chains, after energy minimization (left). The chain axes are essentially perpendicular to the plane of the paper. The slightly distorted (because of minimization) cellulose I unit cell is illustrated. This particular shape was chosen to maximize the number of neighboring chains for the total number of chains. This shape, while not necessarily realistic, reduces the extent of disorder on the surfaces. On the right, the calculated diffraction patterns, both from before and after energy minimization, are compared with the experimental data from a loosely-packed sample.

In Figure 1, the intensity from both the calculated patterns before 12° 2Θ can be understood as low-angle scattering that is caused by the sharp edges of the isolated crystal model. Otherwise there is an interesting, if not totally satisfactory correlation between the red line and the black, experimental line. Peak positions in the green line are shifted from the corresponding ones in the red line because of the shrinkage in the unit cell dimensions that resulted from energy minimization with AMBER/GLYCAM04. The diffraction patterns from models with seven and 19 chains did not correspond well to the observed pattern, while a model with 49 chains (a continuation of the above 37-chain model with six added chains both above and below) gave a better correspondence, although low-angle scattering is still a problem. In Figure 1, the calculated peaks have a similar width, both wider than the experimental peak. This indicates that the model is too small, but that the lack of order resulting from energy minimization does not substantially increase the peak width – it is more connected to the model size. Even the 49-chain models gave peaks that were too wide.

Summary

This work, still in its early stages, is able to provide, by trial and error, indications of how crystallites in cotton might appear. Our work has shown a substantial sensitivity to the shapes of the model crystals as well as the sizes. We anticipate that we will be able to move from the empirical summary deductions from X-ray studies with values such as 80% crystallinity, to knowledge of the actual structural differences among different varieties of cotton or different types of chemical or physical treatments.

Acknowledgement

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