



FIBER DIFFRACTION AND SMALL-ANGLE SCATTERING ON SINGLE CELLULOSE FIBERS

M. MÜLLER, M. BURGHAMMER AND C. RIEKEL

ESRF, EXPERIMENTS DIVISION

Microdiffraction experiments at the ESRF Microfocus beamline (ID13) on single cellulose fibers have already been reported in 1995 [1]. Since then, a considerable amount of fiber diffraction experiments has been performed and the experimental setup has been further developed. The present article will show some of the most recent experimental results on cellulose.

Cellulose fibers, both native and artificially produced, play a major role in daily life. They are present in textile fabrics (cotton, linen, viscose), paper and construction materials (wood). Detailed structural information down to the level of a single fiber are needed in order to understand and to optimize the unique mechanical properties of these materials.

At ID13, monochromatic beams of 10 μm and 2 μm in diameter (produced presently by an ellipsoidal mirror and subsequent beam definition by collimator or glass capillary [1], respectively) are used for position-resolved diffraction and – more recently – for small-angle scattering experiments [2]. Ideally, information on three different length scales is obtained simultaneously [3]:

- (i) The sample is scanned on the micrometer scale, corresponding to optical microscopy.
- (ii) Wide-angle diffraction contains information on crystallographic parameters such as cell constants or

orientation.

(iii) Small-angle scattering is sensitive to inhomogeneities on intermediate length scales (here, typically 1 nm to 10 nm).

The so-called « scanning set-up » on ID13 is, therefore, particularly suitable for the investigation of hierarchically structured materials like cellulose.

Cellulose molecules aggregate forming small crystals called *microfibrils* (a few nm in diameter). The morphology of native and artificial cellulose fibers, i.e. the arrangement of the microfibrils, is of great variability. Many fibers are further structured on a microscopic scale. In the following, three examples will be given to demonstrate how the x-ray microbeam is used in order to obtain information on the different hierarchical levels of cellulose organisation.

The investigation of a *single viscose rayon fiber* (F295, Fibro[®], Courtaulds Research and Technology) demonstrates the advantage of the x-ray method with respect to selected area electron diffraction [4]. A single fiber is used in the experiment, and no tedious and time-consuming sample preparation like embedding and

sectioning is necessary. In addition, more quantitative diffraction diagrams can be obtained due to the weaker interaction of x-rays with matter (i.e. less beam damage and no multiple scattering).

MICROSTRUCTURE SEEN BY ELECTRON MICROSCOPY

The fiber, having a diameter of 9 μm , was scanned with a 2 μm beam in steps of 2 μm . Figure 1 shows a scanning electron microscopic image of the fiber with a characteristically serrated surface. The two circles signify the areas illuminated by x-rays in the center of the fiber and at its edge, respectively. Below each circle, the respective fiber diffraction diagrams (cellulose II structure, see also [1]) are found as insets. There is a clear indication of a « skin-core » microstructure for this viscose fiber: The orientation of the cellulose microfibrils at the fiber edge is better, resulting in better defined Bragg reflections in the diffraction diagram. From transmission electron micrographs, there is evidence for a 2 μm thick skin layer [4]. Using this number, the core/skin volume ratio for the skin + core pattern (Figure 1) can be estimated. A « pure core » diffraction

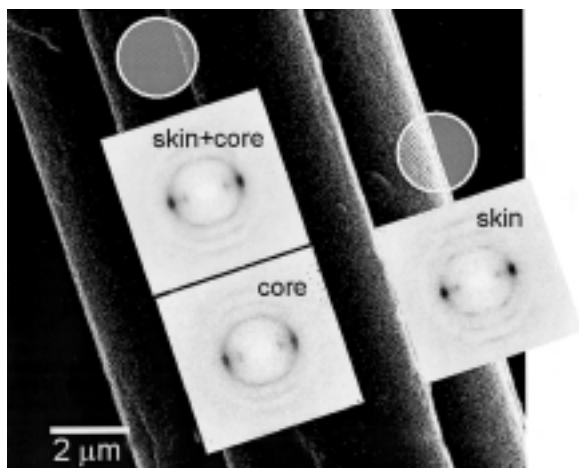


Fig. 1: Skin-core microstructure of a viscose rayon fiber (diameter 9 μm). In the skin layer with a thickness of about 2 μm the cellulose crystals are far better oriented than in the fiber core, resulting in sharper diffraction spots in the fiber diffraction diagram. (Wavelength 0.782 nm, 2 μm beam, image-intensifier CCD detector, 96 s exposure.).



Fig. 2: Scattering curve of a single native flax fiber on a double-logarithmic scale (azimuthal integration of the two-dimensional scattering pattern; wavelength 0.96 nm, 10 μm beam, CCD detector, 240 s exposure). Data in the small-angle region (SAXS) as well as high-order Bragg reflections (WAXS region) were obtained simultaneously on a single detector.

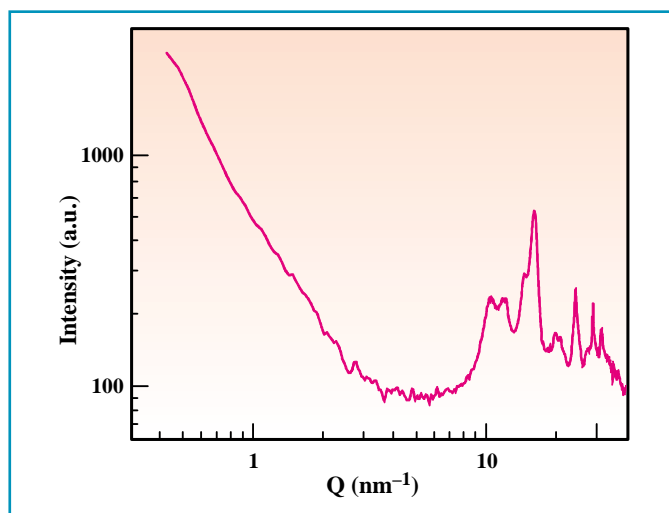


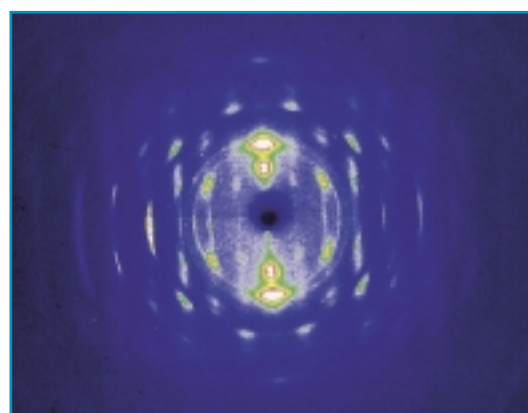
diagram (Figure 1) is then obtained by taking the difference of the centre and the edge patterns with the appropriate scaling. It can now clearly be seen that the orientation of the cellulose microfibrils inside the fibre core is much worse (by a factor of two) than in the skin layer. Note that a quantitative fiber diagram has already been obtained from a very small volume of cellulose (of the order of 10 μm^3 for the pattern at the fiber edge).

MICRODIFFRACTION

The main interest in *single flax fibers* (average diameter 20 μm) concerns the disorder present in all native cellulose specimens, both inside the microfibrils and in their arrangement in the fiber. It is, therefore, necessary to extend the microdiffraction experiments into the SAXS-range. It has recently been shown that both a fiber diagram and a small-angle scattering pattern can be simultaneously recorded on a single CCD detector with a 10 μm beam [3]. The scattering curve, resulting from azimuthal integration, is shown in Figure 2. A range of d-spacings from 15 nm to 0.21 nm is covered. The small- and wide-angle regions are not clearly separated, but connected by a continuous streak of intensity, which is in fact concentrated on the equator of the diagram (see also Figure 3). This scattered intensity is – together with a diffuse maximum below the Bragg reflections at $Q \sim 15 \text{ nm}^{-1}$ – probably due to disordered cellulose molecules between the ordered (crystalline) microfibrils. As most of these molecules are located on the surfaces of the microfibrils, they retain their alignment with the fiber axis. This one-dimensional order gives rise to the orientation of the corresponding scattering pattern.

A second experiment on flax explored the present limits of the signal-to-noise ratio in single fiber diffraction [3]. A small beam stop (400 μm in diameter) was moved very close (5 mm)

Fig. 3: Fiber diffraction pattern of a single flax fiber at 100 K (wavelength 0.782 nm, 10 μm beam, CCD detector, 120 s exposure). The fiber axis was oriented nearly horizontally and corresponds to the meridian of the diffraction diagram; the equator is perpendicular to the fiber axis. The resolution limit is $d = 0.113 \text{ nm}$ (009 reflection on the meridian).



to the sample in order to keep the air scattering background signal at a minimum. Using a liquid nitrogen cryostream, the fiber was cooled to 100 K. The low temperature reduces thermal vibrations of the atoms in cellulose and, thus, enhances the intensity of high-order Bragg reflections. Figure 3 shows the measured fiber diagram. In the meridional direction, the 009 reflection ($d = 0.113 \text{ nm}$) is observable, whereas along the equator the 600 ($d = 0.131 \text{ nm}$) is the highest indexed reflection. These observed smallest d-spacings correspond to the diffraction limit of the cellulose crystals. The excellent signal-to-noise ratio enables furthermore the observation of diffuse scattering along the layer lines of the diffraction diagram. This diffuse intensity is an indication of defects inside the microfibrils, which are probably related to cellulose biosynthesis. A quantitative analysis of these very recent data is under way.

Cellulose is just one example of hierarchically structured biopolymers. The method described here can be equally well applied to a large field of problems in biopolymer science.

Studies on wood, chitin, starch, spider silk and collagen are current topics of research at the Microfocus beamline. Of particular interest for future microdiffraction studies using beams in the micrometer and sub-micrometer range is the breakdown of fiber symmetry which has already been observed for certain of these systems, chitin [5] being one example. ■

REFERENCES

- [1] P. Engström, C. Riekkel, H. Chanzy, *ESRF Newsletter* **24**, 8-9 (1995).
- [2] C. Riekkel, P. Engström and C. Martin, *Journal of Macromolecular Science - Physics* **B37**(4), 587-599 (1998).
- [3] M. Müller, C. Czihak, M. Burghammer, C. Riekkel, *J. Appl. Cryst.*, submitted.
- [4] M. Müller, C. Riekkel, R. Vuong, H. Chanzy, *Polymer*, in press.
- [5] M. Burghammer, H. Chanzy et al., unpublished.

ACKNOWLEDGEMENTS

The authors wish to thank H. Chanzy (CERMAV-CNRS Grenoble) for many fruitful discussions.