



	Experiment title: Anisotropy of the elastic properties of cellulose fibres	Experiment number: SC-2148
Beamline: ID13	Date of experiment: from: 20.09.06 to: 23.09.06	Date of report: 05.03.07
Shifts: 9	Local contact(s): Michael Krisch	<i>Received at ESRF:</i>
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Report:

Cellulose is the most abundant biopolymer on earth and the main building material of plant cell walls. It is a semicrystalline biopolymer with nanocrystals (the so-called *microfibrils*) embedded in a softer matrix of disordered cellulose [1]. Cellulose microfibrils in bast fibres such as flax (linen) and ramie have a typical diameter of 4-6 nm and a length of about 0.1 μm . They are highly oriented along the molecular axis of the molecules parallel to the macroscopic fibre axis [2].

In order to fully understand and model the mechanical properties of plant cell walls, those of the hard particles, the crystalline microfibrils, are of major importance. They are usually studied by means of *in situ* stretching experiments using X-ray diffraction with synchrotron radiation. In our previous experiments, both fibre bundles were investigated with larger beams (HASYLAB, DESY) and single fibres with microbeams (ID13, ESRF) [3,4]. As a result, the strain inside the cellulose crystals was found to be a factor of 3 to 5 smaller than the macroscopic fibre strain. The calculation of the microfibril Young's modulus from these values requires further knowledge of the stress distribution in the composite and of its morphology. Thus, our values for the elastic constants as well as those of other authors using X-ray diffraction are based on assumptions (e. g. constant stress distribution in the composite) that are difficult to prove [3,5,6]. Similar problems occur when band shifts in Raman scattering are interpreted in terms of the elastic modulus [7]. Theoretical values for the elastic constants of cellulose crystals vary strongly with the force field used in the calculations [8,9]. – In summary, reported values for the longitudinal Young's modulus of crystalline cellulose range from 90 to 170 GPa, a variation in disagreement with the structural uniformity of native crystalline cellulose [1].

The idea of the ID28 experiment reported here was to measure the phonon dispersion in cellulose fibres using inelastic X-ray scattering (IXS) and thus determine the sound velocity v_p . The effective elastic modulus C is then simply derived, knowing the density of crystalline cellulose, $\rho = 1.625 \text{ g/cm}^3$, by $C = \rho v_p^2$.

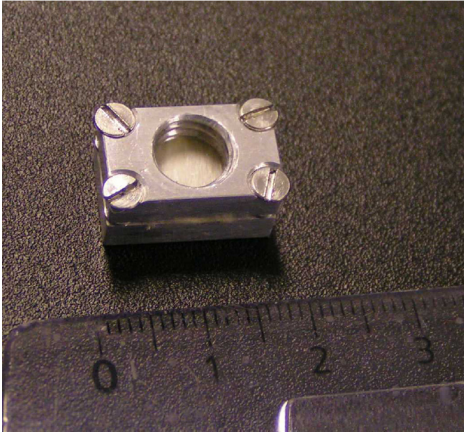


Fig. 1: Oriented cellulose fibres (total thickness 0.5 mm) mounted in an aluminium sample holder for IXS experiments.

The sample consisted of sheets of parallel flax fibres. Sample size was $0.5 \times 10 \times 10 \text{ mm}^3$ with oriented fibres mounted in an aluminium support frame (Fig. 1). The bundle orientation was checked beforehand by X-ray diffraction in the laboratory (orientation distribution with 17° FWHM). Mounting the sample inside the ID28 standard vacuum chamber minimised air scattering and eliminated the influence of adsorbed water. The oriented fibres were measured in two orientations, both with horizontally oriented fibres, with the scattering vector **Q perpendicular** (orientation 1; fibre direction almost along the X-ray beam) and **parallel** (orientation 2; fibres perpendicular to the beam) to the crystal c -axis, respectively. In the first case, scattering from phonon modes involving predominantly motions in the direction of the molecular chains (c -axis) is suppressed, as already proven in INS experiments on cellulose [10].

The experiment at beamline ID28 was carried out utilizing the Si (999) backscattering-reflection of the monochromator and the analysers (overall instrumental energy resolution of $\sim 3 \text{ meV}$). In the two orientations, IXS spectra were recorded at 20 different Q -values (4 analyser settings, $\Delta Q \approx 1.5 \text{ nm}^{-1}$) within the first two Brillouin zones in order to determine the longitudinal acoustic phonon branches.

In orientation 1, we derived an average transverse (i. e., perpendicular to the fibre axis) sound velocity, v_{pt} , from a sinusoidal fit in the first Brillouin zone (Fig. 2). Considering the high structure factor of the 200 equatorial cellulose reflection, the phonons that could principally be detected in general $[hk0]$ directions are probably dominated by a $[h00]$ contribution. – The definition of the excitations becomes worse in the second zone, even though the limit of a density-of-states is not reached.

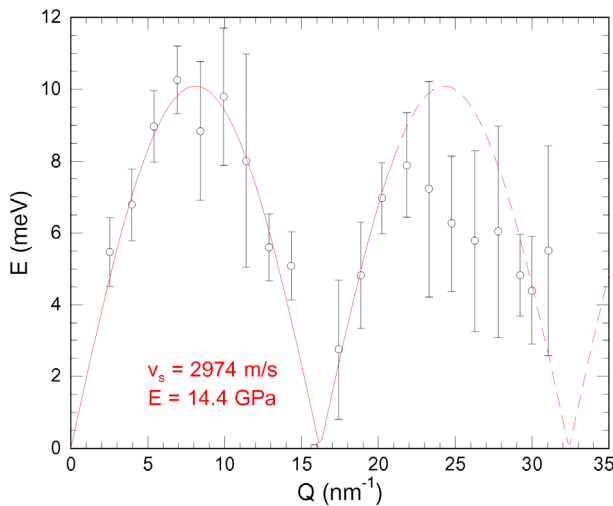


Fig. 2: Phonon dispersion relation in $[hk0]$ direction (measured in orientation 1), probably dominated by $[h00]$ due to the high structure factor of the 200 reflection at 16.3 nm^{-1} . Fit with a sine function up to 21 nm^{-1} yields a sound velocity of $(2974 \pm 83) \text{ m/s}$, corresponding to an effective modulus of elasticity of $(14.4 \pm 0.8) \text{ GPa}$. The data in the first Brillouin zone are much clearer than those in the second one.

In the other orientation (2), the phonon intensity was highest close to the meridional reflections 002 and 004 (Fig. 3a). In the reduced zone scheme (Fig. 4), the four excitations close to 002 and 004 are found on a straight line, yielding a longitudinal (i. e., along the fibre axis) velocity of sound v_{pl} . The 2D plot (Fig 3a) also reveals a problem of the experiment: The elastic line had to be subtracted from the spectra (shaded area in Fig. 3a) in order to reliably determine the phonon energies. Fig. 3b is a logarithmic plot of the two spectra close to 004, exhibiting very strong elastic contribution. These are very probably due to the high amount of disordered material in native cellulose fibres.

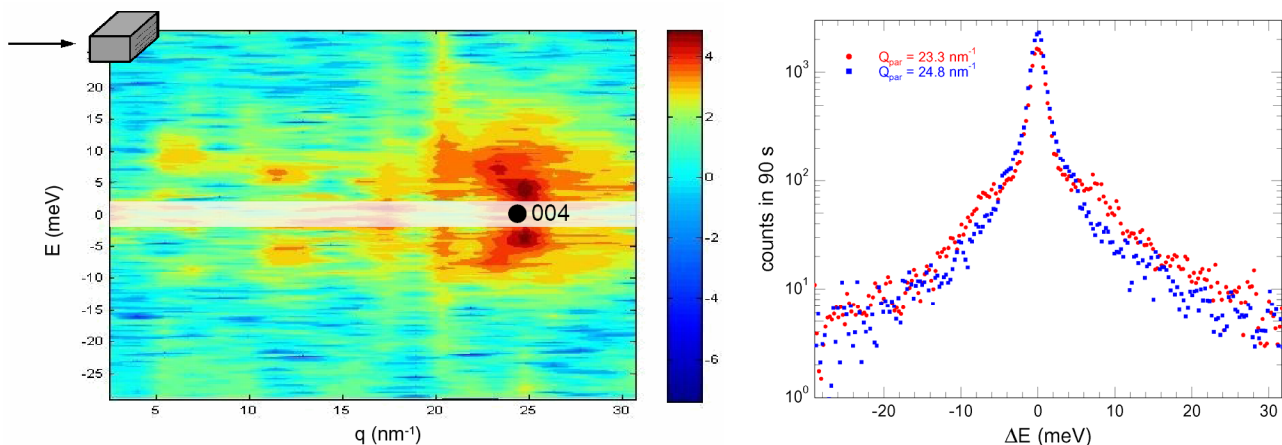


Fig. 3: (a) Inelastic X-ray spectra of oriented cellulose fibre with Q along $[00l]$ (orientation **2**). (b) The elastic lines are so strong that phonon frequencies were determined from spectra with the elastic line subtracted.

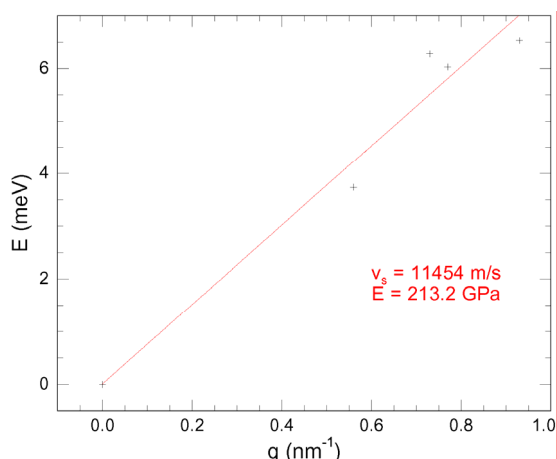


Fig. 4: Phonon dispersion relation in $[00l]$ direction (measured in orientation **2**). The phonon intensity is only high close to the reciprocal lattice points 002 and 004 (meridional reflections of cellulose fibres), the phonons have been folded back into the first Brillouin zone. A sound velocity of (11454 ± 1291) m/s, corresponding to an effective longitudinal modulus of (213 ± 48) GPa, is obtained.

The obtained transverse and longitudinal elastic moduli of native cellulose are $E_t = (14.4 \pm 0.8)$ GPa and $E_l = (213 \pm 48)$ GPa. The transverse modulus of crystalline cellulose, determined here for the first time, is supposed to be dominated by the $[h00]$ direction (see above) where the cellulose molecules sheets are only weakly van der Waals bonded. Calculations gave a transverse modulus of about 10 GPa [6]. The longitudinal modulus of elasticity determined here is larger than previously measured [3,5,6] or calculated [8,9]. Taking into account that “classical” X-ray diffraction experiments rather underestimate the mechanical properties of crystalline material and that present force fields for cellulose cannot predict the crystal unit cell correctly, the elastic constants measured in the present experiment constitute an important step towards a more exact determination of the mechanical properties of cellulose.

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