Crystallinity in ultra thin cellulose films

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In plant cell walls cellulose forms partially crystalline microfibrils with a width of around 3 nm. The crystallization of polymer chains to cellulose I structure occurs during the biosynthesis of cellulose. When one regenerates cellulose, e.g. from a solution, the man-made cellulose II form arises. It is difficult to increase the thickness of the cellulose crystallites: the crystallite width in regenerated cellulose is typically only about two times as large as in native cellulose microfibrils. Here ultrathin cellulose films were made by regenerating trimethylsilyl cellulose (TMSC) which was spin coated on silicon substrates. The structure of cellulose films was characterized with grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity experiments.

Trimethylsilyl cellulose (TMSC) was synthesized from spruce cellulose powder (Fluka). The films were prepared on silicon substrates of the size of 1.5×1.5 cm^2 (Okmetic, Finland). Toluene solutions of TMSC (10 g dm^{-3}) were spin coated at 4000 rpm (acceleration of 2200 rpm/s) onto cleaned substrates. The deposition of the solution was performed on a static substrate and the spinning was retained for 30 seconds. In order to converse TMSC into cellulose [1] the spin coated TMSC films were subsequently exposed to vapor of 2M HCl for 1 min. The thickness of the studied films varied between 2 and 20 nm.

The grazing incidence x-ray diffraction (GIXRD) measurements were carried out at the beamline W1.1 (ROEWI) at HASYLAB. The reflectivity curves were measured with the NaI(Tl)-detector available at the beamline. For GIXD, a transportable image plate (Molecular Dynamics) was used to collect the diffraction patterns. The energy of the x-ray beam was 10.5 keV (1.18 Å) and the incident angle of the beam was 0.165°. The scattering due to air between the sample and the detector was reduced by having the sample in helium atmosphere. The exposure time for the image plate was 20-30 min for each sample. A correction due to measurement geometry was done for the data and a sector of 40° of the two-dimensional diffraction patterns was used in the analysis. The length of the scattering vector (q) was defined as $q=(4\pi/\lambda)\sin\theta$, where θ is half of the scattering angle.

X-ray reflectivity curves showed clear oscillations indicating low surface roughness of the films. GIXD experiments showed that the regenerated cellulose films are weakly ordered. There were no well-resolved diffraction peaks from which the possible crystal structure could be identified. However, on the basis of the diffraction patterns, the films may contain some very tiny cellulose II or III crystallites. Because of the preparation process, the short range order of cellulose chains may differ from that of amorphous cellulose in the native cellulose I microfibrils. On the basis of GIXD results the cellulose structures were the same regardless of the thickness of the film. Exposure to concentrated HCl gas changed the morphology of the film surface, as was revealed by atomic force microscopy studies. On the cellulose chain level, the films were weakly ordered.

Amorphous cellulose is accessible to water and its chemical reactivity differs from that of crystalline cellulose. Thus amorphous cellulose surfaces are of interest from the point of view of applications and biology allowing e.g. studies on the binding of cellulose to other natural polymers of the plant cell wall.

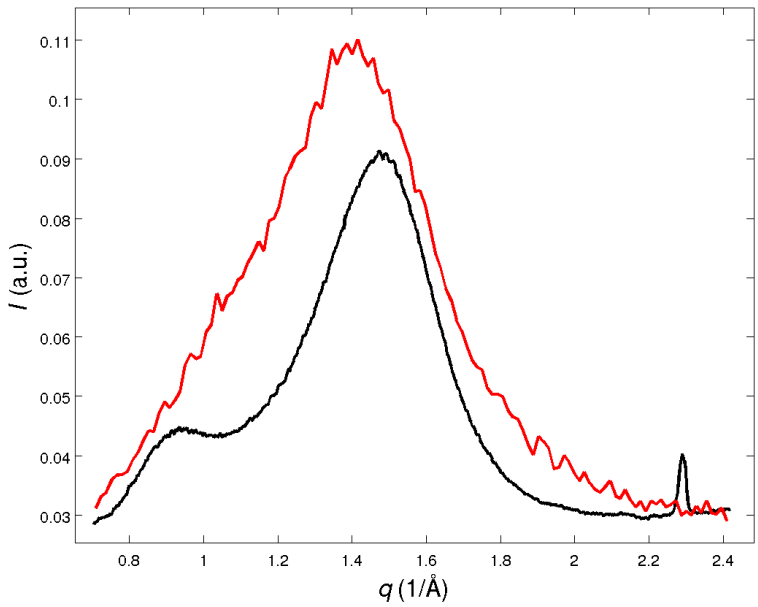

Figure 1: Grazing incidence x-ray diffraction pattern for untreated, as-prepared cellulose film, regenerated from TMSC (black) compared with x-ray diffraction measured from ball-milled microcrystalline cellulose in reflection geometry (red).

References

[1] E. Kontturi, M. Suchy, P. Penttilä, B. Jean, K. Pirkkalainen, M. Torkkeli, R. Serimaa. Amorphous characteristics of an ultrathin cellulose film. Macromolecules, submitted.