In-situ X-ray Diffraction Investigation of Thermal Decomposition of Wood Cellulose

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The hierarchical organisation of wood is known to provide a biomaterial with excellent mechanical properties in spite of its low density. The material wood is built up in several levels of hierarchy [1]. On the micrometre or cell level, wood is a cellular porous solid, built up of tracheids, which are hollow tube-shaped cells with diameters of several micrometres and lengths in the order of millimetres. The cell wall is organised in layers, where the secondary cell wall layer S2 is the thickest one. On the nanometre scale, an analogy can be made with a unidirectional fibre-reinforced composite material, in which the cellulose fibres represent the fibre reinforcement and the amorphous hemicelluloses and lignin are the composite matrix. The crystalline structure of cellulose has been intensively studied in polymer science for almost one century (see [1] and references therein). Pyrolysis of wood in a non-oxidising atmosphere is fairly well characterised from the chemical point of view [2], but there are still only a few studies focusing on structural aspects [3,4].Carbon char from wooden materials is of increasing interest for structural applications due to the potential use of cellular carbon templates in advanced ceramics manufacturing [5].

In the present study the kinetics of cellulose degradation in softwood in the temperature range from 300 to 360°C was studied by *in-situ* X-ray diffraction (XRD) using synchrotron radiation [6]. Spruce wood (*Picea abies* [L.] Karst.) from the stem of an eighty-year old tree with annual rings of regular intervals containing normal wood with small microfibril angle was selected for the investigation of softwood pyrolysis. For measuring *in-situ* XRD patterns in transmission geometry, a special custom-made furnace with mirror heaters was developed by the applicants in cooperation with the beamline staff. Sample heating was performed by commercially available halogen photo optic lamps with elliptical-shaped gold-coated glass mirror reflectors. The concept of mirror heating offers the advantage of a non-contact heating to generate a "hot zone" in free space. Low power consumption, no demand for cooling systems and in particular extremely fast heating and cooling rates of small sample volumes are advantages of mirror lamps. Three mirror lamps were positioned in a copper block of the shape of an equilateral triangle. The wood slice was mounted between two rings of quartz glass and it was positioned at the common focus point of the lamps. The focusing arrangement of the three lamps assured a homogeneous radiation spot of about 5 mm in diameter at the sample position. The temperature was measured by a thermocouple, which was assembled in a quartz glass ring of the specimen holder. The heating cell was enclosed in a steel tube covered with Kapton foils as X-ray windows. Continuous flow of helium provided an inert atmosphere for pyrolysis. *In-situ* XRD measurements were performed at the beamline A2 at HASYLAB/DESY. Monochromatic synchrotron radiation (E = 8.27 keV) was focused by a single mirror and the beam cross section was defined by aperture slits to 250 × 250 μm^2 at the sample position. The two-dimensional XRD patterns covered a total range of the scattering vector q of 4 nm^{-1} < q < 19 nm^{-1}. The length of the scattering vector is given by $q = (4\pi/\lambda)\sin\theta$, with 2θ being the scattering angle and λ the wavelength. The transmission of the sample at each pyrolysis state was determined *in situ* by using an ionisation chamber in front of the heating chamber to monitor the primary X-ray flux and a photodiode mounted in the beamstop to measure the transmitted photons. The scattering data were normalised with respect to primary intensity and corrected for background scattering, electronic noise, transmission and polarisation. Equatorial, meridional and mixed-indices XRD peaks of crystalline cellulose were azimuthally integrated for equal radial distances from the central beam by integrating narrow sectors of the two-dimensional XRD patterns. Figure 1a shows the time dependence of the equatorial XRD peaks at 330°C. The Scherrer sizes of the cellulose microfibrils L_{hkl}, also referred to as widths of the crystallites in the respective crystallographic directions *hkl* were estimated from the integrated width of the XRD peaks. A first-order reaction kinetics law was used to describe the decrease of L_{hkl} with time. Kinetics series at

300, 310, 320, 330, 340, 350 and 360°C were evaluated and an Arrhenius plot provided an activation energy in equatorial direction of 112 ± 17 kJ mol^{-1} (Figure 1b).

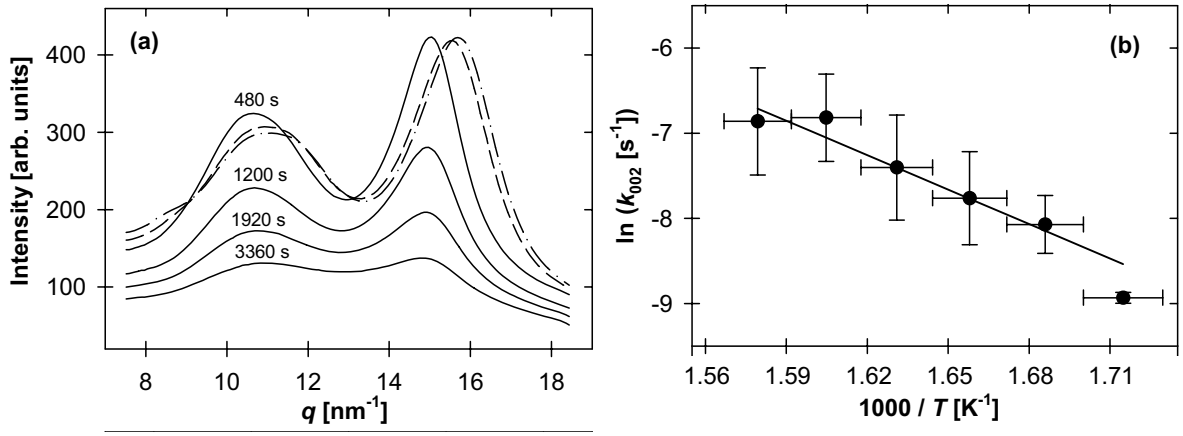

Figure 1: (a) Integrated XRD profiles of equatorial peaks from crystalline cellulose. Dash-dotted lines represent the native sample, dashed lines display the scattering signal after drying at 105°C and solid lines show various states of pyrolysis at 330°C. The numbers given in the Figure refer to the pyrolysis times. (b) Arrhenius plot of the rate constant k_{002} from the time dependence of L_{002}.

The data provided three-dimensional information about the structural degradation of cellulose by evaluating also meridional and mixed reflections. The thermal decomposition of cellulose fibrils in wood is found to occur mainly via a thermally activated decrease of the fibril diameter and may be accompanied by a random breaking of the fibrils into pieces of shorter length (Figure 2) [6]. This is a consequence of the anisotropic nature of the equatorial and meridional bonding forces in cellulose crystallites. The cellulose molecules run parallel along the meridional direction of the monoclinic unit cell and thus merely degrade along this covalently-bonded direction at these low temperatures. The decrease of L_{hkl} in meridional fibril direction might be a consequence of random piecewise breaking up of the crystallites due to local narrowing down of the fibril diameter.

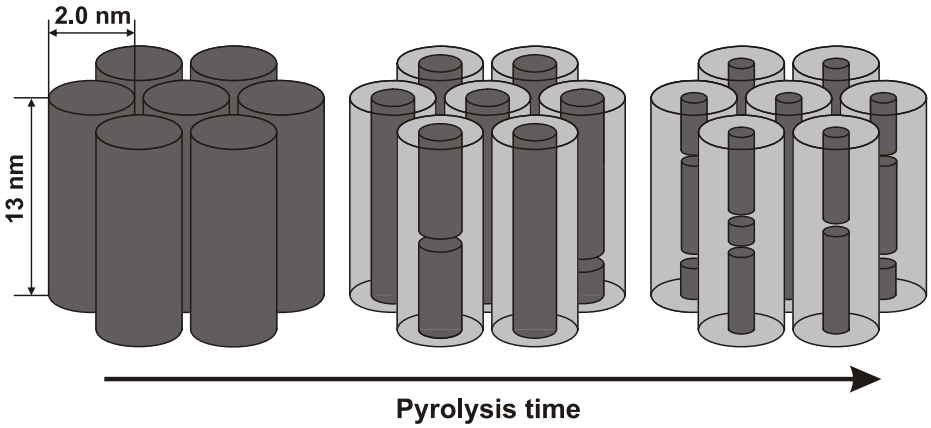

Figure 2: Schematic representation of the thermal degradation of cellulose microfibrils..

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