

## Comment about “The measurement of the micro-fibril angle in soft-wood” by K. M. Entwistle and N. J. Terrill

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In a recent paper “The measurement of the micro-fibril angle in soft-wood,” Entwistle and Terrill [1] describe the use of wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) for measuring the tilt angle of the cellulose fibrils with respect to the longitudinal cell axis (microfibril angle, MFA) of soft wood. The authors present a consistent and detailed mathematical description of the method and experimental results that illustrate the theoretical description. They report their findings as an “improvement to Cave’s method” [2] and cite a total of four papers, where those two being concerned with X-ray scattering date from the 1960s. It must be pointed out that since the pioneering X-ray studies of Cave and Meylan [2, 3] a great number of papers on the use of WAXD and SAXS for determining the MFA have been published. In this comment, we first refer to work which clearly shows that WAXD and SAXS are, in the meanwhile, well-established methods for the determination of MFA’s in wood. Second, we show how to evaluate WAXD and SAXS patterns from rectangular wood cells, which Entwistle and Terrill termed as “not capable of yielding microfibril angles.”

Already in the 1960s, Kantola *et al.* [4, 5] used both WAXD and SAXS for determining the MFA in wood. They investigated the influence of the sample orientation on the scattering pattern and derived Equation 2 in Entwistle and Terrill [1]. Further studies using X-ray diffraction from the 002 as well as the 040 planes of cellulose in wood were carried out for example by Nomura and Yamada [6], Paakari and Serimaa [7] and Sahlberg *et al.* [8]. In a recent paper by Evans [9], it was shown that the asymmetric positions of two poles of one reflection on the detector as they are described by Entwistle and Terrill (see their Equation 1a and 1b) can lead to asymmetric scattering patterns at some sample orientations. Lichtenegger *et al.* [10], took advantage of this asymmetry to determine the fibril orientation in single cell walls in cross sec-

tion. It should also be noted that Entwistle and Terrill were not the first to “explore the potential of small angle X-ray scattering for the measurement of the microfibril angle.” The earliest studies using SAXS on wood were done in the 1950s by Heyn to determine the diameter of elementary fibrils in wood [11–13]. In 1952, Wardrop used SAXS as a means to determine the orientation of the cellulose fibrils [14]. Nomura and Yamada (1972) applied SAXS on dry samples and concluded that part of the scattering signal from samples in the dry state may be due to micropores [15]. This conclusion was further confirmed by Jakob *et al.* [16] who found a great influence of moisture content on the SAXS pattern [16]. Entwistle and Terrill [1] do not state at all whether they used samples in wet or in dry conditions. A detailed analysis of SAXS patterns extracting the information on fibril orientation and diameter can be found in Jakob *et al.* [17, 18]. This technique has been developed further towards a position-resolved method (scanning-SAXS) for studying inhomogeneous samples [19, 20], and was systematically applied to wood [21, 22]. For instance, Equation 3a in Entwistle and Terrill [1] was derived in these papers [21, 22]. In November 1997, an entire workshop dedicated only to the MFA in wood was held in Westport, New Zealand, and several methods to measure MFA measurement including the WAXD and SAXS were presented and discussed there (see *e.g.* [23, 24]).

Finally we would like to add a comment on the evaluation procedure of WAXD and SAXS patterns from rectangular cells oriented at right angles to the beam: Entwistle and Terrill state that at this sample position the side walls are oriented parallel to the beam, yielding a signal that occurs right in the middle of the two other peaks that indicate the MFA. This statement is certainly true, but the additional signal does not necessarily “obscure” the pattern. This may have been different in the early days of X-ray scattering when the statistics of the scattering patterns obtained with the available

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equipment was probably not good enough to do a proper fit of the peaks. However, with the quality of scattering images obtained in the laboratory nowadays, and in particular with synchrotron radiation one gets curves accurate enough to fit the data also in this position. In fact, the curve presented by the authors in Fig. 12 as an example shows the well-known pattern of three distinct peaks on either side [19, 20]. Since we do not have the original data of the authors, we present data of ours that we think have a similar statistics, in order to show how to evaluate such patterns. In Fig. 1 both, the WAXD pattern and the SAXS pattern of a wood sample with an MFA of  $20^\circ$  is shown for two orientations:

with the beam parallel to one set of cell walls ( $\alpha = 0^\circ$ ) (Fig. 1a and b) and at a sample rotation of  $\alpha = 45^\circ$  (Fig. 1c and d). In the right part of the figure, the intensity is displayed as a function of the azimuth  $\phi$ . When the sample is oriented with  $\alpha = 0^\circ$ , this gives three peaks that can be fitted with three Gaussians. The position of the outer peaks relates to the MFA =  $20.4^\circ \pm 0.6^\circ$  in the case of WAXD (Fig. 1a) and  $20.0^\circ \pm 0.6^\circ$  in the case of SAXS (Fig. 1b) respectively [24]. A rotation of the sample by  $\alpha = 45^\circ$  yielded MFA-values of  $21.7^\circ \pm 0.6^\circ$  for WAXD (Fig. 1c), and  $20.4^\circ \pm 0.6^\circ$  for SAXS (Fig. 1d), i.e. identical results within the given accuracy. We therefore do not agree that a

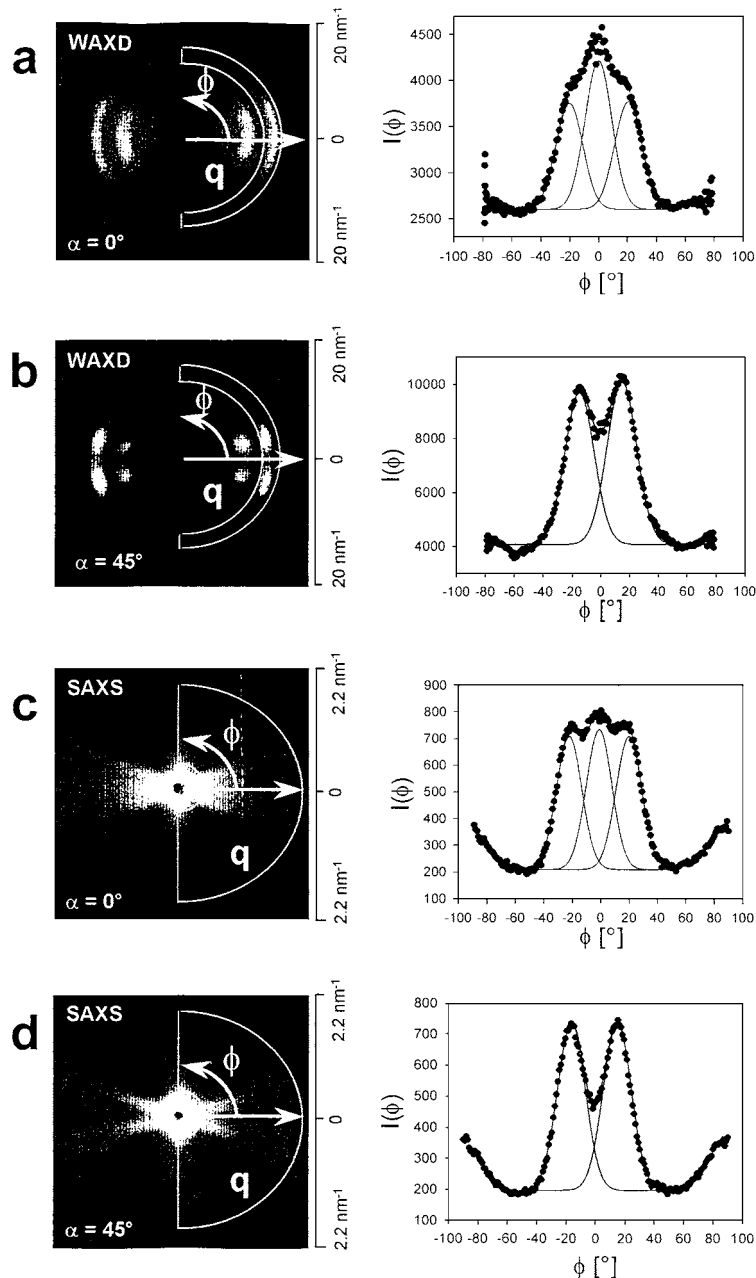


Figure 1 Typical scattering patterns from a Norway spruce sample with a mean MFA of  $20^\circ$ . The longitudinal cell axis was vertical. (a) WAXD pattern recorded with the sample oriented such that the beam hit the rectangular cells at right angles ( $\alpha = 0^\circ$ ). The scattered intensity was integrated over a small range of  $q$  that is covered by the 002 reflection and the intensity was plotted versus the azimuth angle  $\phi$ , as shown in the right part. The resulting three peaks could be fitted with three Gaussians according to theory. The MFA was determined to be  $20.4^\circ \pm 0.6^\circ$ . (b) WAXD pattern recorded at a sample rotation of  $\alpha = 45^\circ$  about the longitudinal cell axis. The diffraction pattern consists of two peaks of high intensity only. Integration of the two-dimensional image yielded a curve that could be fitted with two Gaussians. The MFA was  $21.7^\circ \pm 0.6^\circ$ . (c) SAXS pattern recorded at  $\alpha = 0^\circ$ . The two-dimensional image shows three streaks of high intensity. Integration over the scattering vector  $q$  gave a curve with three peaks that were fitted with three Gaussians, giving an MFA of  $20.0^\circ \pm 0.6^\circ$ . (d) SAXS pattern recorded at  $\alpha = 45^\circ$ . In the scattering pattern one can see two streaks of high intensity. The curve resulting from integration was fitted with two Gaussians. The MFA was determined to be  $20.4^\circ \pm 0.6^\circ$ .

rotation of the sample by  $\alpha = 45^\circ$  is the only way to obtain MFA values directly from the scattering pattern, even though the interpretation of the data is somewhat earlier.

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