A DIRECT X-RAY TECHNIQUE FOR MEASURING MICROFIBRIL ANGLE

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ABSTRACT

A texture goniometer was utilized for measuring the azimuthal intensity distribution of the (040) meridional diffraction from some coniferous wood tissues. A computerized iterative fitting method was used to generate mathematically the experimental diffraction curve and to resolve the (040) diffraction pattern from the composite profile. The mean microfibril angle was then estimated from the shape of the resolved (040) profile.

The technique developed herein is a direct and simple method for determining the mean microfibril angle with a generally satisfactory level of precision. In addition, the technique is applicable to material with a wide range of microfibril angles.

Additional keywords: Pseudotsuga menziesii, Tsuga heterophylla, meridional diffraction, microfibril angle, X-ray diffraction, (040) peak, numerical analysis, mercury reflectance method, texture goniometer.

INTRODUCTION

Microfibril angle is one of the basic ultrastructural characteristics of woody cell walls. It influences a number of wood properties, such as creep (El-osta and Wellwood 1972), modulus of elasticity (Cowdrey and Preston 1966; Hearle 1963), and dimensional stability (Meylan and Probine 1969). In addition, it exerts primary control on the mechanical properties of single wood pulp fibers (Page et al. 1971). It is therefore of some technological importance to provide wood scientists and technologists with a direct X-ray technique by which microfibril angle can be determined on a routine basis.

Most of the available X-ray techniques for determining the average orientation of cellulose crystallites are based on measurement of the intensity distribution on the paratropic planes, such as (002), ($10\bar{1}$), and (101). This requires interpreting the diffraction patterns to obtain an estimate of the average microfibril angle. The following criteria have been utilized to deduce the mean microfibril angle:

(a) half the angular width of the (002) arc at 40% or 50% of its peak height (Meredith 1951; Preston 1952);
(b) half the angular distance (T) between the points of intersection of the tangents at the inflection points with the zero intensity axis of the (002) diffraction pattern (Cave 1966; El-osta et al. 1972; Meylan 1967).

Criterion (a), which was defined to agree with other experimental results, is invalid in the case of a double-peak (bimodal) diffraction diagram and has no sound theoretical basis. Criterion (b), however, has some theoretical justification, but requires a calibration procedure for conversion of the T angle to microfibril angle (Cave 1966). Different species and wood tissues may also require different calibrations (El-osta et al. 1972; Kellogg et al. 1972).

It is worth mentioning here that other X-ray techniques that utilize the paratropic reflection are available for determining the mean microfibril angle. Among these methods is the one developed by Hermans (1949). Utilizing this method, one can determine the orientation factor and the mean inclination angle of cellulose crystallites to fiber axis. This method has been criticized by DeLuca and Orr (1961) on the grounds that it was designed for regenerated fibers. In general, results derived from paratropic planes are not sufficient to describe the orientation of the b-axis of the cellulose I unit cell.

Diffractions arising from the diatropic (040) plane of cellulose I crystallites give the microfibril angle distribution directly. Unfortunately, this type of diffraction is contaminated at its tails by diffractions from the first and third layer lines and the equator which occur at nearly the same Bragg angle (Mann et al. 1960; Radhakrishnan et al. 1969). Furthermore, this kind of diffraction is usually weaker than the diffraction arising from paratropic planes. However, this difficulty can be overcome by using a tilted specimen as will be shown in the material and methods section of this paper.

A few Japanese scientists have used the (040) diffraction pattern to record the distribution of microfibril angle within the cell wall and to determine the mean angle of some wood species (Nomura and Yamada 1972; Sobue et al. 1971; Suzuki 1967; Watanabe and Inoue 1964). Their analytical approach has two main drawbacks. First, they did not take into consideration the aforementioned contamination of the (040) diffraction pattern of cellulose I. Second, their definition of the background was arbitrary and could produce a certain error in calculating the mean microfibril angle.

The purpose of this paper is:

(1) to illustrate a numerical method for resolving the (040) diffraction pattern from the composite profile;

(2) to utilize the resolved (040) diffraction pattern in calculating the mean microfibril angle.

THEORETICAL APPROACH

Measurement of the intensity of diffraction of a particular plane, as a function of the orientation of a specimen relative to the diffraction vector of a diffractometer, yields information about the preferred orientation of the crystallites in the specimen. Such information is normally presented as a stereographic projection of the plane normals, i.e., a pole-figure diagram. The sum total of all orientation in an oriented specimen is referred to as its texture (Alexander 1969). A useful tool for conducting this kind of study is the texture goniometer.

Geometric considerations of the texture goniometer

Considering the schematic diagram presented in Fig. 1, diffraction will be observed under the following conditions:

(a) Crystallographic planes are present in the specimen and their interplanar spacing satisfies the Bragg equation, i.e.,

$$n\lambda = 2d \sin \theta$$

where: n = order of diffraction;
λ = X-ray wave length;
d = interplanar spacing of the set of planes;
θ = angle between diffraction plane and incident X-ray.

In this work, λ and θ are selected such that d must be 2.6A.

(b) The normals to the planes satisfying (a) must lie in the direction of the diffraction vector OA (in the plane of the paper).

In the case of cellulose I, the various planes satisfying (a) and the angle they make with the (040) plane are as follows (Radhakrishnan et al. 1969):

Plane (hkl)	2θ Angle for Cu Kα (degree)	Angle relative to the (040) (degree)
(040)	34.5	0
(032)	34.0	40.6
(230)		
(113)	34.2	75.4
(013)		
(311)		
(212)		
(310)		
(103)	33.5	90
(003)		
(301)		
(20$\bar{2}$)		
(300)		

If a highly oriented wood specimen with a small microfibril angle is placed at 0 (Fig. 1) and oriented such that the tracheid axis coincides with OA, the detector will measure only diffraction from the (040) planes. Upon rotating the specimen gradually through an azimuthal angle ψ about ON (ON is normal to OA and lies in the plane of the paper), the detector output will quickly fall to the background (BG) because the (040) planes will be so oriented as not to satisfy condition (b) above. As the angle ψ increases to about 40° from the original position, diffraction from the (032) and (230) planes will be recorded,[1] since some of the crystallites in the specimen will have these planes so oriented as to satisfy (a) and (b). Similarly, as ψ approaches 75° and 90°, the detector will register some diffraction from planes of the type (113) and (103), respectively.

In a wood specimen with a lower degree of orientation and broader microfibril angle distribution, the ability to resolve the separate diffractions mentioned above breaks down. The result is a composite profile, the main portion of which is due to diffraction from the (040) plane.

Numerical analysis for resolving (040) diffraction peak

The aim of the numerical analysis used herein is to generate the experimental diffraction diagram mathematically and then resolve the (040) peak from it. Before proceeding further, it is necessary to define the geometry of the technique used. The geometry is as follows (Fig. 2):

(a) The specimen axis is taken parallel to the direction of e_3 (OA in Fig. 1).
(b) The axis of specimen rotation (ON in Fig. 1) is coincident with the direction of e_1.

[1] It is assumed that the microfibril axis coincides with the crystallographic "b" axis (Sisson 1935).

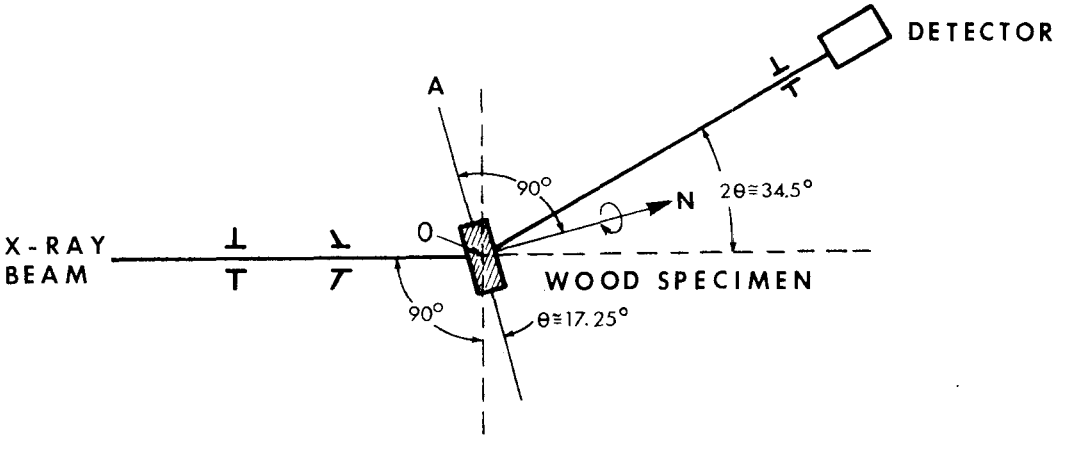

FIG. 1. Conditions for diffraction from the contaminated (040) plane in wood specimen.

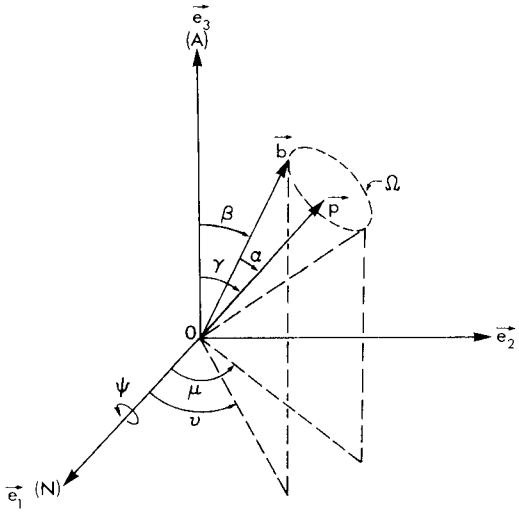

FIG. 2. Geometry of the X-ray technique and the specimen systems.

(c) The microfibril axis direction ($\vec{b}$) is given by the microfibril angle β and the azimuthal angle ν. This direction coincides with the normal to the (040) plane.

(d) There is also another general plane P_α the normal of which ($\vec{P}$) makes an angle α with $\vec{b}$. The direction of $\vec{P}$ is defined by γ and the azimuthal angle μ.

Generally, the unit vector $\vec{P}$ is given by:

$$\vec{P} = \sin\gamma\cos\mu\,\vec{e}_1 + \sin\gamma\sin\mu\,\vec{e}_2 + \cos\gamma\,\vec{e}_3. \quad (1)$$

For the plane P_α to give rise to diffraction, its normal ($\vec{P}$) must become parallel to OA (Fig. 1), through a rotation ψ $\vec{e}_1$. The rotated vector can be written as follows:

$$\vec{P}_r = \sin\gamma\cos\mu\,\vec{e}_1 + [\cos\psi\sin\gamma\sin\mu - \sin\psi\cos\gamma]\,\vec{e}_2 + [\sin\psi\sin\gamma\sin\mu + \cos\psi\cos\gamma]\,\vec{e}_3. \quad (2)$$

Accordingly, the diffraction occurs when the components in the directions of $\vec{e}_1$ and $\vec{e}_2$ become zero, i.e.:

$$\sin\gamma\cos\mu = 0 \quad \text{and} \quad (3)$$
$$\cos\psi\sin\gamma\sin\mu - \sin\psi\cos\gamma = 0. \quad (4)$$

To satisfy equation (3), for the general case of $\gamma \neq 0$.

$$\cos\mu = 0 \quad \text{or} \quad \mu = \pi/2, 3\pi/2. \quad (5)$$

From equations (5) and (4),

$$\sin(\psi \pm \gamma) = 0. \quad (6)$$

Thus, the rotation that is required to bring P_α plane in a position for diffraction is given by

$$\psi = \pm\gamma \pm n\pi \quad (7)$$
where: $n = 0, 1, \ldots$.

Equations (5) and (7) can be utilized to construct the components of the diffraction profiles produced by planes having Bragg's angle near 17.25°.

1. Plane (040)

In this case, $\alpha = 0$, $\gamma = \beta$ and $\mu = \nu$. Application of equation (5) indicates that the diffraction from the (040) plane is possible only from microfibrils in planes normal to the direction ON (Fig. 1). This condition, whereby the X-ray beam falls on the tangential face of the wood specimen, is satisfied by:

(a) microfibrils in the tangential walls of the specimen,

(b) microfibrils having zero angle in the radial walls and

(c) if, through weaving in and out of the plane of the radial walls, some microfibrils lie in a plane parallel to the plane of rotation. However, contribution to diffraction profile from these microfibrils is probably small and would not materially affect the result.

According to equation (7), the required specimen rotation for a given microfibril with an angle β is:

$$\psi = \pm\beta \pm n\pi. \quad (8)$$

2. General plane P_α

In the general case, the plane P_α is defined as making an angle α with the plane (040). However, there exists an infinite number of directions that make an angle α with $\vec{P}$. This family of directions gener-

ates a conical surface Ω (Fig. 2). The vector $\vec{b}$ can be expressed in the following manner:

$$\vec{b} = \sin\beta\cos\nu\,\vec{e}_1 + \sin\beta\sin\nu\,\vec{e}_2 + \cos\beta\,\vec{e}_3; \quad (9)$$

and, if P_α is in a position to satisfy the condition for diffraction, the vector $\vec{P}$ can be written as follows, according to equations (1) and (5):

$$\vec{P} = \pm\sin\gamma\,\vec{e}_2 + \cos\gamma\,\vec{e}_3. \quad (10)$$

Since the family of vectors $\vec{b}$ on the surface Ω satisfies the condition:

$$\vec{P}\cdot\vec{b} = \cos\alpha, \quad (11)$$

the following relationship is obtained:

$$\cos\alpha = \pm\sin\gamma\sin\beta\sin\nu + \cos\beta\cos\gamma. \quad (12)$$

Let us consider the case whereby an X-ray beam falls on the tangential face of a wood specimen:

a: *For microfibrils located in one pair of tangential walls ($\nu = \pi/2,\ 3\pi/2$, Fig. 2)*

For those walls equation (12) becomes:

$$\cos\alpha = \cos(\beta - \gamma), \quad (13)$$

$$\text{from which } \gamma = \beta \pm \alpha, \quad (14)$$

and according to equation (7) the required rotation for producing diffraction from the P_α plane of these microfibrils is given by:

$$\psi = \beta \pm \alpha \pm n\pi \text{ for } \nu = \pi/2, \text{ and} \quad (15)$$
$$\psi = -\beta \pm \alpha \pm n\pi \text{ for } \nu = 3\pi/2,$$
where: $n = 0, 1, \ldots$.

b: *For microfibrils located in one pair of radial walls*[2] *($\nu = \pi, 2\pi$)*

For those walls equation (12) becomes:

$$\cos\alpha = \cos\beta\cos\gamma \quad (16)$$

and according to equation (7) the required rotation for producing diffraction from the P_α plane of these microfibrils is given by:

$$\psi = \pm\arccos(\cos\alpha/\cos\beta) \pm n\pi \quad (17)$$
where: $n = 0, 1, \ldots$.

c: *For microfibrils located in walls with ν other than $\pi/2$, π, $3\pi/2$, or 2π.*

Equation (7) and (12) can again be used to determine the required rotation for producing diffraction from the P_α plane for those microfibrils. Equation 12, however, becomes in this case a transcendental equation for γ and cumbersome to solve. For simplicity, this contribution to the diffraction profile will not be considered here. This approximation is equivalent to taking the cross section of the tracheid to be rectangular in shape. Since the true shape is not precisely known, a more precise model is not required. This approximation is not expected to significantly affect the results since it is related only to minor contributions from planes other than (040).

Limiting the angles ψ, β, and α to values between 0 and $\pi/2$, the composite diffraction profile at ψ can now be obtained by superposition of results derived from equations (8), (15), and (17). This profile consists of diffraction from:

(a) (040) plane of microfibrils in tracheid tangential wall ($\nu = \pi/2$) and and also in the radial wall for $\beta = 0$ with:

$$\beta = \psi \quad (18)$$

(b) P_α plane of microfibrils in the tracheid tangential wall at ($\nu = \pi/2$) with:

1. $\beta = \psi - \alpha$ if $\psi \geq \alpha$
2. $\beta = \psi + \alpha$ if $\psi + \alpha \leq \pi/2$ (19)

(c) P_α plane of microfibrils in the tracheid tangential wall ($\nu = 3\pi/2$) with:

1. $\beta = \alpha - \psi$ if $\psi < \alpha$
2. $\beta = \pi - (\psi + \alpha)$ if $\psi + \alpha > \pi/2$ (20)

(d) P_α plane of microfibrils in the tracheid radial walls ($\nu = \pi,\ 2\pi$) with $\beta = \arccos(\cos\alpha/\cos\psi)$ if $\psi \leq \alpha$ (21)

[2] The authors wish to thank Dr. F. El-Hosseiny of the PPRIC for his useful comments.

Thus, if

$I_4(\beta) = (040)$ intensity distribution as a function of the microfibril angle β,

$I_\alpha(\beta) = P_\alpha$ intensity distribution as a function of β,

$I(\psi)$ = intensity distribution as a function of ψ, and considering that the three groups of planes occur at $\alpha_1 = 40.6°$, $\alpha_2 = 75.4°$ and $\alpha_3 = 90°$ from (040) plane, then the observed composite intensity at ψ can be written as follows:

$$\begin{aligned} I(\psi) = {} & I_4(\psi) \\ & + \sum_{i=1}^{2} \Big\{ I_{\alpha_i}(\psi - \alpha_i)\,\Delta(\psi - \alpha_i) \\ & \quad + I_{\alpha_i}(\alpha_i - \psi)\,\Delta(\alpha_i - \psi) \\ & \quad + I_{\alpha_i}(\psi + \alpha_i)\,\Delta[\pi/2 - (\psi + \alpha_i)] \\ & \quad + I_{\alpha_i}[\pi - (\psi + \alpha_i)]\,\Delta(\psi + \alpha_i) - \pi/2] \\ & \quad + I_{\alpha_i}\left[\arccos\left(\frac{\cos\alpha}{\cos\psi}\right)\right]\Delta^*(\alpha_i - \psi)\Big\} \\ & + I_{\alpha_3}(\pi/2 - \psi) + I_{\alpha_3}(\pi/2) \quad . \end{aligned} \tag{22}$$

where the step functions $\Delta(x)$ and $\Delta^*(x)$ are defined in the following manner:

$$\begin{aligned} &\Delta(x) = 1 \quad \text{if } x > 0 \\ &\Delta(x) = 1/2 \quad \text{if } x = 0 \\ &\Delta(x) = 0 \quad \text{if } x < 0 \\ &\Delta^*(x) = 1 \quad \text{if } x \geq 0 \\ &\Delta^*(x) = 0 \quad \text{if } x < 0. \end{aligned} \tag{23}$$

Assuming that the intensity distribution function I_4 and, in general, I_α are Gaussian centered at angle β_0, corresponding to the greatest density of microfibrils, then these distributions can be expressed by:

$$\begin{aligned} I_4(\beta) &= H_1^2 e^{-H_2^2(\beta - \beta_0)^2} \\ I_{\alpha_1}(\beta) &= H_3^2 e^{-H_4^2(\beta - \beta_0)^2} \\ I_{\alpha_2}(\beta) &= H_5^2 e^{-H_6^2(\beta - \beta_0)^2} \\ I_{\alpha_3}(\beta) &= H_7^2 e^{-H_8^2(\beta - \beta_0)^2} \end{aligned} \tag{24}$$

Substituting equations (24) into equation (22) gives the intensity observed at specimen rotation angle ψ as a function of the parameters H_1^2 through H_8^2 and β_0:

$$\begin{aligned} I(\psi) = {} & H_1^2 e^{-H_2^2(\psi - \beta_0)^2} \\ & + H_3^2 \Big\{ e^{-H_4^2(\psi - \alpha_1 - \beta_0)^2}\,\Delta(\psi - \alpha_1) \\ & \quad + e^{-H_4^2(\alpha_1 - \psi - \beta_0)^2}\,\Delta(\alpha_1 - \psi) \\ & \quad + e^{-H_4^2(\psi + \alpha_1 - \beta_0)^2}\,\Delta[\pi/2 - (\psi + \alpha_1)] \\ & \quad + e^{-H_4^2[\pi - (\psi + \alpha_1) - \beta_0]^2}\,\Delta[\psi + \alpha_1 - \pi/2] \\ & \quad + e^{-H_4^2\left[\arccos\left(\frac{\cos\alpha}{\cos\psi}\right) - \beta_0\right]^2}\,\Delta^*(\alpha_1 - \psi)\Big\} \\ & + H_5^2 \Big\{ e^{-H_6^2(\psi - \alpha_2 - \beta_0)^2}\,\Delta(\psi - \alpha_2) \\ & \quad + e^{-H_6^2(\alpha_2 - \psi - \beta_0)^2}\,\Delta(\alpha_2 - \psi) \\ & \quad + e^{-H_6^2(\psi + \alpha_2 - \beta_0)^2}\,\Delta[\pi/2 - (\psi + \alpha_2)] \\ & \quad + e^{-H_6^2[\pi - (\psi + \alpha_2) - \beta_0]^2}\,\Delta[\psi + \alpha_2 - \pi/2] \\ & \quad + e^{-H_6^2\left[\arccos\left(\frac{\cos\alpha}{\cos\psi}\right) - \beta_0\right]^2}\,\Delta^*(\alpha_2 - \psi)\Big\} \\ & + H_7^2 \Big\{ e^{-H_8^2(\pi/2 - \psi - \beta_0)^2} + e^{-H_8^2(\pi/2 - \beta_0)^2} \Big\} . \end{aligned} \tag{25}$$

The model used herein differs from that employed by Radhakrishnan et al. (1969) in that they assumed that all intensity distribution functions of equations (24) had the same shape and differed only by a scale factor. This assumption required the use of only five parameters in their equation. It was both their observation and ours that this is too restrictive and contrary to experience. In addition they did not take into consideration the contribution to their diffraction profile from microfibrils located in the other walls (i.e. radial wall in this study).

The parameters H_1^2 through H_8^2 and β_0 can be computed by a nonlinear least-squares method of fit. Thus, if $I_D(\psi_i)$ is the observed intensity for an angle of ψ_i, the parameters can be computed from the condition that

$$U = \sum_{i=1}^{NA} \{[I_D(\psi_i) - BG(\psi_i)] - I(\psi_i)\}^2 \tag{26}$$

be a minimum, where NA is the number of observations, $BG(\psi_i)$ is the background, and $I(\psi_i)$ is the net intensity calculated by