DETERMINATION OF FIBRIL ANGLE DISTRIBUTION IN WOOD FIBERS: A COMPARISON BETWEEN THE X-RAY DIFFRACTION AND THE POLARIZED MICROSCOPE METHODS

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ABSTRACT

The fibril angle distribution of a black spruce sample was determined by the reflectance method on the polarized microscope. This was compared with the azimuthal distribution of intensity obtained from the (002), (101), and ($10\bar{1}$) planes of the X-ray pattern of the corresponding piece of wood. Obviously, the X-ray intensities do not give directly the fibril angle distribution function of the sample. However, using for example Cave's theory, one can predict the X-ray distribution of intensity from the fibril angle distribution function, or vice-versa, assuming that the sample is made of cylindrical fibers.

Additional keywords: *Picea mariana*, cellulose fibers, quantitative analysis, reflectance, orientation, polarization microscopy, X-ray diffraction, statistical distribution.

INTRODUCTION

Cellulose fibers are made of four principal cell-wall layers, termed the primary (P), outer secondary (S_1), middle secondary (S_2) and inner secondary (S_3) layers. Each secondary layer is made of cellulose fibrils embedded in a lignin and hemicellulose matrix, and has a particular fibrillar orientation. Since the majority of the cell-wall material (80–95% depending upon the tree, growth season, and other variables) is contained in the S_2 layer, the mechanical properties of the fiber will depend largely upon the structural organization of this layer and in particular upon the angle of orientation of its fibrils, the so-called fibril angle of the fiber.

Experimental evidence of the dependence of the mechanical properties of cellulose fibers upon fibril angle has been given by several groups working on single fibers (Spark et al. 1958; Cowdrey and Preston 1966; Tamolang et al. 1967; Page et al. 1972), or sheets of paper made from fibers having different fibril angles (Guha 1961; Watson and Dadswell 1964). From these measurements, it is clear that fibril angle is an important variable.

Consequently a large number of papers have been devoted to fibril angle determination. Methods involve the use of light microscopy (Bailey and Vestal 1937; Meylan 1967), polarized microscopy (Preston 1934; Wardrop and Preston 1947; Manwiller 1966; Page 1969; Crosby et al. 1972; El-Hosseiny and Page 1973), and X-ray diffraction techniques (Matano 1936; Matano 1937; Berkley and Woodyard 1938; Preston 1952; Creely et al. 1956; DeLuca and Orr 1961; Cave 1966; Meylan 1967; Duckett and Tripp 1967; Sobue et al. 1971; Nomura and Yamada 1972; El-Osta et al. 1973). All of the microscopy techniques are long and tedious. The most satisfactory

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one is probably the method of Page (1969) based on the impregnation of mercury in the lumen of the fibers and their examination by reflectance. This technique is direct, although one must be aware of possible deviations in the case where the thickness of the S_1 and S_3 layers is non-negligible (El-Hosseiny and Page 1973). In addition, it is not applicable to a full piece of wood and is still time-consuming.

The main advantage of the X-ray technique is its rapidity. But so far, the use of this method has been limited since the relationship between the X-ray intensity curve and the fibril angle distribution function has not been clearly established. Empirical relations such as associating to the fibril angle the angle where 40%, 50% or some other percent of the intensity on the equator of the (002) plane is found, have been proposed (Berkley and Woodyard 1938; Creeley et al. 1956; DeLuca and Orr 1961; Cave 1966; Meylan 1967; Duckett and Tripp 1967; Sobue et al. 1971). These methods are most useful from a practical point of view since they permit one to compare several samples. But they are inadequate from a fundamental point of view since they are not theoretically justified.

Some other workers suggested the direct use of the (040) reflection of the pattern. Although the recording of the intensity of this plane is experimentally difficult and corrections for overlapping reflections are needed, the average fibril angles calculated by this method seem to agree with the corresponding values measured from Page's method (Sobue et al. 1971; Nomura and Yamada 1972; El-Osta et al. 1973). However, one prefers whenever possible, to use strong paratropic reflections and the present paper will consider that particular problem. Attention will also be given to fibril angle distribution functions which peak at zero degrees as is frequently the case for softwood samples (Page 1969; Prud'homme et al. 1975).

It is then the purpose of the present paper to compare the fibril angle distribution function as obtained experimentally by the reflectance method on the polarized microscope to the measured distribution in X-ray intensity of the (002), (101), and ($10\bar{1}$) planes for a black spruce wood sample. It will be shown that using Cave's diffraction theory (Cave 1966), one can relate the X-ray intensity measurements to the fibril angle distribution function when the fibers are cylindrical in shape. For clarity, Cave's theory will be briefly outlined in the next section.

THEORY

Let us consider the diffraction geometry defined in Fig. 1. An incident X-ray beam vector falls on a sample whose chain axis is along the vector b. A diffraction vector r is defined at a Bragg angle 2θ. The vector p is a unit vector normal to the reflecting plane. From Fig. 1, one can write:

$$\underline{s_0} = -\underline{i} \tag{1}$$

$$\underline{b} = (\cos\omega \sin\beta)\underline{i} + (\sin\omega \sin\beta)\underline{j} + (\cos\beta)\underline{k} \tag{2}$$

$$\underline{r} = -(\cos 2\theta)\underline{i} + (\cos\phi \sin 2\theta)\underline{j} + (\sin\phi \sin 2\theta)\underline{k} \tag{3}$$

X-ray diffraction will be produced if a) the Bragg law is obeyed, namely if

$$n\lambda = 2d \sin\theta \tag{4}$$

where n is the diffraction order, λ is the wavelength of the incident beam, and d is the interplanar distance of the plane considered giving diffraction at the angle 2θ; and if b) r is in the plane formed by the normal vector of the reflecting plane and the incident beam vector. This leads to (Cave 1966)

$$\underline{p} = (\sin\theta)\underline{i} + (\cos\theta \cos\phi)\underline{j} + (\cos\theta \sin\phi)\underline{k}. \tag{5}$$

For the (002) plane, one can write that

$$\underline{b} \cdot \underline{p} = 0 \tag{6}$$

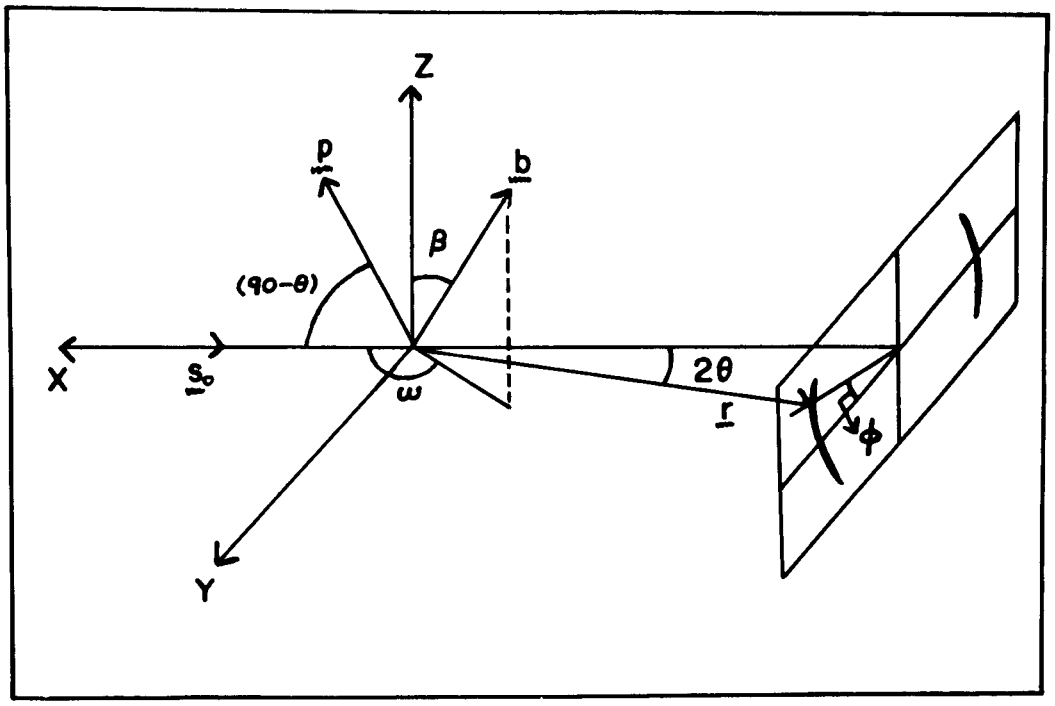

FIG. 1. Schematic representation of the diffraction geometry.

since it is assumed that the distribution of (002) planes around the fibril axis is uniform.

Then, using equations (2), (5) and (6) one gets the condition

$$\tan\theta\cos\omega + \sin\omega\cos\phi + \cot\beta\sin\phi = 0 \qquad (7)$$

Eq. (7) is the expression originally derived by Cave (1966). It relates for the crystallographic plane (002) (angle 2θ fixed at 22.6°), the azimuthal position of the diffracted ray (angle ϕ) to the location of the fibril angle in the fiber defined by the angles β and ω. The dispersion of crystallite orientation about the fibril axis is assumed to be negligibly small.

It can be written that the diffracted intensity of the (002) plane is given by

$$I(\phi) = \sum_{\omega}\sum_{\beta} F(\phi, \omega, \beta)\, N(\beta) \qquad (8)$$

where $F(\phi,\omega,\beta)$ is equal to zero if Eq. (7) is not satisfied, and is equal to one if it is satisfied, and $N(\beta)$ is the fibril angle distribution of the sample.

EXPERIMENTAL

Measurements were made on a black spruce (*Picea mariana*) wood sample. The sample was delignified using a holocellulose treatment. A portion of the chip was separated manually, solvent-exchanged in ethanol, and dried. On the optical microscope, no distortion in the orientation of the fibers could be seen, and moreover, the fibers appeared as circular in shape. Another portion of the same chip, of the same annual ring, was defibered and used for the mercury reflectance measurements.

The mercury reflectance measurements were made following the technique described by Page (1969).

X-ray data were recorded on a Picker (FACS-1 system) diffractometer using the Cu K_α radiation. The instrument was controlled (PDP-8 mini-computer) by a program described by Desper (1969). The recorded values of intensity were corrected

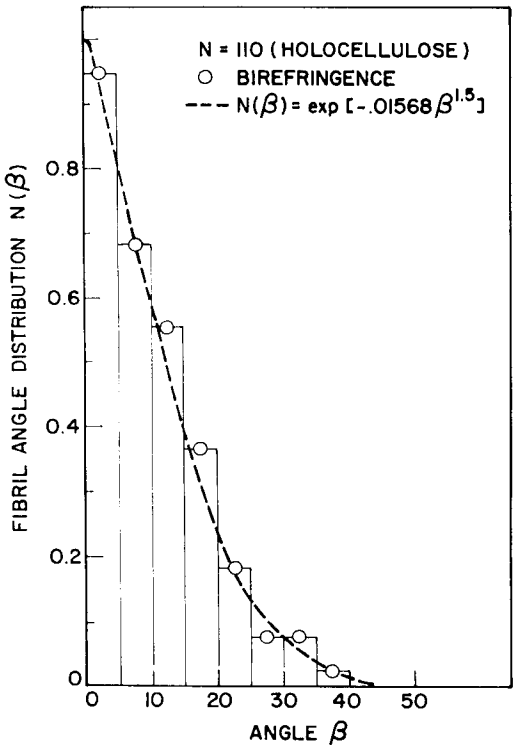

FIG. 2. Fibril angle distribution function as a function of angle for a black spruce sample, as obtained from the microscope reflectance method.

for background diffraction by a graphical technique involving radial scans of the intensity at various azimuthal angles. The normal of the sample was tilted through the diffraction angle θ with respect to the incident beam.

RESULTS AND DISCUSSION

The mercury reflectance data are reported in Fig. 2. A histogram is obtained which can be described by the function

$$N(\beta) = \exp\left[-0.0157\ |\beta|^{1.5}\right] \qquad (9)$$

This function peaks at zero degrees. In Fig. 2, this maximum has been arbitrarily set at a value of unity. A total of 110 fibers was analyzed.

For the wood sample, the measured X-ray distribution of intensity of the (002), (101), and $(10\bar{1})$ planes is reported in

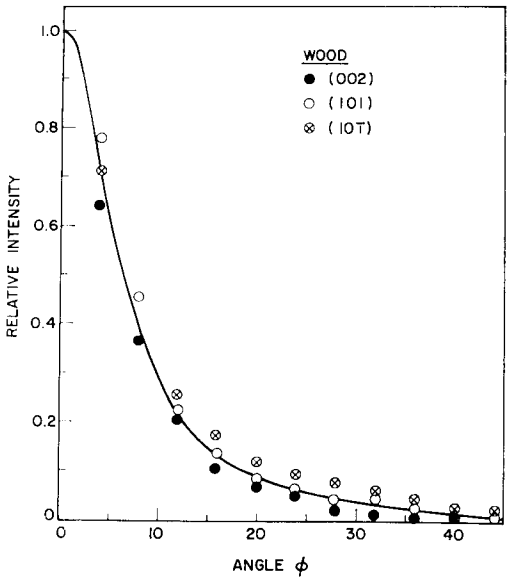

FIG. 3. Experimental distribution of intensity as a function of angle for the (002), (101), and $(10\bar{1})$ planes of a wood sample.

Fig. 3 as a function of the angle ϕ. Some scatter in the data can be seen but it is mainly due to the difficulty in correcting the data for the background intensity. This can be done fairly accurately for the (002) plane which is very intense, but it is much more difficult for the (101) and $(10\bar{1})$ planes, which are weak. Considering this experimental limitation, we can conclude from Fig. 3 that no preferred orientation of the paratropic planes is present in the sample (Sisson 1935). The X-ray intensity curves have been arbitrarily normalized to unity at zero angle.

A direct comparison between the microscopy and the X-ray measurements is made in Fig. 4 where the fibril angle distribution function, Eq. 9, is plotted as well as the distribution of intensity of the (002) plane of the wood sample. It is seen that the X-ray curve falls much more rapidly as a function of angle than the fibril angle distribution function.

In order to see if this difference in behavior can be explained by Cave's theory, we made calculations on simple systems. For example, let us consider a single cylin-

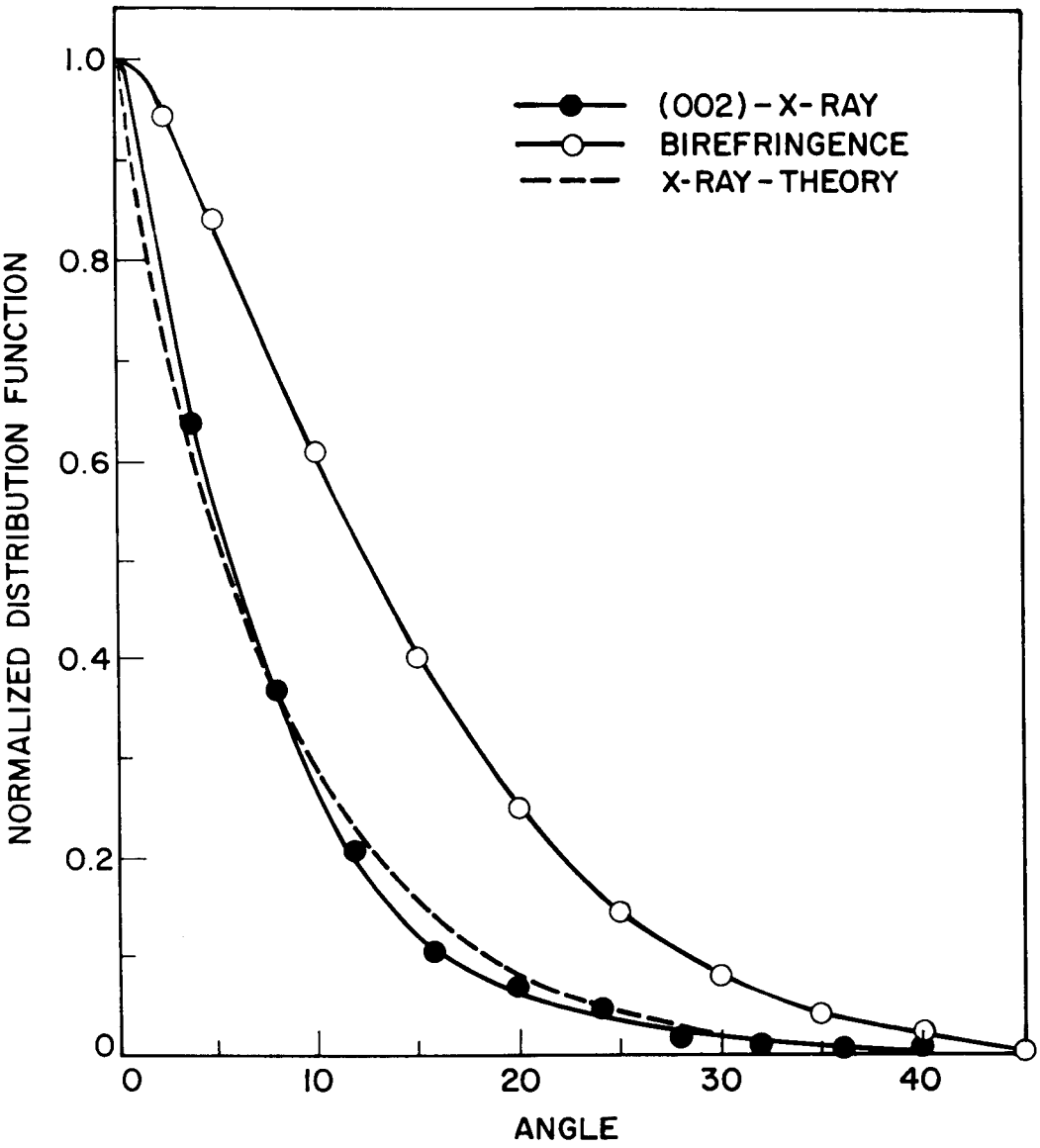

FIG. 4. Comparison between the measured fibril angle distribution function as obtained by the reflectance method and the X-ray intensity data of the (002) plane for a wood sample. The dotted line is the theoretical X-ray intensity curve.

drical fiber having a fibril angle of 29 degrees. This implies solving Eqs. (7) and (8) for all values of ω in the range 0–360 degrees and representing $N(\beta)$ by a delta function (Fig. 5, top). This gives rise to a diffraction curve $I(\phi)$ which has a maximum of intensity around 28 degrees, no intensity at angles larger than 29 degrees, and increasing intensity values from 0 to 27 degrees. This indicates that the diffraction from a single circular fiber having a well-defined fibril angle β_0 will not give an X-ray curve centered at β_0, but a diffuse diffraction curve at angles smaller than β_0. Similarly, if $N(\beta)$ is represented by a box function (Fig. 5, center) covering

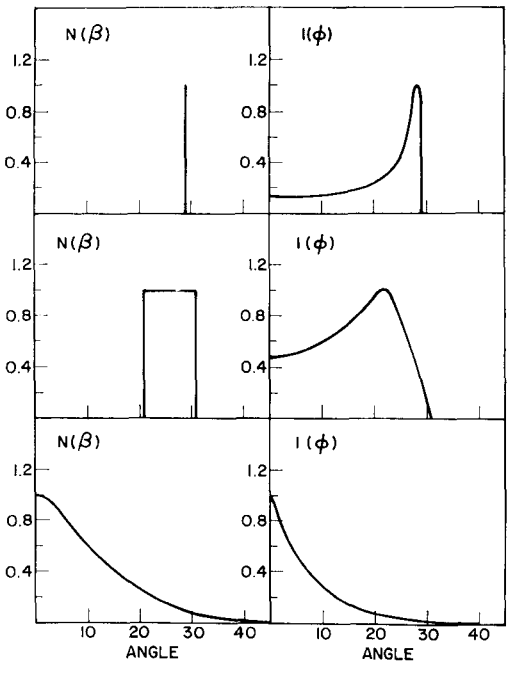

FIG. 5. Comparison between several fibril angle distribution functions $N(\beta)$ and the corresponding X-ray intensity functions $I(\phi)$ for circular fibers.

angles in the interval 21–31 degrees, no diffracted intensity is found at angles larger than 31 degrees, a maximum in intensity is seen around 22 degrees, and decreasing values of intensity are observed at smaller angles. Additional calculations are presented by Cave (1966) for several $N(\beta)$ Gaussian functions.

These calculations are in complete agreement with several experimental results found in the literature on cellulose single fibers (Duckett and Tripp 1967; Radhakrishnan and Patil 1968), models for cellulose single fibers (Preston 1952), and synthetic fibers (Cooper et al. 1968; Radhakrishnan et al. 1969). This means that the (002) reflection of the X-ray pattern will present a maximum in intensity at an angle ϕ larger than zero degrees only if the fibril angle distribution function is sharp and centered at an angle β significantly larger than zero degrees. Otherwise, the X-ray intensity curve will peak at the equator of the pattern as in Figs. 3 and 4.

A final calculation was made (Fig. 5, bottom) considering the distribution of fibril angle given by Eq. (9). Again, we considered an ensemble of cylindrical fibers since all values of ω are equally weighted when applying Eq. (8). This calculation leads to an X-ray curve where the intensity peaks at $\phi = 0$, and decreases rapidly with increasing angle. In order to compare this calculation with the experimental results, this curve is also plotted in Fig. 4 (dashed line). A fair agreement is obtained between the experimental and theoretical X-ray curves, even if some of the approximations made in the calculation were relatively crude. In particular, we neglected to consider the contribution of the S_1 and S_3 layers to the X-ray intensity distribution. This might not create a serious problem since most of the diffraction occurs in the range 0–35 degrees where these layers should not contribute much, and since the S_1 and S_3 layers are usually very thin for this species of wood (El-Hosseiny and Page 1973). We also considered that the fibers are made of perfect cylinders. The differences seen between the experimental and theoretical X-ray curves may be primarily due to this assumption. On the other hand, since a fair agreement is obtained, the model seems to be qualitatively appropriate, at least for the case investigated. Of course, the comparison made in Fig. 4 between the X-ray and the polarized microscope fibril angle distribution functions is also subjected to the assumptions made in the application of the latter method: neglect of the presence of the S_1 and S_3 cell-wall layers and assumption that the fibril angle is unique within each fiber.

CONCLUSIONS

In view of the results presented above and in agreement with previous measurements, it is clear that the X-ray intensity measurements for the paratropic reflections do not give directly the fibril angle distribution function. The X-ray curve must be corrected in some fashion. This correction is related to the geometry of the fibers in

the sample. In some cases, as in the present one, the fibers may be considered as cylindrical in shape. We have shown that knowing the fibril angle distribution function, the X-ray intensity curve can be predicted using Cave's theory. Conversely, when the cylindrical approximation holds, one can calculate a series of X-ray curves assuming different fibril angle distributions until a fair agreement is obtained between the experimental and theoretical X-ray intensity results. Then, the fibril angle distribution is known.

The application of the X-ray technique relies very heavily on the geometry of the fibers of the sample. Since in many cases, the shape of the fibers is uncertain (square or circular), then in order to determine the fibril angle distribution function of the sample, the reflectance method on the polarized microscope must be preferred. An alternative method would be to develop X-ray techniques which would permit one to decide which geometrical model best describes the fibers of the sample. Even if this is beyond the scope of the present work, this seems to be a reasonable possibility which should be pursued further. If this can be done, Cave's theory can be used in the same manner as suggested for cylindrical fibers.

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tion or transportation uses? Such questions will be asked of us not by today's wood users, but by industrialists and consumers who are today using materials other than wood. In the past we have not given such alternatives thorough technical study, supposing always that economic controls would regulate materials uses. Please note, however, that economics was not one of the criteria for materials use during the big crisis mentioned earlier!

Will we in SWST be courageous enough and wise enough to anticipate the assignments that lie ahead for us and to organize ourselves for them in a positive and constructive fashion? Are we preparing to assume responsibility as materials scientists of the future, who know how wood can best serve the needs of mankind in a world where all materials are scarce? It is a broader task than we have so far envisioned for ourselves.

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