

# The Determination of Cellulose Spiral Angle by Small-Angle X-Ray Scattering from Structurally Characterized *Acacia mangium* Cell Wall

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**Abstract**—The spiral angle of the elementary cellulose fibril in the wood cell wall, often called microfibril angle, (MFA). Microfibril angle in hardwood is one of the key determinants of solid timber performance due to its strong influence on the stiffness, strength, shrinkage, swelling, thermal-dynamics mechanical properties and dimensional stability of wood. Variation of MFA (degree) in the  $S_2$  layer of the cell walls among *Acacia mangium* trees was determined using small-angle X-ray scattering (SAXS). The length and orientation of the microfibrils of the cell walls in the irradiated volume of the thin samples are measured using SAXS and optical microscope for 3D surface measurement. The undetermined parameters in the analysis are the MFA, ( $M$ ) and the standard deviation ( $\sigma_\Phi$ ) of the intensity distribution arising from the wandering of the fibril orientation about the mean value. Nine separate pairs of values are determined for nine different values of the angle of the incidence of the X-ray beam relative to the normal to the radial direction in the sample. The results show good agreement. The curve distribution of scattered intensity for the real cell wall structure is compared with that calculated with that assembly of rectangular cells with the same ratio of transverse to radial cell wall length. It is demonstrated that for  $\beta = 45^\circ$ , the peaks in the curve intensity distribution for the real and the rectangular cells coincide. If this peak position is  $\Phi_{45}$ , then the MFA can be determined from the relation  $M = \tan^{-1}(\tan \Phi_{45} / \cos 45^\circ)$ , which is precise for rectangular cells. It was found that 92.93% of the variation of MFA can be attributed to the distance from pith to bark. Here we shall present our results of the MFA in the cell wall with respect to its shape, structure and the distance from pith to park as an important fast check and yet accurate towards the quality of wood, its uses and application.

**Keywords**—Small-Angle X-Ray Scattering, Microfibril Angle, MFA, rectangular cell wall and real cell wall, *Acacia mangium*.

## I. INTRODUCTION

THE cell wall of plant are composed of small cellulose structural units called microfibrils. The angle between the cellulose fibrils and the longitudinal cell axis, the microfibril angle (MFA), has been shown to be a crucial factor that influence the modulus of elasticity and the dimensional

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stability of wood [9]. Reference [5] stated that the microfibril angle of the  $S_2$  layer in the fibre cell wall is known to be one of the main determinants of the thermal and dynamic-mechanical properties of the hardwood. Reference [6] reported that the microfibril angle changed as a function of the position in the tree. The mean microfibril angle of *Pinus massoniana* decreased more gradually as the distance increased from the pith and reached the same level in mature wood [6]. The varied wood resource of the future will require more definitive information about the microfibril angle to improve selection and utilization. X-ray diffraction and SAXS have the potential to be much more rapid methods to determine MFA than is microscopic measurement [2].

*Acacia mangium* wood is classified as a hardwood. It is the major fast growing plantation species for timber and pulp in Asia. Botanically *Acacia mangium* comes from family Leguminosae and sub-family mimisoideae. It has a wood density ranging from 420 to 600 Kg/m<sup>3</sup> and specific gravity of 0.65

X-ray diffraction is a well-established method for the determination of the mean microfibril angle [3]. Additionally, Reference [2] also utilized the SAXS to investigate the spiral in the wood cell wall, but there primary assumption in the analysis is that the wood cell walls are square. It is necessary to take in to account the detailed cell structure in order to interpret diffraction and scattering data [1]. This involved using quantitative image analysis or SEM to measure the length and the orientation of the microfibrils in the irradiated volume of the thin samples. From the data, the angle of the peak scattering intensity  $\Phi_p$  was calculated for a sample irradiated in a direction of  $45^\circ$  to the radial and transverse direction. It was thereby demonstrated that the MFA could be calculated from the formula (1).

$$M = \tan^{-1}(\tan \Phi_p / \cos 45^\circ) \quad (1)$$

where:  $M$  the MFA in  $S_2$  layer, with an error about  $1^\circ$ . The relation is exact for rectangular cells [2].

## II. MATERIALS AND METHODS

The wood samples used in this study were selected from 3, 5, 7, 9, 10, 11, 13 and 15-year-old of *Acacia mangium* plantation from Sabah Forestry Development Authority (SAFODA). Two trees from each compartment were selected

providing a total 16 trees for this study. Two discs of 40 mm were taken at breast height of the stem for each tree. In total, eight knot-free discs were labeled and stored in plastic bags for further sample preparation.

*A. Sample Preparation*

A 4cm × 6cm rectangular block was obtained from each disc at different angles of grain. The samples subsequently stored under controlled temperature and relative humidity (23 °C ± °C 1and 55% ±3%) to achieve equilibrium moisture content about 9%. Thin strips of uniform thickness about 50 microns were cut along the radius rotary microtome. The sample dimensions were 20mm length × 10mm width.

*B. Measuring MFA Using Small-Angle X-Ray Scattering Technique*

Samples of 9 different orientations were cut. The angle β shown is between the wider face of the sample and the radial direction. The samples were irradiated with the X-ray beam has a circular cross-section of 0.6mm in diameter directed normal to the face, β is the angle between the normal to the radial plane and the direction of the X-ray beam. The various cell-wall orientations were obtained by cutting specimens with different angles, so that the scattered radiation would pass through the same length of specimen material in all cases. Without any further treatment, it is encapsulated in plastic foil to keep them from drying and shrinking in the vacuum chamber of the x-ray equipment. A SAXS device (HMBG-SWAX, SAXS PW 3830 X-Ray generator) was used to determine the MFA in each of the eight investigated trees. The measurements were carried out in point focus geometry using Cu Kα radiation of wave length 1.54 nm. The beam width at the sample position was 200 μm. A position detector was used to record the scattering patterns. The distance of the sample to the detector was 5.14 mm. The experimental set-up consisted of 40 Kv and 20 mA. The incoming x-ray beam had a circular cross-section of 0.6 mm in diameter.

*C. Theory*

The equations used to calculate the scattered intensity and MFA were derived by Reference [2] and using a peak fit method developed by Reference [7]. Recently, the MFA was calculated based on the value of parameter T using X-ray diffraction technique [5].

In Fig 1, z is the direction of the cell axis, y is the radial direction and χ is the transverse direction. A cell wall will shown with two sets of S<sub>2</sub> microfibrils f<sub>1</sub> and f<sub>2</sub> lying at the microfibril angle M to the cell axis direction z. The incident X-ray beam is directed along χ axis. The normal to the cell wall lies at an angle α to the direction of the X-ray beam. The azimuth angle Φ<sub>1</sub> for the scattered intensity from the fibril f<sub>1</sub> is given by:

$$\tan \Phi_1 = - \cos \alpha \tan M \tag{2}$$

The corresponding azimuth angle Φ<sub>2</sub> for scattering from f<sub>2</sub> is given by:

$$\tan \Phi_2 = - \cos(\alpha + \pi) \tan M = \cos \alpha \tan M \tag{3}$$

and so Φ<sub>1</sub> = - Φ<sub>2</sub> and the scattered intensity is symmetrical about Φ = 0°.

A sample is cut so that the radial direction is at an angle β to the front face of the wood section. The X-rays are directed normal to the front face. For a cell wall lying at an angle θ to the radial direction, the value of α is:

$$\alpha = (\beta + \theta) \tag{4}$$

The azimuthal angle for scattering from f<sub>1</sub> fibrils in the cell wall is given from equation (5) by:

$$\tan \Phi_1 = - \cos(\beta + \theta) \tan M \tag{5}$$

For scattering from the f<sub>2</sub> microfibrils, Φ<sub>2</sub> is given from equation (6) by

$$\tan \Phi_2 = \cos(\beta + \theta) \tan M \tag{6}$$

Measurement on 9 samples will be used for the angles:

β = 0, 10, 20, 30, 35, 40, 45, 50 and 90°.

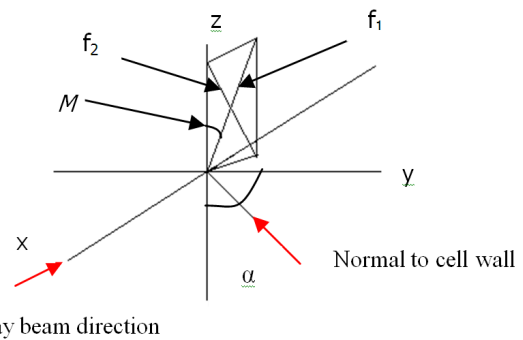


Fig. 1 Diagram showing the relationship between a cell wall, the S<sub>2</sub> microfibrils and the direction of the X-ray beam [2]

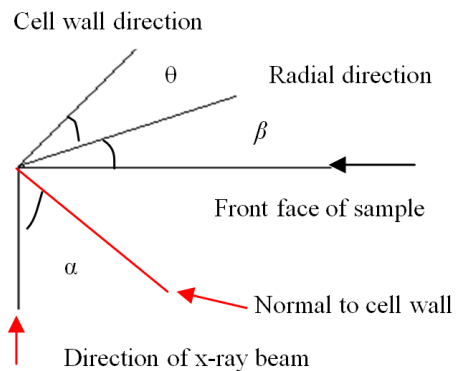


Fig. 2 Diagram showing the relation between front face of the thin sample, the radial direction (β), the cell-wall direction (θ) and the direction of the X-ray beam normal to the face of sample [2]

### III. RESULTS

Fig. 5 presents the determination of MFA by plotting intensity  $I$  against the azimuthal variation of scattered intensity. The azimuthal angle  $\Phi$  ranging from  $-90^\circ$  to  $90^\circ$ ; outside this range the scattered intensity is very small. Table 1 reports the estimated values for MFA and the orientation angle of the grain,  $\beta$ . As can be seen there is reasonable consistency between the values derived from the nine samples. It's clear that the lower values of  $\beta$  gives lower values of MFA and that the higher flanks of the intensity distributions are critical values of the  $\beta$ . That mean, for values of  $\beta$  less than  $45^\circ$ , the values of MFA are increased as the grain angle increased. For the  $\beta$  greater than  $45^\circ$ , the data of Table I indicates that the value of MFA is slightly less than that estimated as less than  $45^\circ$ . In Figure 5, a typical intensity distribution for  $\beta = 45^\circ$  versus the azimuthal angle  $\Phi$ . The higher peak arises from the  $S_2$  layer and the lower peak is generated by  $S_1$  and  $S_3$  microfibrils. Table 1 indicates that possibly the value of estimated MFA using SAXS technique is slightly less than that for the grain orientation,  $\beta$ . In Fig. 5,  $\sigma_\Phi$  is the half-width at inflection point. The width  $T$  has been shown to be correlated to the MFA [7]. The "T" parameter was developed for wide-angle diffraction data but here no reason in principle why it should not be used for SAXS intensity distribution. Here the MFA values were estimated from the reference [7] equation as following:

$$MFA = 0.6 T \quad (7)$$

$$T = MFA + 2 \sigma_\Phi \quad (8)$$

#### A. The Comparison between Measured Value of MFA for the Real Cell Wall and the Rectangular Cell Wall

It was found that the MFA of intensity distribution for the real cell of *Acacia mangium* used and the rectangular structure cell wall in a direction at  $\beta = 45^\circ$  were close together.

The intensity for  $\beta = 45^\circ$  is plotted in Figure 5. The peak intensity at  $\Phi_{45} = 24^\circ$ . The relation between this azimuthal angle and MFA for the perfect rectangular cells is given by [4].

$$MFA = \tan^{-1} \left( \frac{\tan \phi_{45}}{\cos 45} \right) \quad (9)$$

$$MFA = \tan^{-1} \left( \frac{0.445}{0.707} \right)$$

$$MFA = 32.16^\circ$$

The measured value of the cell wall of *Acacia mangium* MFA=  $29.4^\circ$ , so the use of the relation for rectangular cells to interpret the measured data gives a good estimate of MFA. Fig. 3 shows a 3dimensional module of wood at 10 mm from pith center used for the MFA estimation while Fig. 4, shows the scattering graphs obtained from *Acacia mangium* wood taken from different trees.

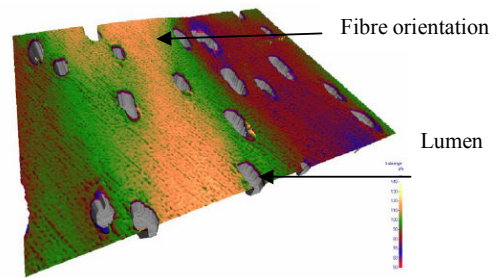


Fig. 3 The Pseudo colored 3D module wood at 10 mm from pith center, used for x-ray scattering test

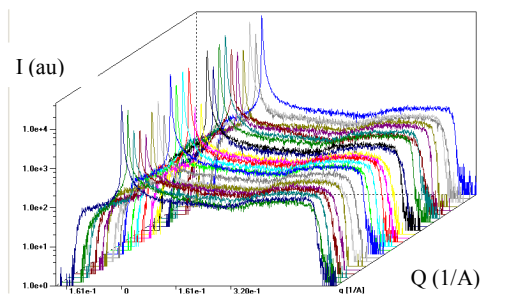


Fig. 4 Scattering graphs obtained from *Acacia mangium* wood at age 3, 5, 7, 9, 10, 11, 13 and 15-year-old from pith and bark regions. (I) the intensity and (Q) scattering factor

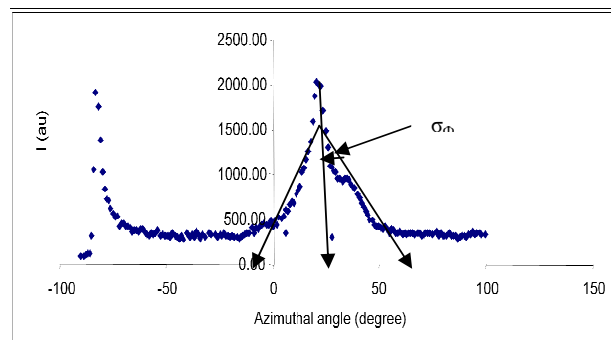


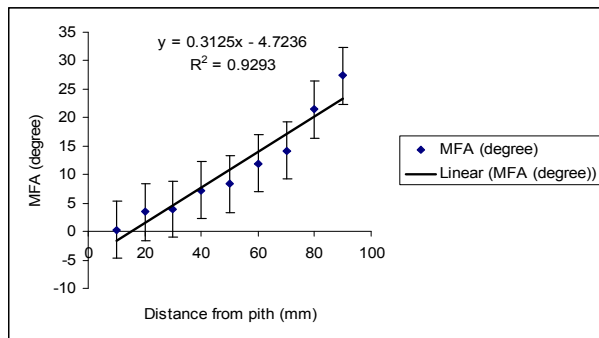
Fig. 5 The intensity distribution for  $\beta = 45^\circ$  is plotted against azimuthal angle. MFA= $29.4^\circ$  and  $\sigma_\Phi = 9.8^\circ$

The strong relationship between MFA and the distance from pith to bark which has previously been shown using XRD [8] was confirmed in this study using SAXS when the regression analysis showed that a straight line fit the data very well. It was found that 92.93% of the variation of MFA can be attributed to the distance from pith to bark of wood model 10-year-old as shown in Figure 6. Based on the results obtained from the *Acacia mangium* wood model of 10-year-old, this study can deduce the results for other samples of different age. This observation supports those of reference [4] who found that MFA in *Betula pendula* Roth varied from  $10^\circ$  to  $18^\circ$  with the distance from pith towards bark.

TABLE I

ESTIMATED MFA AND THE STANDARD DEVIATION  $\sigma_{\phi}$  FOR EACH VALUE OF  $B$ 

Sample No.	Distance from pith (mm)	$\beta$ ( $^{\circ}$ ) $\pm$ 0.5 $^{\circ}$	MFA ( $^{\circ}$ ) Mean MFA=24.2 $^{\circ}$	$\sigma_{\phi}$
1	10	0	18.0	6.0
2	20	10.0	19.8	6.6
3	30	20.0	19.2	6.4
4	40	30.0	22.2	7.4
5	50	35.0	24.0	8.0
6	60	40.0	25.8	8.6
7	70	45.0	29.4	9.8
8	80	50.0	28.8	9.6
9	90	90.0	30.6	10.2

Fig. 6 The relationship between MFA and the distance from pith in *Acacia mangium* wood of 10-year-old

#### IV. DISCUSSION

The results show that MFA varied from 18.0 $^{\circ}$  at distance 10.0 mm from the pith center to 30.6 $^{\circ}$  at 90.0 mm from the pith. The highest MFA has been found near the outer bark at the breast height of the tree. This result supports the statement made by [3] who found that MFA in hardwoods were lower than in softwoods. This was shown in *Norway spruce* where MFA after the 7<sup>th</sup> year ring varies between 6 $^{\circ}$  to 10 $^{\circ}$  [1]. *Acacia mangium* wood as a hardwood contains vessel elements in which the MFA can be higher. On this basis, The MFA values measured in this wood model is reasonable. The presence of vessels, especially in high abundance might be expected to increase x-ray diffractometric estimates MFA for hardwoods in comparison to softwoods [4]. Removal of the contribution of vessels from the average values found in hardwoods might therefore result in an even lower value of MFA for the fibres [2].

#### V. CONCLUSION

MFA can be used a good indicator to estimate of hardwoods and softwood based on its value [8]. Wood containing fibres with an MFA of 30 $^{\circ}$  or below have been termed hardwoods wood, while wood containing fibres with MFA of 30 $^{\circ}$  or more have been termed softwoods [4]. This can be proved again in *Acacia mangium* wood from Sabah where the mean value of MFA from pith to bark was found to be 24.2 $^{\circ}$  in the wood disc of 10-year-old.

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