## THE BIREFRINGENCE OF WOOD PULP FIBRES AND THE THICKNESS OF THE S<sub>1</sub> AND S<sub>3</sub> LAYERS

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## ABSTRACT

The birefringence of pulped softwood fibres has been measured and found for several species to decrease with decreasing cell-wall thickness. This is explained theoretically by the compensation of the retardation of light in the  $S_2$  layer by the transversely wound  $S_1$  and  $S_3$  layers. These layers are of similar thickness for all fibres and thus have a greater effect on thin-walled fibres. Measurement of birefringence over a range of fibre wall thicknesses permits a determination of the thickness of the  $S_1$  and  $S_3$  layers, and the results are in good agreement with data from other methods.

Additional keywords: Fibres, cellulose fibres, softwoods, birefringence, optical properties, fibrils, angles, cell-wall thickness, fibre structure, microstructure, cell walls, primary walls, secondary walls.

#### INTRODUCTION

The structure of a softwood fibre is shown in Fig. 1 (Kerr and Bailey 1934). It consists of a tenuous primary wall, P, heavily encrusted with lignin to form the middle lamella, ML, and three secondary layers, S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>, composed of cellulosic fibrils embedded in an amorphous matrix of hemicellulose and lignin. The  $S_1$  and  $S_3$ layers are thin and the fibrils are wound almost transversely to the fibre axis. The  $S_2$  layer comprises most of the cell wall and its fibrils are wound in a helix at an angle, termed the fibril angle, to the fibre axis. The fibrils are largely crystalline and are aligned in the secondary layers so that wood fibres are in general birefringent. The magnitude of the birefringence depends on the relative thicknesses of the layers, ML-P, S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>, and the orientation and birefringence of each layer. A theoretical equation has been derived for the birefringence of wood fibres of low fibril angle and verified experimentally. From birefringence measurements a precise measure of the average combined thickness of the  $S_1$  and  $S_3$  layers can be derived.

#### THEORY

We will consider a wood pulp fibre viewed between crossed polars in a microwood and FIBER

scope, the axis of which is perpendicular to the fibre axis. The fibrils of  $S_2$  make an angle  $\theta$  with the fibre axis. The S<sub>1</sub> layer is generally considered to comprise several layers of fibril angle 70-80° with alternating S and Z helices. The optical behaviour of such a structure is approximately equivalent to a single layer of fibril angle 90°. For the analysis given here, the fibrils of  $S_t$  are thus assumed to be perpendicular to the fibre axis. The S<sub>3</sub> layer is treated similarly. Plane polarized light entering a birefringent layer of the fibre is split into ordinary and extraordinary components that travel at different velocities. These components are subsequently split again as they pass each layer boundary. The complete theory of the state of the emergent light is complicated. Generally, it belongs to the theory of "elliptical retarders" and the term "birefringence" is not used for such structures. The problem simplifies if we consider only fibres for which the fibril angle of the  $S_2$  layer is zero. Then polarized light is split into two components on entering the fibre, vibrating in the directions parallel and perpendicular to the fibre axis, but is not split again as it passes through the various layers. Such a fibre is a linear retarder and the term "birefringence" is defined as the difference between the refractive indices for light

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beams vibrating parallel and perpendicular to the fibre axis.

Since the  $S_1$  and  $S_3$  layers have their directions of maximum refractive index perpendicular to that of the  $S_2$  layer, they in part compensate for the retardation in the  $S_2$  layer.

The retardation R of the fibre thus becomes

$$R = 2(\mu_2 t_{S_2} - \mu_1 t_{S_1} - \mu_3 t_{S_3}) \quad (1)$$

where  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$ , are the birefringences and  $t_{s_1}$ ,  $t_{s_2}$ ,  $t_{s_3}$  are the thicknesses of the  $S_1$ ,  $S_2$ , and  $S_3$  layers, respectively. We assume that the middle lamella is unoriented and its birefringence is zero.

The light path 2T is given by

$$2T = 2\left(t_{S_1} + t_{S_2} + t_{S_3} + t_{ML+P}\right) \quad (2)$$

where T is the total thickness of a single cell wall.

Birefringence of the fibre  $\mu_{\rm f}$  is then given by

$$\mu_{f} = \frac{R}{2T}$$
$$= \frac{\mu_{2} t_{S_{2}} - \mu_{1} t_{S_{1}} - \mu_{3} t_{S_{3}}}{t_{S_{1}} + t_{S_{2}} + t_{S_{3}} + t_{ML+P}} . (3)$$

We wish now to consider fibres pulped by a process of complete delignification. The middle lamella, being composed mostly of lignin, is dissolved during pulping and can be ignored. We will assume that the chemical composition and degree of molecular orientation of the pulped  $S_1$ ,  $S_2$ , and  $S_3$  layers are similar, so that

$$\mu_1 = \mu_2 = \mu_3 = \mu_0 .$$
 (4)

Then

$$\mu_{f} = \mu_{0} \left[ 1 - 2 \frac{\left[ t_{S_{1}} + t_{S_{3}} \right]}{T} \right] \quad (5)$$

Insofar as the assumption of the constancy of chemical composition between the layers is invalid, the thicknesses  $t_{s_1}$  and  $t_{s_3}$  can be regarded as equivalent rather than absolute thicknesses.



FIG. 1. Schematic representation of a single fibre of wood showing the arrangement of the cellulosic microfibrils in the various layers of the cell wall.

The theory given above is only strictly correct for fibres of zero fibril angle. We have applied the theoretical equation of Hsu et al. (1947) to the general case when the fibril angle is not zero and have verified that no serious error arises provided the fibril angle is smaller than  $10^{\circ}$ . Our experimental verification was carried out on fibres of fibril angle between  $0^{\circ}$  and  $10^{\circ}$ .



FIG. 2. Interference micrograph taken in fringe field conditions for measurement of wall thickness at a specified location on the fibre.

The theory predicts that the birefringence of fibres will be a function of the thickness, T, of the cell wall. The nature of the function depends on the relationship between  $t_{s_1}$ ,  $t_{s_3}$ , and T. We will consider three cases.

I. The thicknesses of S<sub>1</sub> and S<sub>2</sub> are a constant proportion of the total thickness T.

$$t_{S_1} + t_{S_2} = K_1 T$$
 (6)

Hence,

$$\mu_{f} = \mu_{0} (1 - 2 K_{1}) . \qquad (7)$$

In this case the birefringence of all fibres is the same, but is lower than the birefringence of cell-wall material  $\mu_0$ , by a factor that depends on the ratio of the thicknesses of the layers.

II. The  $S_1$  and  $S_3$  layers are of constant thickness and the variation in the total thickness T, from fibre to fibre, comes from variation in the  $S_2$  layer.

$$t_{S_1} = K_2, \quad t_{S_3} = K_3$$
 (8)

Hence,

$$\mu_{f} = \mu_{0} \left( 1 - 2 \frac{(K_{2} + K_{3})}{T} \right) .$$
 (9)



FIG. 3. Plot of birefringence against reciprocal of cell-wall thickness for black spruce fibres, 60% yield kraft, chlorite bleached.

In this case the birefringence varies with T, the thickest fibres having a birefringence that approaches that of cell-wall material.

III. The S<sub>1</sub> and S<sub>3</sub> thicknesses are partly constant and partly variable with T.

$$t_{S_1} + t_{S_2} = K_4 + K_5 T$$
 (10)

Hence,

$$\mu_{f} = \mu_{0} \left( 1 - 2 K_{5} - \frac{2K_{4}}{T} \right) . \quad (11)$$

Here, the birefringence of the fibre varies with T as in case II, but even for the thickest fibres the birefringence does not approach that of the cell-wall material.

The relevance of the three cases will be apparent in the analysis of the data.

## EXPERIMENTAL

Wood pulp fibres of several softwood species were pulped as indicated in Table 1. The pulps were dried in the form of loose filtered mats and impregnated with mercury for the determination of fibril angle. The pulps were resuspended and fibres were dried individually between a cover glass and microscope slide. The fibril angle of each fibre was determined, by the method of Page (1969), and only those fibres with fibril angle less than 10° were accepted.



FIG. 4. Plot of birefringence against reciprocal of cell-wall thickness for unbeaten and beaten black spruce fibres, 60% yield kraft, chlorite bleached. The regression lines have a common intercept.

Birefringence was determined from two measurements, thickness, T, and retardation in polarized light, R. The dry fibres were first observed in a Leitz interference microscope in fringe field conditions using transmitted light. The shift in the fringes caused by the light passing through the fibre was measured by using a compensating calibrated wedge, adjusted to bring the fringes in the fibre to the same position as the fringes in the background. This measurement gives the value (n - 1)2Twhere n is the mean refractive index of the fibre and 2T is the length of the light path through the fibre. T was calculated assuming a value of 1.570 for n. The maximum error in T arising from this assumption was estimated at 2%. A Polaroid photograph was taken of every fibre to



FIG. 6. Plot of birefringence against reciprocal of cell-wall thickness for balsam fir holocellulose.

record the exact location of the point of measurement, which was generally at a point in the fibre axis in a region where the lumen did not contain mercury droplets. A typical print is shown in Fig. 2.

The slide was then transferred to a polarizing microscope and the region of measurement located. The retardation in transmitted polarized light, R, was determined by orienting the fibre at 45° to the crossed polars and using a calibrated Ehringhaus compensator to achieve extinction. The birefringence is given by

$$\mu_{f} = n_{H} - n_{L} = \frac{R}{2T}$$
. (12)

The experimental error in birefringence and 2T was determined from separate measurements by two operators on the same fibre. The mean error in birefringence was 0.001 and in 2T,  $0.07\mu$ m.



FIG. 5. Plot of birefringence against reciprocal of cell-wall thickness for Douglas-fir holocellulose.



FIG. 7. Plot of birefringence against reciprocal of cell-wall thickness, for black spruce holocellu-lose.



FIG. 8. Plot of birefringence against reciprocal of cell-wall thickness for white pine holocellulose.

## RESULTS AND DISCUSSION

The theory for cases II and III predicts a linear relationship between birefringence and the reciprocal of the wall thickness. All the data are therefore plotted in this way in Figs. 3 to 10. Since R and T are the measured variables, regression lines were obtained of the form  $R = a_0 + a_1T$ , and were subsequently transposed to the form  $\mu_t = b_0 + b_1/T$ , for presentation on the graphs.

## Black spruce kraft pulp, chlorite bleached

For this pulp, the data fall on a line of negative slope, supporting the theory, as shown in Fig. 3. The distinction is not clear, however, between case II, in which the thickness of the  $S_1$  and  $S_2$  layers are constant and case III, in which the thicknesses are partly constant and partly variable. Neither is it certain that the bire-fringence is being controlled according to



FIG. 9. Plot of birefringence against reciprocal of cell-wall thickness for shortleaf pine holo-cellulose.

the theory, and not by a fortuitous relationship between the cell-wall thickness and the degree of orientation of cellulose in the cell wall. For this species, the  $S_3$ layer is of negligible thickness. The matter can therefore be decided by beating the pulp until the  $S_1$  layer is removed. According to case II, the birefringence should then be independent of wall thickness, and equal to the intercept for the unbeaten pulp. The pulp was beaten in a Waring blender for 15 min and this was sufficient to remove the  $S_1$  layer as discerned microscopically from the swelling behaviour in a cupriethylene diamine solution. The results are shown in Fig. 4. Birefringence for the beaten fibres is independent of wall thickness, and within experimental error is equal to the intercept for the unbeaten pulp. Thus it is concluded that for this black spruce sample the mean

Species	Source	Pulping Process		
Black spruce	33rd, 55th and 80th rings of a 110-year-old tree	60% yield kraft chlorite bleached Holocellulose		
Balsam fir	30th and 52nd rings of a 56-year-old tree	Holocellulose		
Douglas-fir	146th, 200th, 295th and 372nd rings of a 379-year-old tree	Holocellulose		
White pine	33rd and 71st rings of a 73-year-old tree	Holocellulose		
Shortleaf pine	20th ring of a 23-year-old tree	Holocellulose		
Loblolly pine	12th ring of a 62-year-old tree	60% yield kraft chlorite bleached		

TABLE 1. Sources of wood pulp fibres studied



FIG. 10. Plot of birefringence against reciprocal of cell-wall thickness for loblolly pine, 60% yield kraft, chlorite bleached.

thickness of the  $S_1$  layer is independent of the total thickness of the cell wall, as in case II.

## Douglas-fir, balsam fir, black spruce holocellulose

Data for samples of these species are given in Figs. 5, 6, and 7. They all show the same linear relationship established above. From the regression line, two quantities of interest can be derived. The intercept on the ordinate gives directly the birefringence of the delignified cell-wall material. The slope of the line gives the combined thickness of the  $S_1$  and  $S_2$  layers. These quantities together with their limits of error are shown in Table 2.

The magnitude of the birefringence of the cell wall has special significance for it can yield information on the degree of orientation of its chemical components. This aspect will be discussed in detail in a subsequent paper. The close similarity of the intercept on the ordinate for the three species suggests that Douglas-fir and balsam fir also obey the relationship of case II, with the  $S_1$  and  $S_3$  layer thicknesses being independent of the  $S_2$  layer thickness.

The combined thicknesses of the  $S_1$  and  $S_3$  layers differ significantly between species with an average around 0.21 $\mu$ m. Although no attempt has been made to confirm this value independently, it is in good agreement with published data, obtained from electron microscopy of sections. The  $S_1$  layer is given by Meier (1955) as 0.20 $\mu$ m and by Jayme and Fengel (1962) as between 0.12 and 0.35 $\mu$ m; the  $S_3$  layer is given as 0.07–0.08 $\mu$ m by Jayme and Fengel (1962) and 0.10–0.15 $\mu$ m by Liese (1960).

# White pine and shortleaf pine holocellulose

The behaviour described earlier is not followed for all species. Figure 8 shows that for white pine no correlation exists between birefringence and the reciprocal of cell-wall thickness.

Thus this species obeys the equation derived for case I, for which the thickness of the  $S_1$  and  $S_3$  layers increases proportionately with the total thickness of the cell wall. The sparse data of shortleaf pine given in Fig. 9 show a similar pattern.

If it is assumed that the value of birefringence of the pulped cell wall is 0.056, the combined  $S_1$  and  $S_3$  layers are for white pine 0.38 $\mu$ m (or 18% of the total wall thickness) and for shortleaf pine 0.9 $\mu$ m (or 20% of the total wall thickness). No independent data are available for

TABLE 2. Birefringence and  $S_1 + S_2$  layer thicknesses for Douglas-fir, balsam fir, and black spruce

Opena Leat	kirefringenee of the cell-wall material	95% confidence limits of birefringence		S <sub>1</sub> + S <sub>3</sub> layer thickness (micromoter)	95% confidence limits of S <sub>1</sub> + S <sub>3</sub> thiomess (micrometer)	
		From	То		From	'l'o
botation=file	0.055%	0.0523	0.0583	0,249	0.169	J.328
ballun für	$O_{\bullet}(O_{2}^{*}(e^{it}))$	0.0532	0.0588	0.169	0.103	0.236
hinek apruee	0.056.5	0.0555	0.0575	0.206	0.188	0.225

white pine, but the very high value for shortleaf pine is consistent with published work on a similar species, longleaf pine, which indicates that the  $S_1$  and  $S_3$  layers are unusually thick. The electron micrographs of latewood fibres published by Mark (1967) and Dunning (1969) show  $S_1$  and  $S_3$  layers that are each of the order of 0.5–1.0 $\mu$ m thick.

## Loblolly pine, 60% yield kraft, chlorite bleached

Not all pines follow the pattern of the previous section. The data of loblolly pine (Fig. 10) fall on a line of significant slope, similar to the data of spruce and Douglasfir and balsam fir.

## CONCLUSION

The birefringence of holocellulose fibres is controlled by the relative thicknesses of the  $S_1$ ,  $S_2$ , and  $S_3$  layers. For four softwoods, the  $S_1$  and  $S_3$  layers although variable from fibre to fibre, are independent of the total wall thickness, whereas for two species, white pine and shortleaf pine, their thickness increases with total wall thickness. Measurement of birefringence permits a precise determination of the average combined thicknesses of these layers, and the results are in good agreement with previous data.

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