

Determination of S_2 -fibril-angle and fiber-wall thickness by microscopic transmission ellipsometry

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PULP FIBERS ARE MADE OF ONE primary wall enveloped in lignin to form the middle lamella and three secondary walls, S_1 , S_2 , and S_3 layers (Fig. 1) (1). All the three secondary walls are concentric and composed of cellulosic microfibrils embedded in an amorphous matrix of hemicelluloses and lignin. The most important wall is the middle layer S_2 , since it contains 80–95% of the fiber material (2, 3), so that a wood pulp fiber can be approximately described by the S_2 layer. The crystalline microfibrils of the S_2 layer trace a steep spiral around the fiber axis, and the microfibrils of the front and back walls of the S_2 layer are crossed. The angle between the fibrillar direction and the fiber axis ϕ is termed the fibril angle or micellar angle of the fiber.

The experimental evidences provided by a number of investigations [see, e.g., (4–9)] indicate that the fibril angle ϕ is closely related to the mechanical properties of the fibers such as the strength, the elastic modulus, and the shrinkage. Polarized-light microscopy has proven useful for measuring fibril angle over the years. The main difficulty with this technique is that a single, whole fiber represented by the S_2 layer has two walls. Plane polarized light entering the front wall is split into two orthogonal components travel-

ing at different velocities. These components are split again as they pass the back wall. It has been very difficult to measure the whole fiber without any pretreatment. In fact, all the existing polarizing microscope methods (1–3, 10–13) are applicable only to one fiber-wall measurement. The most commonly used MEP (major extinction position) method (1) needs to expose a fiber wall, to cut one wall away, and leave the other one available for examination. Various methods of removing fiber wall have been reported [see, e.g., (13)]. The most satisfactory method so far is the variant MEP method of (2), in which mercury droplets are injected into the lumen under high pressure. The deposited mercury droplets will function as small mirrors, reflecting the polarized light so that it passes through only one wall. This technique is still time-consuming (3) and requires a high-pressure apparatus for impregnating the fibers with mercury. Because of being one-wall measurements, the existing polarized-light methods may cause change in the fiber material. Any physical or chemical treatment may alter the fiber geometry or properties to some extent. What is even worse, they require tedious and time-consuming pretreatment of samples, making the methods very impractical for actual pulp testing. Besides, the existing methods are inaccurate.

The two orthogonal components traveling in the S_2 layer have a relative phase retardation ^{3} when emerging from the S_2 layer because of dif-

ABSTRACT

A new method based on the transmission ellipsometry for determining the fibril angle of single, intact pulp fibers is described with the emphasis on its practical importance. Requiring no sample pretreatment, the new method is simple, fast, more accurate than the existing polarized-light methods, and nondestructive of the fiber material. Besides the fibril angle, useful information about the cell-wall thickness and related properties such as fiber flexibility and coarseness can be obtained by this method. Measurement results are presented and compared.

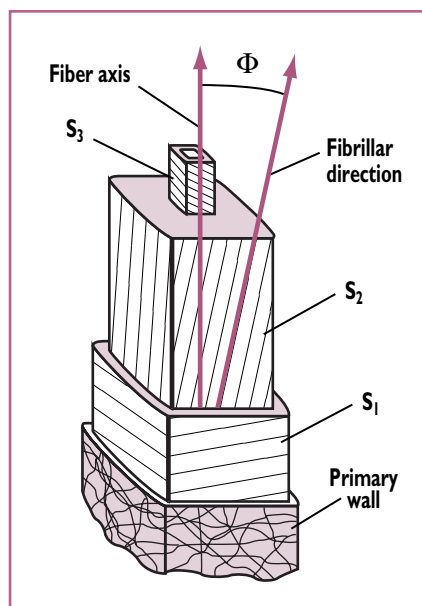
Application:

A new method is described with the emphasis on its practical importance, which can be used for determining the fibril angle of single, intact pulp fibers and obtaining useful information about the cell-wall thickness without sample pretreatment.

ferent velocities. The retardation ^{3} is proportional to the fiber-wall thickness. The wall thickness is important, as it is related to the fiber flexibility and is directly tied to the coarseness value of the fiber. The wall thickness is usually measured by cutting fibers into thin sections. If the retardation ^{3} can be determined, a nondestructive measurement of the wall thickness is possible. However, to measure the retardation ^{3} using the existing methods, one of the two cell walls must be removed, and the fibril angle needs to be known [see, e.g., (1)].

Recently, a new technique based on the transmission ellipsometry developed for measuring the fibril angle and the relative phase retardation of single, intact pulp fibers was reported (14). This method permits a two-fiber-wall measurement and requires no sample pretreatment. It is relatively simple, fast, and non-

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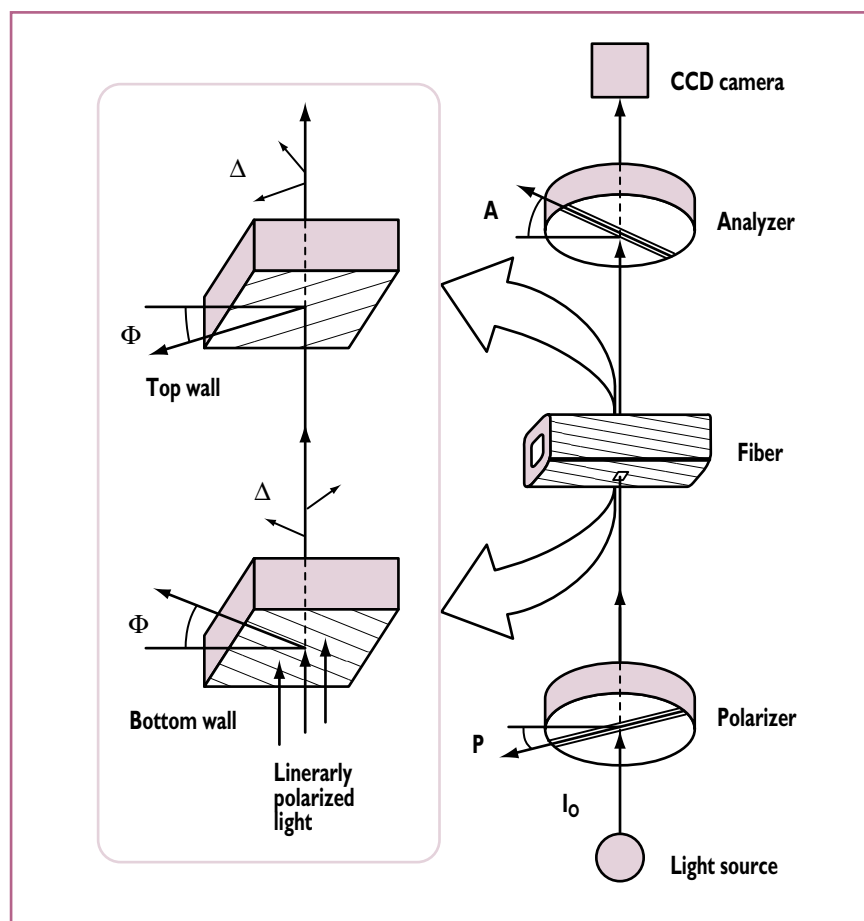


1. Schematic representation of the layer structure of a single wood fiber: ϕ , fibril angle.

destructive of the fiber material. The physical principle of the new method is described and preliminary experimental results are presented in (14). In this paper, more extensive measurement results obtained by this method are reported with the emphasis on its practical importance.

METHOD

The equipment required for applying the new method is a conventional polarizing microscope equipped with a CCD (charge-coupled device) camera or microscope video camera (Fig. 2). The fiber to be investigated is located between the polarizer and analyzer of the microscope. The fiber can be wet or dry. The light from the light source of the microscope, with constant intensity I_0 , is linearly polarized by the polarizer. The linearly polarized light sequentially passes through the two walls of the fiber to be measured. In general, the fibril angles of the two opposite walls of a fiber are similar but of opposite sense, and the thickness of



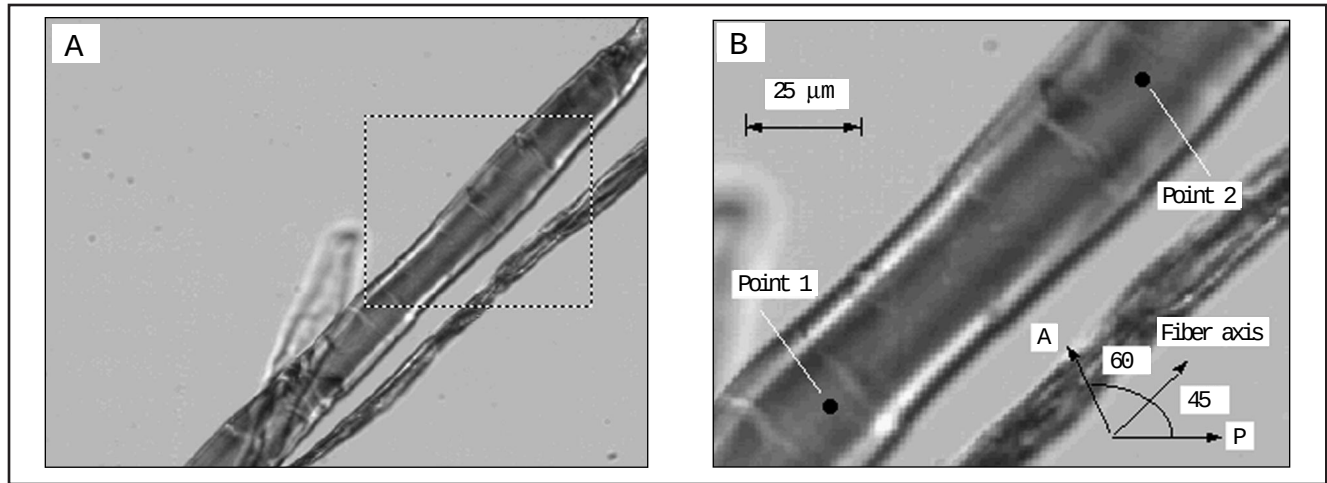
2. A single pulp fiber represented by the S_2 layer in a polarizing microscope. The two fiber walls are described by two linear retarders of the same relative retardation δ and the same orientation angle ϕ (fibril angle) with opposite senses [see text].

both of the walls can be assumed to be nearly equal. Moreover, it is assumed that it is possible to examine a homogenous region in the middle of the fiber, so that the influence of light scattering and refraction from the fiber wall can be ignored in practice. Under these conditions, the polarization properties of the two walls can be approximately described by two linear retarders in cascade with crossed optical axes (Fig. 2). These two retarders have the same relative retardation δ , which is related to the thickness of the fiber wall and the birefringence of the wall material according to:

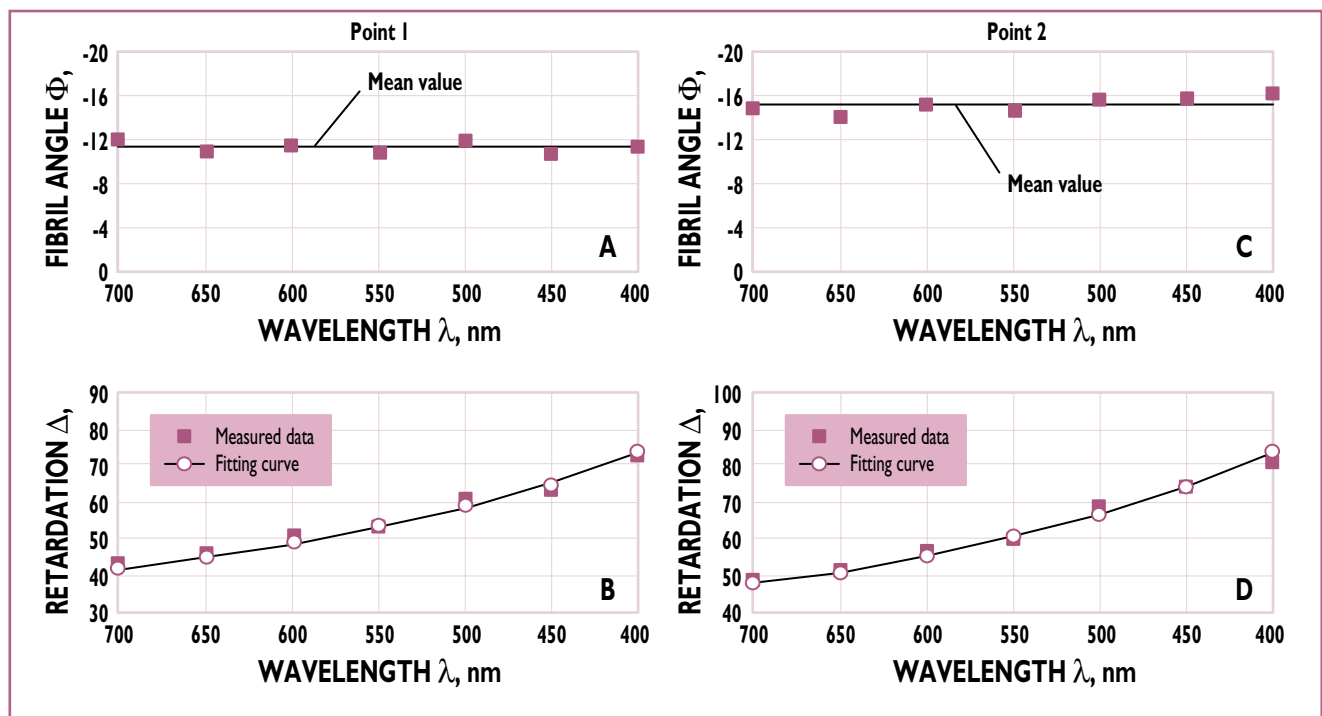
$$\delta = (360^\circ/\lambda) \cdot d \cdot (n_1 - n_2) \quad (1)$$

where d is the fiber-wall thickness,

n_1 and n_2 the refractive indices for the light vibrations parallel and perpendicular to the microfibril direction, respectively, and $n_1 - n_2$ is the birefringence of the S_2 layer. The birefringence is related to the chemical composition of the wall material and mainly results from cellulose and hemicelluloses. The orientation angles of the optical axes of these two retarders have the same value as the fibril angle ϕ of the fiber, but with opposite senses. With the help of the two-retarder model of a whole fiber, the light intensity recorded by the camera behind the analyzer can be deduced. According to (14), with the fiber axis as the coordinate axis and the polarizer at azimuth $P = 45^\circ$,



3. A: Polarizing micrograph ($\lambda = 600$ nm) of a bleached Kaukas pine springwood pulp fiber. B: Measured fiber segment (650X), where the intensity $I(A)$ was measured at the two marked points in the center region.



4. Measured fibril angle ϕ and relative retardation Δ of the pulp fiber in Fig. 3B vs. wavelength λ . A: ϕ and B: Δ for point 1; and C: ϕ and D: Δ for point 2.

the intensity $I(A)$ after the analyzer (azimuth A) is as follows:

$$I(A) = (I_0/2) \{1 + T_1 \cdot \sin 2A + T_2 \cdot \cos 2A\} \quad (2)$$

where

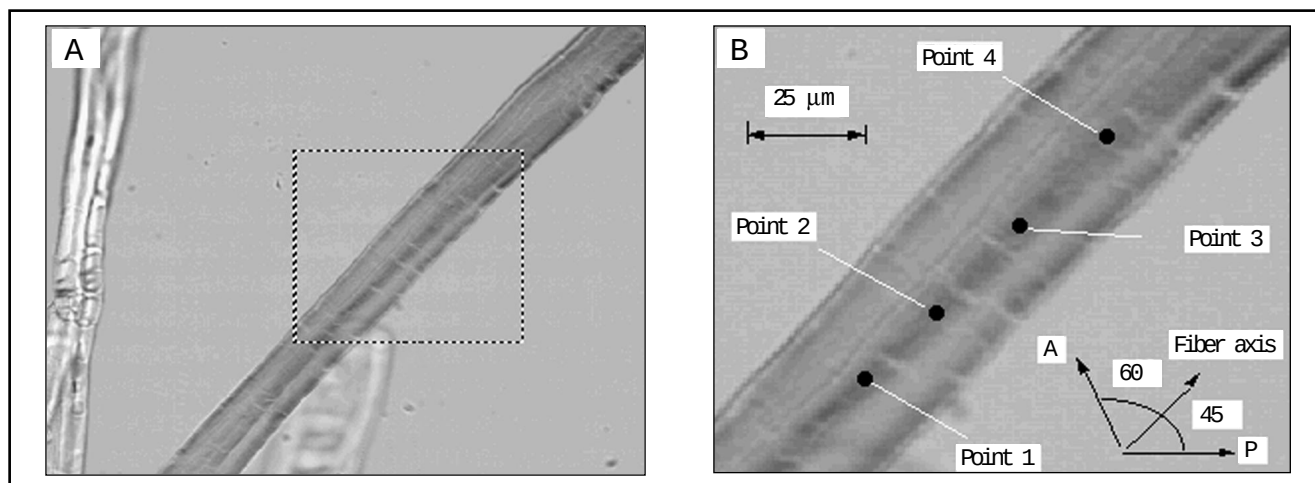
$$T_1 = 1 + 8 \cos^2(2\phi) \cdot \sin^2(3/2) \cdot [\cos^2(2\phi) \cdot \sin^2(3/2) - 1] \quad (3a)$$

$$T_2 = 2 \cdot \sin(4\phi) \cdot \sin^2(3/2) \cdot [2 \cos^2(2\phi) \cdot \sin^2(3/2) - 1] \quad (3b)$$

Because in most cases the fibers are

not straight, the concept of a local fiber axis has to be introduced. For a curved fiber, the axis of a short fiber segment straight enough is defined as a local axis of this fiber.

Based on Eqs. 2 and 3, there are two alternative ways to determine ϕ and Δ . Because the harmonic part of



5. A: Polarizing micrograph ($\lambda = 600$ nm) of a bleached Kaukas pine springwood pulp fiber showing large difference of the fibril angle. B: Measured fiber segment (650X), where the intensity $I(A)$ was measured at the four marked points in the center region.

$I(A)$ depends only on ϕ and ^{3} , the least-square principle can be used to obtain the best estimates for these parameters. For this, the intensity $I(A)$ within one whole period 180° has to be registered. The estimates for ϕ and ^{3} in Eq. 2 are then obtained based on the least-square curve fitting. Another method for determining ϕ and ^{3} is based on the formulas given in (14):

$$\tan 2\phi_1 = \frac{-2T_2}{[-2(1 + T_1)]}, \quad T_1 \approx \pm 1 \quad (4a)$$

$$\tan 2\phi_2 = \frac{-2T_2}{[-2(1 + T_1)]}, \quad T_1 \approx \pm 1 \quad (4b)$$

$$\cos^3_1 = 1 - \frac{(1 - (1 + T_1)/2)}{\cos^2(2\phi_1)} \quad (5a)$$

$$\cos^3_2 = 1 - \frac{(1 - (1 + T_1)/2)}{\cos^2(2\phi_2)} \quad (5b)$$

where the intermediate quantities T_1 and T_2 are to be determined by using the four light intensities $I(A = 0^\circ)$, $I(A = 45^\circ)$, $I(A = 90^\circ)$, and $I(A = 135^\circ)$ according to the following relations:

$$T_1 = \frac{[I(A = 45^\circ) - I(A = 135^\circ)]}{[I(A = 45^\circ) + I(A = 135^\circ)]} \quad (6a)$$

$$T_2 = \frac{[I(A = 0^\circ) - I(A = 90^\circ)]}{[I(A = 0^\circ) + I(A = 90^\circ)]} \quad (6b)$$

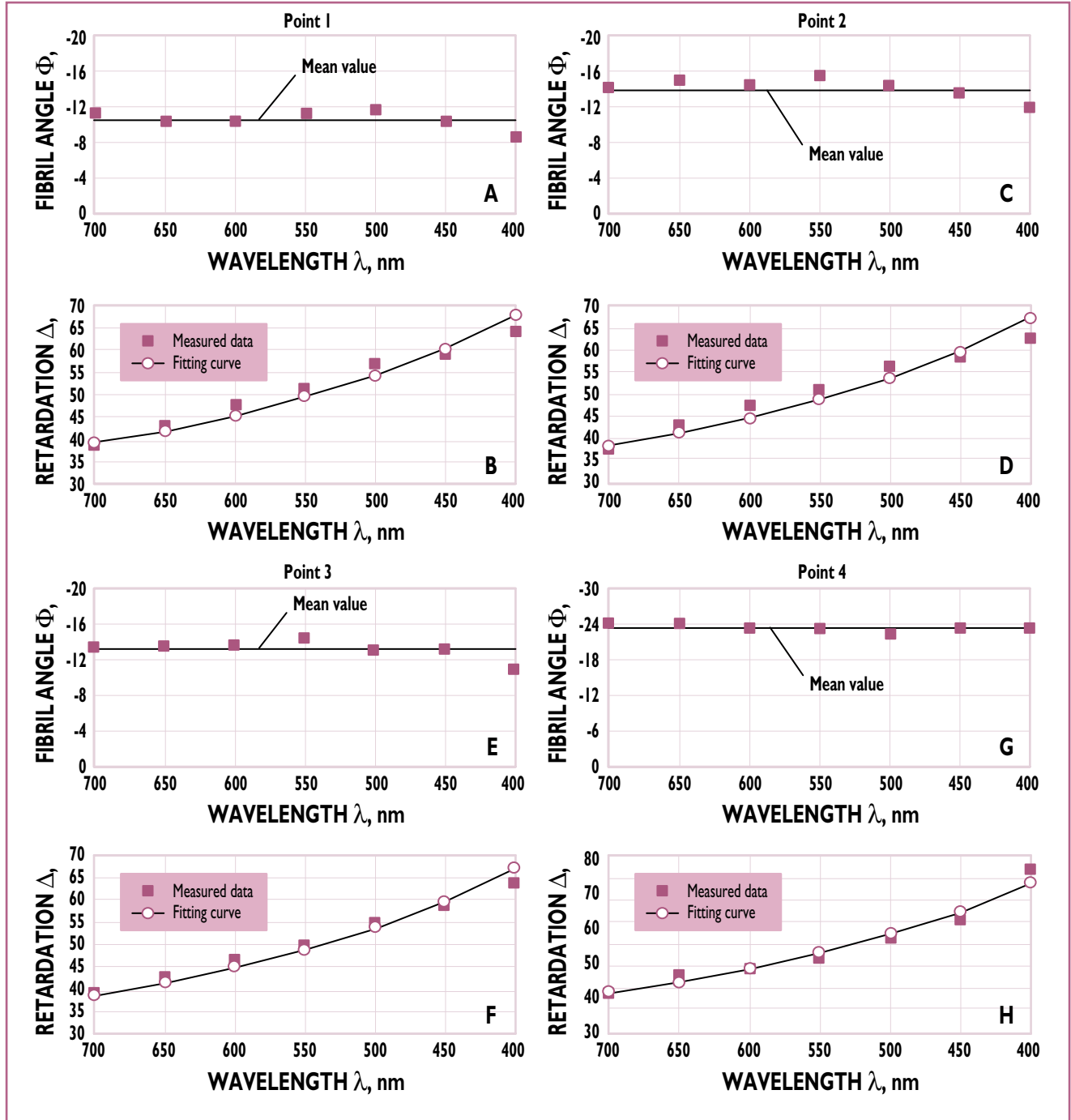
By means of Eqs. 4 and 5, the fibril angle ϕ and the relative retardation ^{3} of the fiber sample can be calculated when $T_1 \approx \pm 1$. The calculation will yield two solutions for ϕ and ^{3} . Only one of them has physical significance, the other one is a useless mathematical by-product. One way to distinguish the physically relevant solution from the mathematical by-product is to repeat the measurement with another wavelength λ according to (14). This is based on the fact that for a linear retarder the orientation angle of the optical axis (the fibril angle ϕ in our case) is independent of the light wavelength employed, while the retardation ^{3} is related to the wavelength used according to Eq. 1.

Equations 4 and 5 are not valid when $T_1 = \pm 1$. The amplitude of the sinusoidal fluctuation of $I(A)$ reaches its maximum when $T_1 = \pm 1$ ($T_2 = 0$ in this case). As pointed out in (14), the errors rapidly increase when the amplitude of $I(A)$ becomes large. Fortunately, however, such a critical case can be avoided by changing the wavelength used. With the change of the wavelength, the retardation ^{3} changes (see Eq. 1) and, accordingly, the intensity $I(A)$ can be made to

vary more smoothly.

RESULTS

Using the new method we measured some bleached sulfate pulp fibers (Kaukas Mill, Lappeenranta, Finland) by an imaging ellipsometer described in more detail in (14). The pulp fibers were fractionated into springwood and summerwood fibers by means of a centrifugal cleaner (Laboratory of Pulp Technology, Helsinki University of Technology). The fibers to be measured were immersed in a mixture of water and glycerin between a microscope slide and cover glass without any other preparation, and the slide was placed between the polarizer and analyzer of the imaging ellipsometer. Later it was proven that even dry fibers can be measured using this method. The local fiber axis of the fiber segment to be measured was oriented to be parallel to the selected coordinate axis. The polarizer was fixed at the position $P = 45^\circ$. The analyzer was rotated and the light intensities $I(A = 0^\circ)$, $I(A = 45^\circ)$, $I(A = 90^\circ)$, and $I(A = 135^\circ)$ were recorded. The measured intensity data were digitized to 256 gray levels by an image-processing unit, and the results for ϕ and ^{3} were calculated using Eqs. 4 and 5.



6. Measured fibril angle ϕ and relative retardation Δ of the pulp fiber in Fig. 5B vs. wavelength λ . A: ϕ and B: Δ for point 1; C: ϕ and D: Δ for point 2; E: ϕ and F: Δ for point 3; and G: ϕ and H: Δ for point 4.

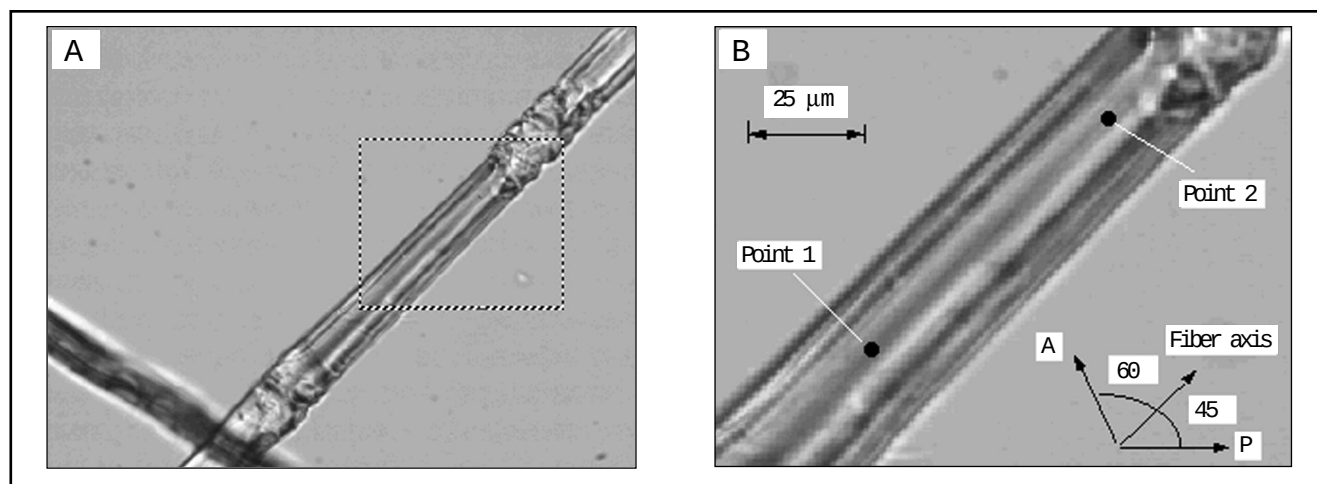
As mentioned previously, to distinguish the physically relevant solution ϕ and Δ from the mathematical by-product, the same measurement should be repeated with at least two light wavelengths. For a more con-

vincing demonstration, the wavelength λ of the light was changed from 400 to 700 nm with a step of 50 nm by sequentially inserting band-pass filters into the optical path of the ellipsometer. The measurement

procedure was repeated for each wavelength. From Eqs. 4 and 5, two solutions for ϕ and Δ were obtained for each wavelength. As an example, the intermediate results of a fiber (Fig. 3A) from the springwood frac-

Wavelength, nm	POINT 1				POINT 2			
	$\phi_1, ^\circ$	$\Delta_1, ^\circ$	$\phi_2, ^\circ$	$\Delta_2, ^\circ$	$\phi_1, ^\circ$	$\Delta_1, ^\circ$	$\phi_2, ^\circ$	$\Delta_2, ^\circ$
400	-11.3	72.4	5.0	116.6	-16.0	80.8	7.6	119.8
450	-10.6	63.1	3.5	123.1	-15.6	74.0	6.2	122.6
500	-11.9	60.8	3.4	126.5	-15.6	69.3	5.3	125.5
550	-10.8	53.3	2.4	131.6	-14.5	59.9	3.7	130.3
600	-11.5	50.8	2.2	134.3	-15.2	57.2	3.4	133.1
650	-11.0	46.4	1.8	137.7	-14.0	51.6	2.6	135.9
700	-12.1	44.0	1.7	140.6	-14.6	48.2	2.3	139.2

1. Intermediate results of a measured springwood fiber vs. the wavelength (based on the fiber in Fig.3)



7. A: Polarizing micrograph ($\lambda = 600$ nm) of a bleached Kaukas pine summerwood pulp fiber. B: Measured fiber segment (650X), where the intensity $I(A)$ was measured at the two marked points in the center region.

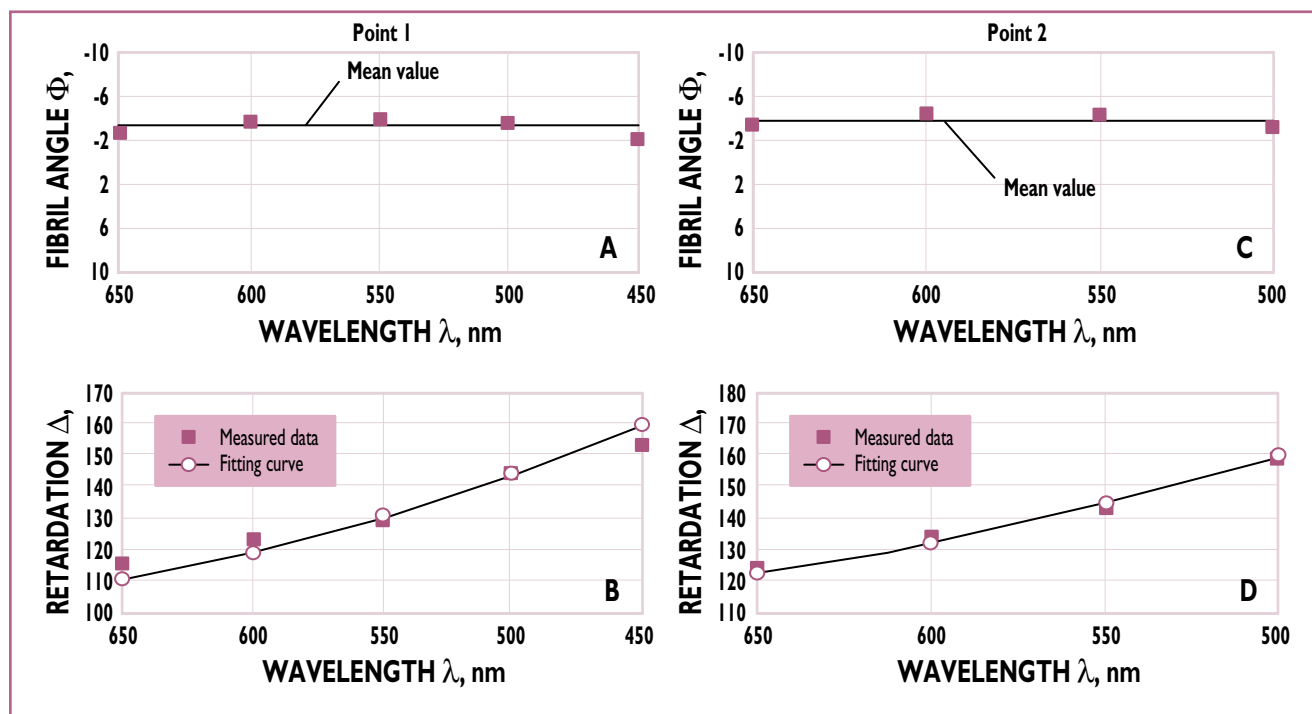
tion are presented in Table I. A segment of the fiber is magnified in Fig. 3B, and the two marked points in the center region were measured. The first group of results, ϕ_1 and ϕ_2 , in Table I (both for points 1 and 2) are the real results, because the ϕ_1 values are practically equal and the ϕ_2 values decrease with the increase of the wavelength (see Eq. 1). On the other hand, for the second group, ϕ_2 and ϕ_3 , the two criteria are not fulfilled, especially for the ϕ_3 data. The minus sign of the ϕ data in the chosen coordinate system means that the helix formed by the microfibrils of the S_2 layer is right-handed. The measurement results, ϕ_1 and ϕ_2 , in Table I are schematically described as a

function of the light wavelength in Figs. 4A–D and compared with their mean values or the best-fit curves. The mean of all the measured ϕ values is equal to -11.3° for point 1 and -15.1° for point 2. It can be seen from Fig. 4B and Fig. 4D that the measured values of ϕ coincide well with their respective best-fit curves.

Because the new method is the first one that enables the two-cell-wall measurement, the existing polarized-light methods cannot be simply used to give some comparative results for reference. Another reason for not using the existing methods is that they seem to be very inaccurate: the results obtained by different methods are significantly

different [see, e.g., (10, 15)], even if the results are based on several tens of repeated measurements. To evaluate our measurement results, fortunately, we can use the two criteria used for distinguishing the measurement result from the mathematical by-product. If the two criteria can be satisfactorily fulfilled, especially in a broad wavelength bandwidth, this is also indirect experimental evidence for this new method.

From Table I or Fig. 4, one can see that the fibril angles of the fiber at the two measured points are obviously different. This indicates that the fibrillar direction varies not only from fiber to fiber but also from point to point within one fiber. Even



8. Measured fibril angle ϕ and relative retardation Δ of the pulp fiber in Fig. 7B vs. wavelength λ . A: ϕ and B: Δ for point 1; and C: ϕ and D: Δ for point 2.

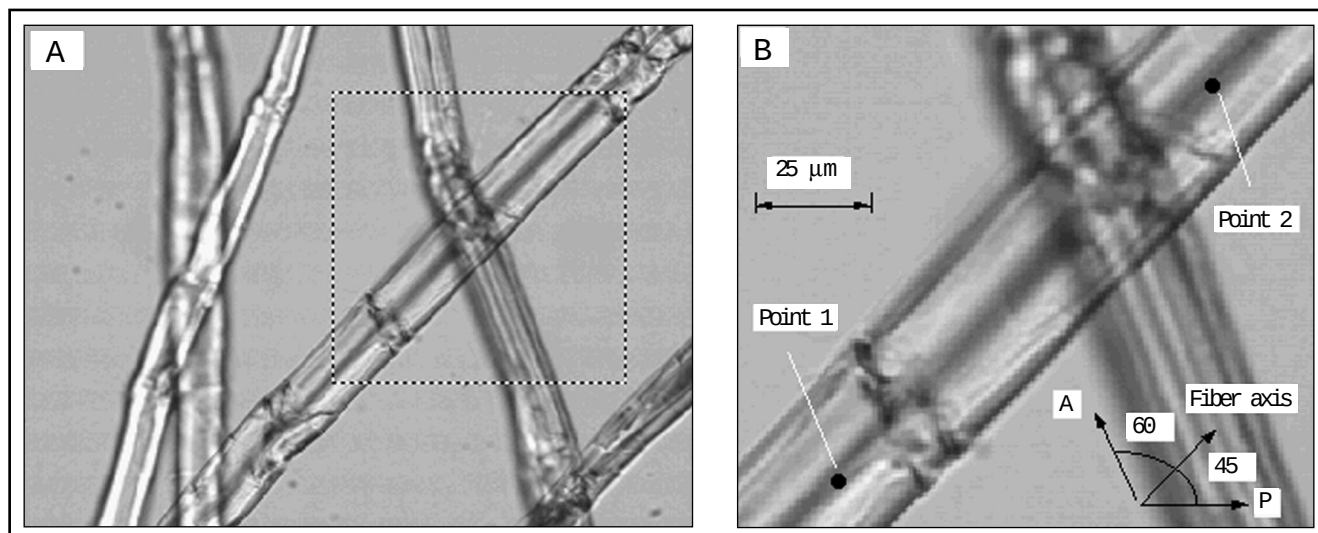
within a single fiber, the fibril angle can vary depending on the actual measurement point. As an example, Fig. 5 presents another fiber from the springwood fraction: its fibril angle varies from point to point as can be seen in Fig. 6. Four points marked in Fig. 5B in the center area were measured. Although these points are very near to each other, the measured fibril angles are far from equal, especially those for point 1 and point 4. The mean ϕ is -10.5° for point 1 and -23.4° for point 4. On the other hand, the wall thickness at these points, which are proportional to the Δ values, do not differ very much from one another.

The retardation Δ of a fiber is proportional to the wall thickness (Eq. 1). Thus, by measuring the retardation, an estimation for the wall thickness can be obtained provided that the birefringence of the wall material can be assumed constant. For an accurate determination of the wall thickness, it is necessary to know

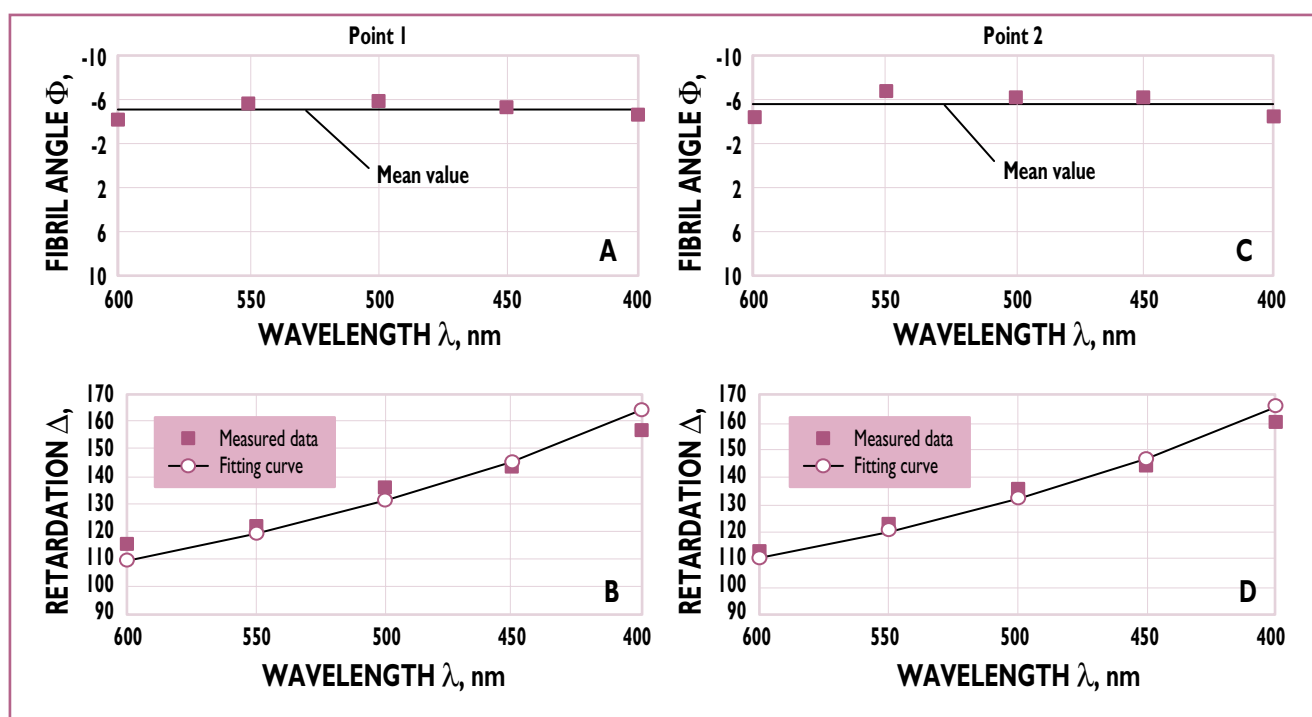
both the birefringence, $n_1 - n_2$, and the retardation, Δ . However, as the birefringence is related to the relative contents of cellulose, hemicelluloses, and lignin in a fiber, one can assume that the birefringence varies less from point to point and fiber to fiber than the wall thickness does. In general, wood fibers grow faster in the spring than in the summer. Therefore, the average wall thickness of the summerwood fibers should be greater than that of the springwood fibers. For a comparison, Fig. 7 shows a measured fiber from the summerwood fraction. The measurement results for ϕ and Δ of this fiber are presented in Figs. 8A–D. The results for some wavelengths were not accepted because they exhibited relatively large errors. The cause of this kind of error is explained in (14). Such a critical case does not limit the applicability of this method because it can be avoided simply by changing the wavelength range. This has been proven to be feasible by

the results shown in Fig. 8; two wavelengths are generally enough to be able to choose the correct measurement results.

To have a better comparison of the wall thickness, it is convenient to calculate the product $d(n_1 - n_2)$ of the wall thickness, d , and the birefringence, $(n_1 - n_2)$, since the retardation, Δ , is a quantity related to the light wavelength used. The product $d(n_1 - n_2)$ was determined based on the fit of the Δ data and using Eq. 1. The determined $d(n_1 - n_2)$ is equal to 199.1 nm and 221.6 nm for points 1 and 2 of the fiber in Fig. 7, while that of the fiber in Fig. 4 is 82.1 nm and 92.7 nm at points 1 and 2. The summerwood fiber in Fig. 7 is much thicker than the springwood fiber in Fig. 3 if the birefringence of their wall material do not differ very much from each other. According to (16), for pine fibers no correlation exists between the birefringence and the wall thickness, and the measured results for the birefringence do



9. A: Polarizing micrograph ($\lambda = 600$ nm) of a bleached Kaukas pine summerwood pulp fiber having small fibril angle. B: Measured fiber segment (650X), where the intensity $I(A)$ was measured at the two marked points in the center region.



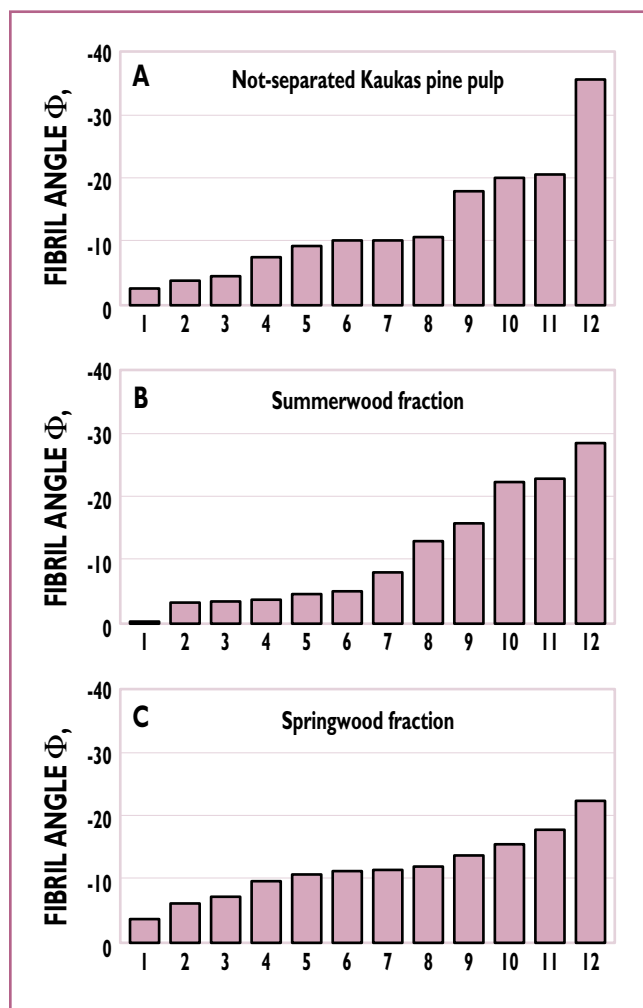
10. Measured fibril angle ϕ and relative retardation Δ of the pulp fiber in Fig. 9B vs. wavelength λ . A: ϕ and B: Δ for point 1; and C: ϕ and D: Δ for point 2.

not significantly vary from fiber to fiber. If the birefringence is known, the wall thickness can be estimated immediately. For example, if the birefringence ($n_1 - n_2$) of the measured pine fibers is assumed to be 0.05

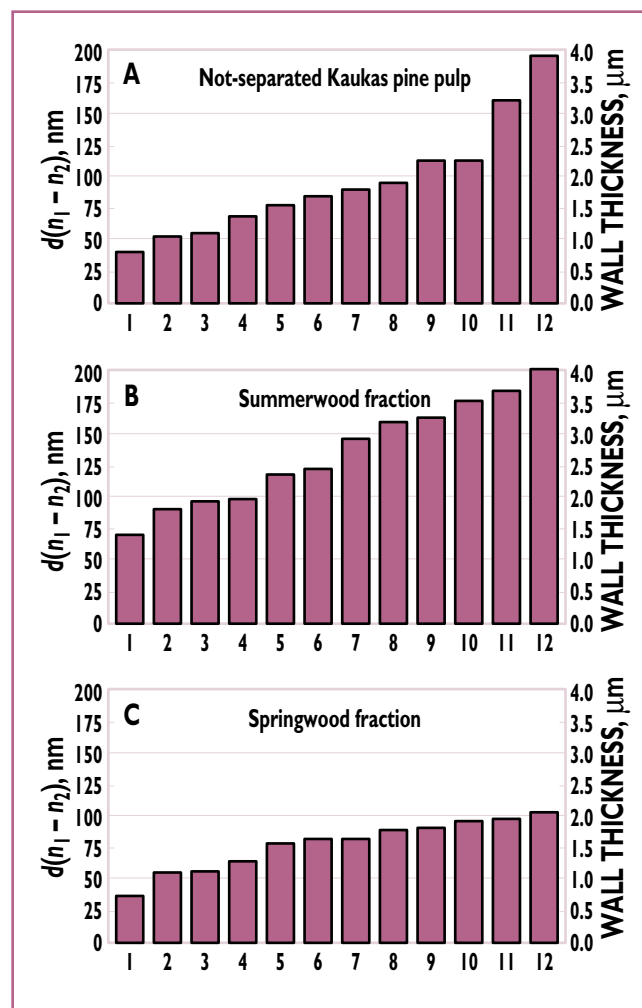
referred to the measurement results given in (16), the springwood fiber in Fig. 3 should have a wall thickness of 1.64 μm or 1.85 μm at point 1 or point 2, respectively, while the wall

thickness of the summerwood fiber in Fig. 7 should be 3.98 μm or 4.43 μm at point 1 or point 2, respectively.

According to (10), the thick-walled summerwood fibers with



11. Distribution (arranged according to the magnitude) of the measured fibril angle ϕ of A: the original Kaukas fibers, B: the fibers from the summerwood fraction, and C: the fibers from the springwood fraction.



12. Distribution (arranged according to the magnitude) of the measured product $d \cdot (n_1 - n_2)$ and the wall thickness d (if the birefringence $n_1 - n_2 = 0.05$) of A: the original Kaukas fibers, B: the fibers from the summerwood fraction, and C: the fibers from the springwood fraction.

small fibril angles are the most difficult materials to measure by any usual method. However, our measurements indicate that the new method works well both with springwood and summerwood fibers. The summerwood fiber shown in Fig. 7 is a demonstration example. Figure 9 is another measured summerwood fiber. This fiber also had a thick wall and small fibril angle. The results for ϕ and d of the fiber are described in Figs. 10A–D.

For comparison, 12 fibers were measured for each fraction of the

original not-separated Kaukas fibers, the springwood and summerwood fibers. The determined fibril angle ϕ and the product $d(n_1 - n_2)$ or the wall thickness d (assuming the birefringence $n_1 - n_2 = 0.05$) for these fibers are given in Figs. 11 and 12. It is understood that the springwood fraction contains more springwood fibers, while summerwood fibers predominate in the summerwood fraction. This fact has been reflected in the results of $d(n_1 - n_2)$ in Fig. 12. Based on the assumption that the birefringence of the wall material for

the springwood and summerwood fibers does not vary remarkably, the mean wall thickness of the fibers in the springwood fraction is smaller than that of the original, not-separated fibers and much smaller than that of the fibers from the summerwood fraction. The regularity of the fibril angle is not so clear because the number of the measured fibers is probably far from sufficient. Right now, the measurement takes about 4–5 min per fiber. We hope to increase the speed to 5–10 fibers per minute by automating the measure-

KEYWORDS

Angles, cell wall thickness, cellulose fibers, fibrils, measurement, microscopy, nondestructive testing, retardation, test methods, test equipment, transmission, transmittance.

ment and data-processing procedures.

DISCUSSION AND CONCLUSION

The measurement results for both ϕ and ^{3} were in good agreement with the theoretical description. The new method allows a quantitative determination of ϕ and ^{3} , and requires no sample preparation. It is relatively simple, fast, accurate, and non-destructive of the fiber material. Based on the determination of ^{3} , the method enables one to acquire information about the wall thickness and related fiber properties such as flexibility and coarseness. For the new method, the fiber to be measured can be wet or dry, and the thick-walled summerwood fibers with small fibril angle are as easily measurable as thin-walled springwood fibers. **TJ**

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