

Micro-model of paper

Part 1: Bounds on elastic properties

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ABSTRACT: *A micro-model of paper with the cell wall taken as a composite with continuous cellulose microfibrils embedded in a matrix of hemicellulose and lignin is presented. Part 1 presents the derivations for the upper and lower bounds on the elastic and shear moduli and the moisture expansion coefficients of assemblages of cell-wall elements. The upper and lower bounds are established by considering the two extreme configurations of the cell-wall elements—the series and parallel arrangements. The anisotropy is accounted for by a distribution function for the orientations of microfibrils.*

KEYWORDS: *Anisotropy, bibliographies, cell walls, computation, elastic strength, fibrils, hemicelluloses, lignins, mathematical models, mechanical properties, moisture content, paper sheets, stiffness.*

A sheet of paper may be thought of as being composed of fiber segments, bonds, and voids (1). **Figure 1** illustrates this concept. For sheets of low apparent density, the fiber segments are thought to dominate the way in which the sheet responds to a load. For high-density sheets, with an apparent density approaching that of the fiber cell wall, the mechanical deformation is considered to be governed by the response of the bonded material.

Theories that describe or predict the mechanical response of paper may be classified broadly as network

theories (2–7) and continuum theories (8–10). Continuum theories do not take the presence of voids into account, whereas network theories fall short when the fibers are too closely packed to act as elements of a network. Network models successfully predict the elastic and post-elastic responses of low-density sheets (11, 12). Before these predictions are possible, however, the models require many geometrical and material parameters that are difficult to obtain. More recently, finite-element analysis has been used in the analysis of fiber networks to pro-

vide useful insights on the mechanical response of low-density sheets (13, 14).

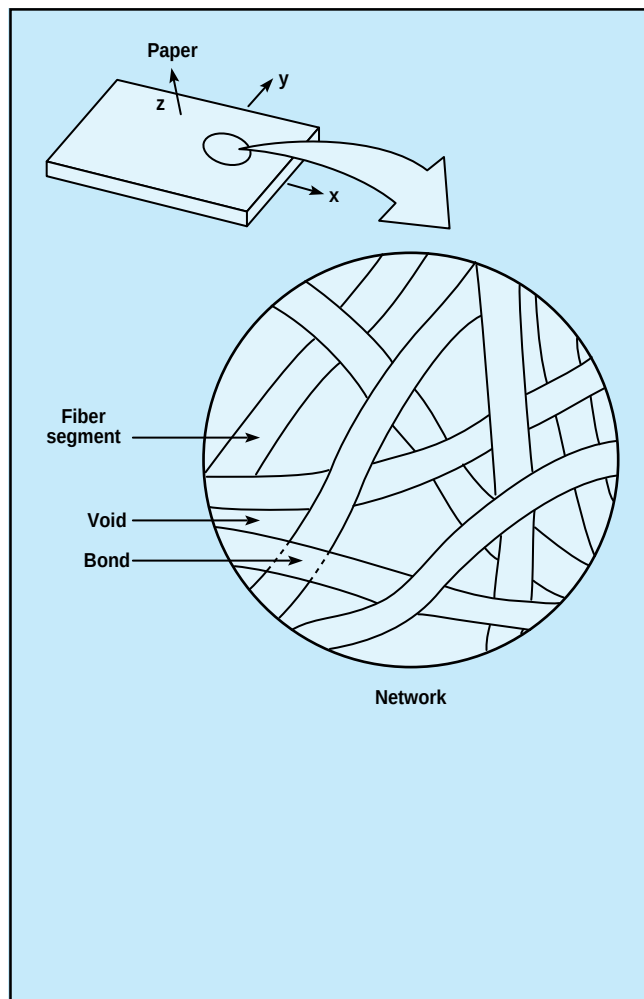
Our main objective with this work is to predict the elastic constants (or the small strain constants) and the moisture expansion coefficients of sheets ranging from medium to high density. These predictions are to be based on structural and material properties that can be measured by tests on the fibers and paper.

The laminate model is a type of continuum model that has been used with some success (9, 10, 15). However, the laminate model overpredicts the elastic moduli of paper even when accounting for the void content (15). Laminate and network models are based on the assumption of a uniform field of strain throughout the paper sheet. In reality, there are substantial variations in local strain in a sheet under stress or in one undergoing changes in moisture content. The bonded regions and free segments will have different stiffnesses, and there will be local concentrations of strain as a result of voids. The overprediction of the elastic stiffnesses of paper is not surprising because the assumption of uniform strain leads to upper bounds on the elastic stiffnesses (16). Conversely, the assumption of uniform stress leads to lower bounds on the elastic stiffnesses. The actual response of paper should be somewhere between these two extremes.

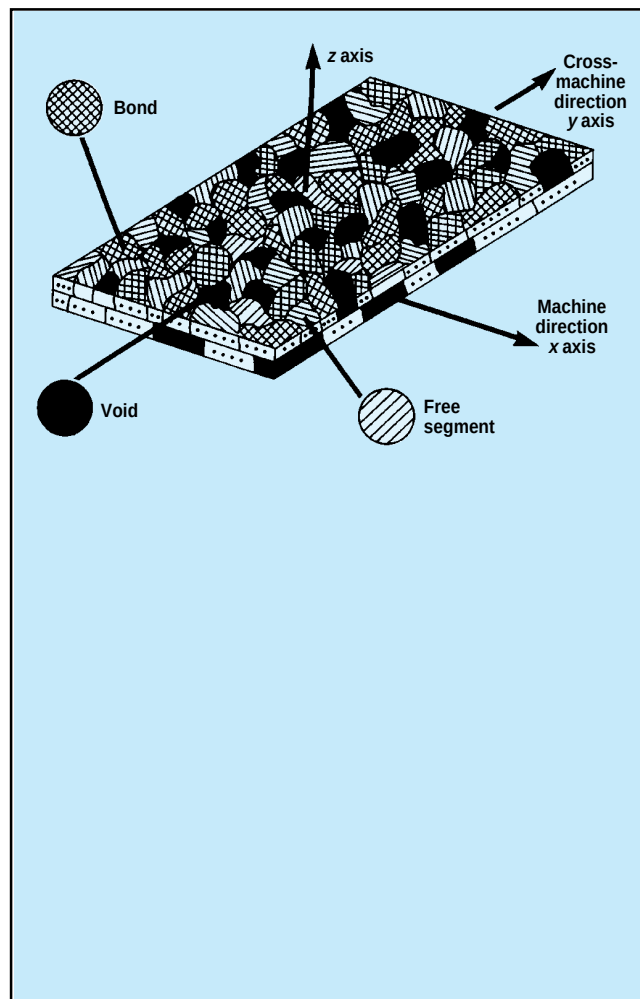
The micro model we propose is a “mosaic” type model. As depicted in **Fig. 2**, the paper is considered to be

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1. Fiber segments, bonds, and voids in a sheet of paper



2. The structure of paper in the mosaic concept



composed of three elements: bonds, fiber segments, and voids. The bonds are assumed to have uniform strain, similar to a laminate of fiber cell-wall plies. The segments are assumed to have uniform stress, behaving as cell-wall material connected in series.

Based on these two assumptions, we derive in Part 1 of this study the appropriate mechanical properties and the moisture expansion coefficients of the bonds and fiber segments. We also examine the effects of microfibril orientation and the influence of moisture content on the bounds.

Bounds on paper properties

Series model

Figure 3 shows cell-wall elements of different orientations θ_k (for $k = 1, 2, \dots, n$) connected in series. The cell-wall material is considered to be composed of the S_2 layer of the wood fiber. The series configuration corresponds to a uniform stress and leads to lower bounds on the effective moduli of the assemblage of cell-wall elements.

The material is taken to be linearly and orthotropically elastic (or elastic in the x , y , and z directions). The plane-of-stress constitutive relation for an off-axis, orthotropic element is (17):

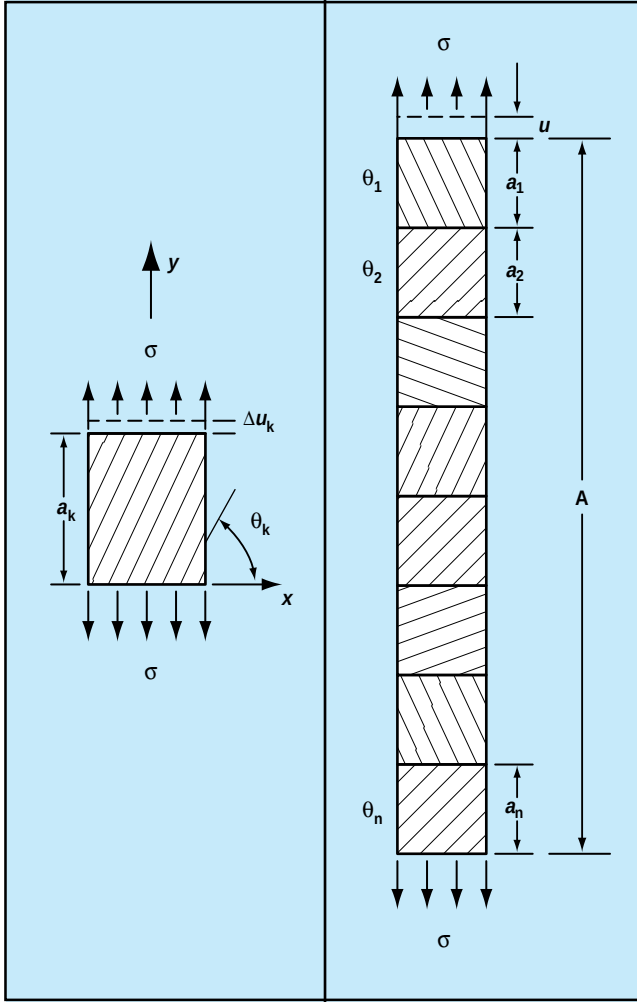
See pg. 164 for equation (1)

where $S_{ij}^* = S_{ij}^*(\theta_k)$ are the off-axis compliance elements of the cell-wall material. Listed elsewhere are the transformation equations from on-axis (S_{ij}) to off-axis compliance elements, along with the expressions for S_{ij} in terms of the principal elastic constants of the cell wall (17).

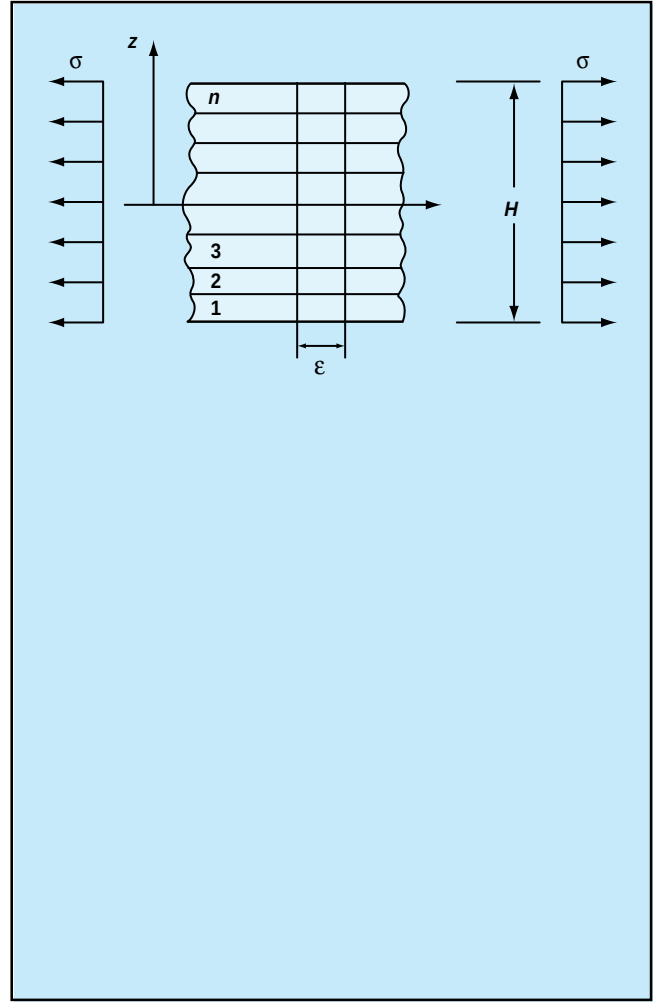
Assembling the cell-wall elements in series (Appendix A) leads to the following expressions for the effective Young's moduli (E_x and E_y), the effective shear modulus (G_{xy}), and Poisson's ratio ν_{xy} :

$$E_x = \frac{1}{\int_{-\pi/2}^{\pi/2} S_{11}^*(\theta) f(\theta) d\theta} \quad (2a)$$

3. Cell-wall elements assembled in series, having uniform stress



4. Cell-wall elements assembled in parallel, having uniform strain



$$E_y = \frac{1}{\int_{-\pi/2}^{\pi/2} S_{22}^*(\theta) f(\theta) d\theta} \quad (2b)$$

$$G_{xy} = \frac{1}{\int_{-\pi/2}^{\pi/2} S_{66}^*(\theta) f(\theta) d\theta} \quad (2c)$$

$$\nu_{xy} = - \frac{\int_{-\pi/2}^{\pi/2} S_{12}^*(\theta) f(\theta) d\theta}{\int_{-\pi/2}^{\pi/2} S_{11}^*(\theta) f(\theta) d\theta} \quad (2d)$$

where $f(\theta)$ is the probability distribution function for the orientation of fibrils, which is assumed to be sym-

metric with respect to the x and y axes.

When the assemblage of cell-wall elements shown in Fig. 3 is subjected to a moisture content change, ΔM , the moisture-induced strains (e_x , e_y , e_{xy}) can be calculated from Eqs. 3a–3c (Appendix B):

$$e_x = \Delta M \int_{-\pi/2}^{\pi/2} \beta_x(\theta) f(\theta) d\theta \quad (3a)$$

$$e_y = \Delta M \int_{-\pi/2}^{\pi/2} \beta_y(\theta) f(\theta) d\theta \quad (3b)$$

$$e_{xy} = \Delta M \int_{-\pi/2}^{\pi/2} \beta_{xy}(\theta) f(\theta) d\theta \quad (3c)$$

The hygroexpansion coefficients, β_x , β_y , and β_{xy} , are defined by

$$\beta_x = e_x / \Delta M \quad (4a)$$

$$\beta_y = e_y / \Delta M \quad (4b)$$

$$\beta_{xy} = e_{xy} / \Delta M \quad (4c)$$

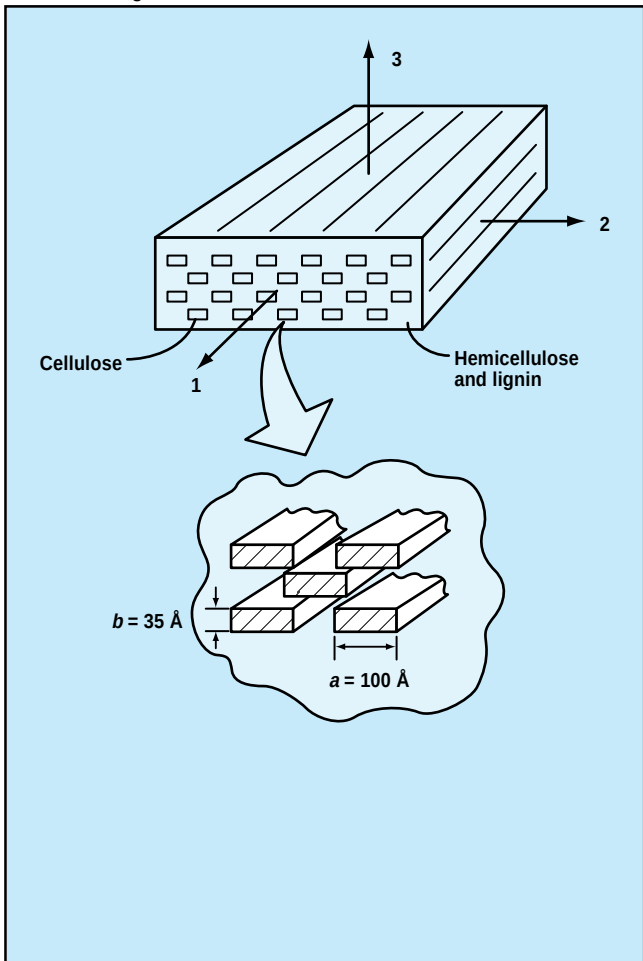
For $f(\theta)$ being symmetric with respect to $\theta = 0$, $e_{xy} = 0 = \beta_{xy}$.

Parallel model

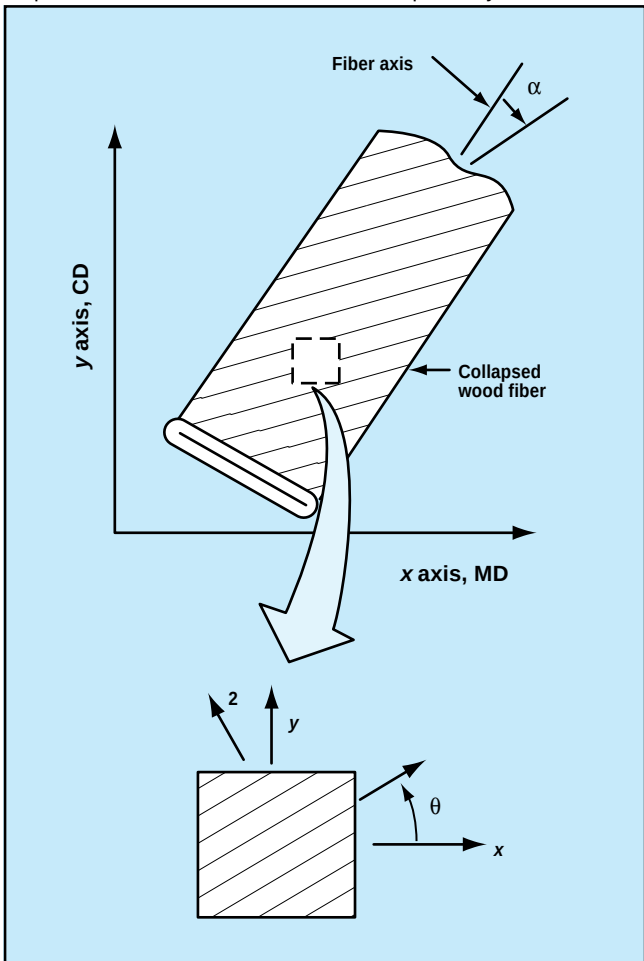
The parallel model illustrated in **Fig. 4** corresponds to a uniform strain field and leads to upper bounds on the effective moduli of the assemblage of cell-wall elements. The cell-wall elements of different orientations θ_k (for $k = 1, 2, \dots, n$) are assembled as a symmetric laminate. The constitutive relation for a symmetric laminate is (17):

See pg. 164 for equation (5)

5. Composite model of the S_2 layer of the fiber cell wall, with the insert showing the dimensions of the cellulose microfibrils



6. Collapsed wood fiber and definition of fibril angles α and θ , with respect to the fiber axis and the x axis, respectively



where (N_x, N_y, N_{xy}) are the mechanical stress resultants and (F_x, F_y, F_{xy}) are the effective hygroscopic stress resultants per unit width of the laminate. $[\epsilon_x, \epsilon_y, \gamma_{xy}]$ are the extensional and shear strains. The i and j variables for A_{ij} are the components of the stiffness matrix given by

$$A_{ij} = \sum_{k=1}^n Q^*_{ij}(\theta_k) h_k \quad (6)$$

where the Q^*_{ij} are the transformed (off-axis) ply stiffness elements, and h_k is the thickness of the k th ply (17).

Assuming that the through-thickness orientations of the microfibrils follow the distribution $f(\theta)$,

$$h_k/H = f(\theta_k) \Delta\theta \quad (7)$$

where H is the total thickness of the laminate and $f(\theta_k) \Delta\theta$ is the fraction

I. Elastic constants and densities of cell-wall constituents (dry)

	Cellulose	Hemicellulose	Lignin
Young's modulus E , GPa	...	8.0	4.0
E_1	134.0	...	...
E_2	27.2	...	...
Poisson's ratio ν	...	0.33	0.33
ν_{12}	0.1	...	...
Shear modulus G , GPa	...	...	...
G_{12}	4.4	...	...
Density, ρ , kg/m ³	1500	1500	1500

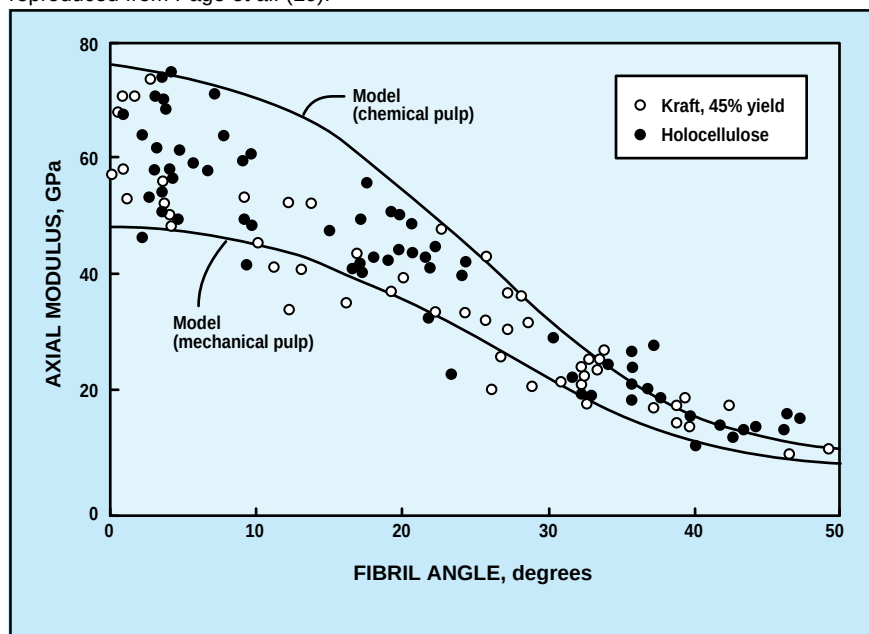
E_1, E_2, ν_{12} , and G_{12} were calculated earlier (20) using the Halpin-Tsai equations (21). Other sources were also consulted (19, 24, 25).

of microfibrils with orientations between the angles θ_k and $\theta_k + \Delta\theta$.

Considering the small dimensions of the cell-wall plies, we can con-

sider the limit when the number of elements (plies) approaches infinity, $n \rightarrow \infty$. Equation 7 becomes

7. Single fiber modulus, E_{Axial} , as a function of the S_2 microfibril angle, α (dry). Data points are reproduced from Page *et al.* (29).



$$dh = H f(\theta) d\theta \quad (8)$$

and the summations in Eq. 6 are replaced by integrals.

The calculations of A_{ij} are simplified if the Q_{ij}^* in Eq. 6 are expressed in terms of the ply invariants U_i (for $i = 1, 2, 3, 4, 5$) (17):

$$A_{11} = H \int_{-\pi/2}^{\pi/2} (U_1 + U_2 \cos 2\theta + U_3 \cos 4\theta) f(\theta) d\theta \quad (9a)$$

$$A_{22} = H \int_{-\pi/2}^{\pi/2} (U_1 - U_2 \cos 2\theta + U_3 \cos 4\theta) f(\theta) d\theta \quad (9b)$$

$$A_{12} = H \int_{-\pi/2}^{\pi/2} (U_4 - U_3 \cos 4\theta) f(\theta) d\theta \quad (9c)$$

$$A_{66} = H \int_{-\pi/2}^{\pi/2} (U_5 - U_3 \cos 4\theta) f(\theta) d\theta \quad (9d)$$

$A_{16} = A_{26} = 0$ because of the symmetry of $f(\theta)$. The effective elastic constants of the assemblage of cell-wall elements are (9):

$$E_x = (A_{11} A_{22} - A_{12}^2) / A_{22} H \quad (10a)$$

$$E_y = (A_{11} A_{22} - A_{12}^2) / A_{11} H \quad (10b)$$

$$G_{xy} = A_{66} / H \quad (10c)$$

$$v_{xy} = A_{12} / A_{22} \quad (10d)$$

When the laminate is subjected to a change in moisture content, the hygroscopic stress resultants in Eq. 5 are (as $n \rightarrow \infty$),

See pg. 164 for equation (11)

where $[Q(\theta)]$ is the transformed stiffness matrix (3 x 3) for a ply and $[\beta(\theta)]$ is the transformed set of moisture expansion coefficients (3 x 1) for a ply (18). The effective moisture expansion coefficients of the laminate ($\beta_x, \beta_y, \beta_{xy}$) are obtained by solving Eq. 5 for the strains (with $N_x = N_y = N_{xy} = 0$), which together with Eq. 4 yields

See pg. 164 for equation (12)

where $F_{xy} = 0 = \beta_{xy}$ for $f(\theta)$ being symmetric with respect to $\theta = 0$.

Micromechanics of the cell wall

The calculations of elastic constants based on the series and parallel models require the elastic constants, S_{ij} and Q_{ij} , of the cell wall as input. The mechanical response of the cell wall is assumed to be dominated by the response of the S_2 layer. The S_2 layer

is considered to be a unidirectional composite with cellulose microfibrils embedded in a matrix consisting of hemicellulose and lignin (19), as Fig. 5 shows. This matrix is thought of as a particulate composite, that is a mixture of hemicellulose and lignin with isotropic material properties.

The Young's modulus of the matrix, E_m , is bounded by (16):

$$1/[(V_{\text{Hemi}}/E_{\text{Hemi}}) + (V_{\text{Lig}}/E_{\text{Lig}})] < E_m < (E_{\text{Hemi}} V_{\text{Hemi}} + E_{\text{Lig}} V_{\text{Lig}}) \quad (13)$$

where E represents Young's modulus and V represents the volume fraction. With initial capital letters, the subscripts "Hemi" and "Lig" on V represent volume fractions of hemicellulose and lignin in the matrix. The subscripts in all lower-case letters "hemi" and "lig" on V represent the corresponding overall volume fractions in the cell wall.

The volume fractions of hemicellulose and lignin in the matrix are given by

$$V_{\text{Hemi}} = V_{\text{hemi}} / (V_{\text{hemi}} + V_{\text{lig}}) \quad (14a)$$

$$V_{\text{Lig}} = V_{\text{lig}} / (V_{\text{lig}} + V_{\text{hemi}}) \quad (14b)$$

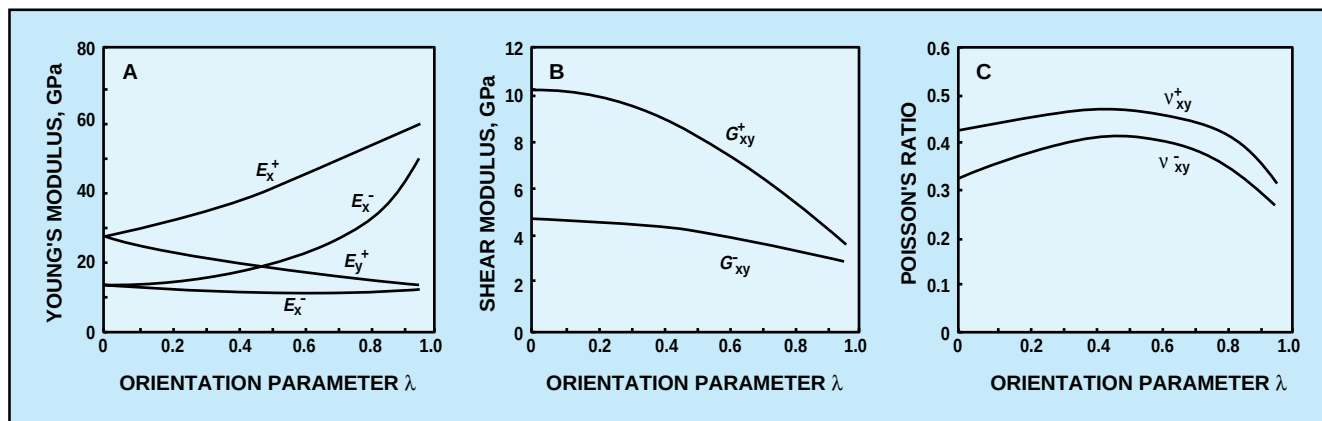
Bounds on the matrix shear modulus, $G_m = E_m / [2(1 + v_m)]$, can be obtained from the bounds on E_m , Eq. 13, and the rule of mixtures estimate of the Poisson's ratio for the matrix,

$$v_m = v_{\text{hemi}} V_{\text{Hemi}} + v_{\text{lig}} V_{\text{Lig}} \quad (15)$$

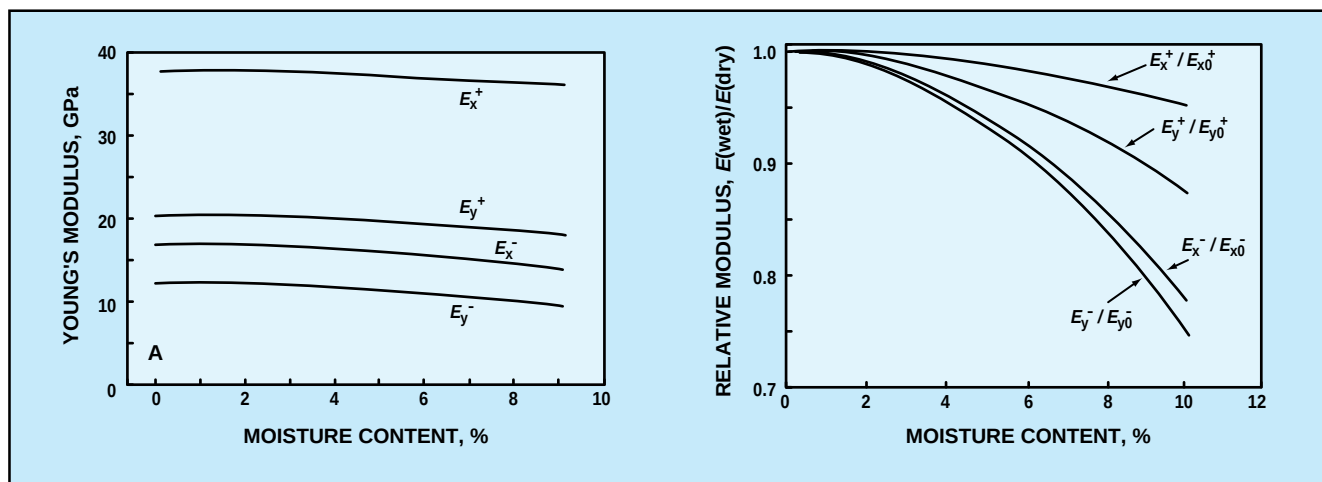
where v_{hemi} and v_{lig} are the Poisson's ratios of hemicellulose and lignin.

The elastic constants of the cell wall (E_1, E_2, v_{12} , and G_{12}) were calculated (20) using the Halpin-Tsai equations (21). The input data used in the calculations of the cell wall constants are the material properties of cellulose, hemicellulose, and lignin listed in Table I. The parameter ξ in the Halpin-Tsai equations was $\xi = 2a/b$ for E_2 and $\xi = (a/b)^{1.732}$ for G_{12} (21). The cross-sectional dimensions a and b of the fibril are given Fig. 5 (22, 23). The calculations were based on the lower and upper bounds on the matrix modulus, E_m , as defined by Eq. 13. Only

8. Bounds on the elastic constants of cell-wall assemblages (dry) vs. the orientation parameter λ for (A) elastic moduli, (B) shear modulus, and (C) Poisson's ratio



9. A: The moduli E_x and E_y decrease with increasing moisture content because of the softening of hemicellulose and lignin. B: The graph with the normalized, or relative, modulus shows more clearly the effects of softening from moisture absorption ($\lambda = 0.375$).



slight differences exist between the predictions based on the upper and lower bounds on E_m (20). The calculations that follow are based on the upper bound estimate of E_m .

Moisture sensitivity of cell-wall constituents

As the amorphous constituents of the cell wall, hemicellulose, and lignin, absorb water, they become softened. The range of moisture contents we considered corresponds to a range of relative humidity of 0–80%. Here, we assume that the cellulose microfibrils are unaffected by water absorbed over this humidity range.

Moisture absorption and the softening of hemicellulose and lignin ac-

cording to experimental data of Cousins (25, 26) are incorporated in the micromechanical calculations of the elastic constants and moisture expansion coefficients of the cell-wall material. Assumptions of isotropic swelling and volume additivity of hemicellulose and lignin are incorporated in Schapery's micromechanical analysis of the moisture expansion coefficients (27) (Appendix B).

Fibril orientation distribution

Shulgasser and Page suggested that the wrapped Cauchy distribution is appropriate for describing the fiber orientation distribution in typical machine-made papers (10, 28). The

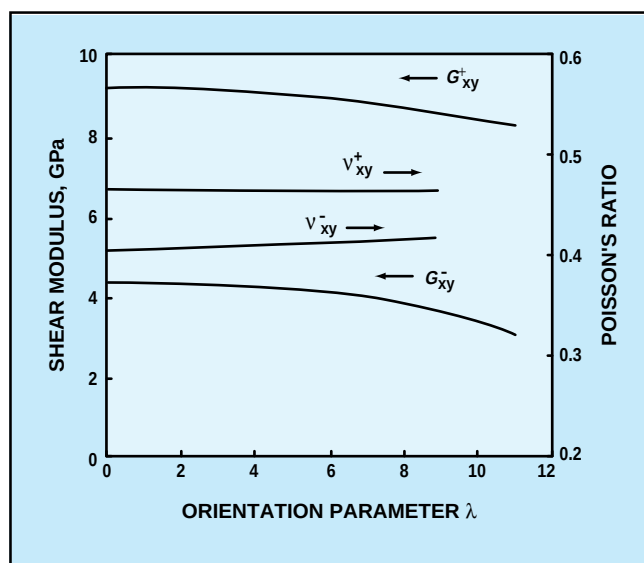
wrapped Cauchy distribution is used to represent the orientation of microfibrils and is given by

$$f(\theta) = (1/\pi) [(1 - \lambda^2)/(1 + \lambda^2 - 2\lambda \cos(2\theta))] \quad (16)$$

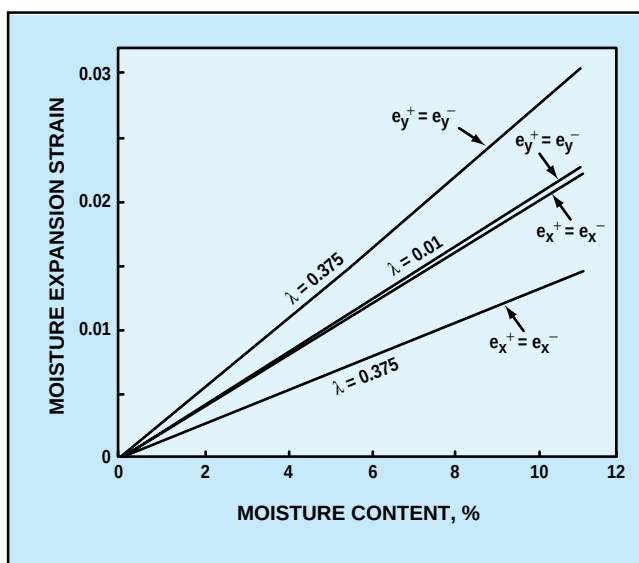
where λ is "the orientation parameter" and θ is the angle between the x axis (machine direction) and a microfibril in the S_2 layer of the cell wall. For isotropy, $\lambda = 0$, and for perfect collimation of the microfibrils, $\lambda = 1$.

As illustrated in **Fig. 6**, the hollow space of a wood fiber, or the lumen, tends to collapse during papermaking, and the fiber assumes a band-shaped laminated structure. As a result of the $\pm \alpha$ orientation of the microfibrils, the microfibrils have on

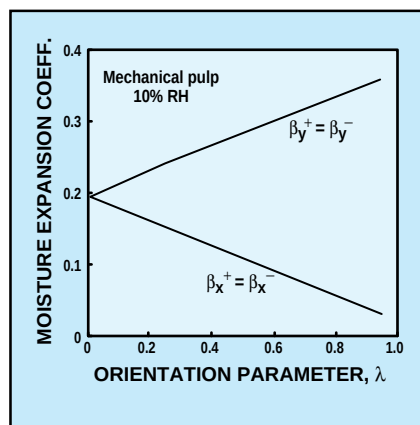
10. Bounds on shear modulus, G_{xy} , and Poisson's ratio, ν_{xy} , as a function of moisture content ($\lambda = 0.375$)



11. Bounds on moisture expansion strains, e_x and e_y , as a function of moisture content ($\lambda = 0.01$ and 0.375)



12. Moisture expansion coefficients, β_x and β_y , as a function of the orientation parameter λ



average the same angle to the x axis as the fiber itself. Therefore, an assemblage of fibers with constant fibril angle should follow the same distribution function as the microfibrils, with the same value of λ in Eq. 16.

Results and discussion

Single fiber modulus

As an initial check of the validity of the mechanical model, we calculated the axial modulus, E_{axial} , of a collapsed wood fiber, based on an angle-

ply laminate model as depicted in Fig. 6. If twisting of the fiber is neglected, E_{axial} is simply given by Eq. 10a.

The ply stiffnesses were calculated for chemical and mechanical pulp fibers based on the mechanical properties for cellulose, hemicellulose, and lignin listed in Table 1, using the Halpin-Tsai equations (21). Volume fractions of the constituents were assumed to be as follows, where the subscripts "cel," "hemi," and "lig" denote cellulose, hemicellulose, and lignin: For chemical pulp, $V_{\text{cel}} = 0.55$ and $V_{\text{hemi}} = 0.45$. For mechanical pulp, $V_{\text{cel}} = 0.36$, $V_{\text{hemi}} = 0.40$, and $V_{\text{lig}} = 0.14$.

Figure 7 shows the axial fiber modulus versus the S_2 microfibril angle. The two curves are the theoretical results for chemical and mechanical pulp fibers. The points are experimental results of Page *et al.* (29) for single holocellulose and kraft fibers of 45% yield. Fibers were occasionally damaged during the process of isolation (29), which explains the experimental scatter. The model predictions capture the decreasing trend of fiber modulus with increased microfibril angle, which indicates that the composite model of the cell wall is feasible.

Bounds on elastic constants and moisture expansion coefficients

To study the bounds on elastic properties and moisture expansion coefficients, we selected a fiber with volume fractions of $V_{\text{cel}} = 0.44$, $V_{\text{hemi}} = 0.30$, and $V_{\text{lig}} = 0.26$. This composition represents mechanical pulp. Table I gives the properties of the fiber wall constituents under dry conditions used in the calculations.

We considered a range of values of the orientation parameter ($0 \leq \lambda \leq 0.95$) in the wrapped Cauchy distribution (Eq. 16). Lower and upper bounds on the elastic constants of the assemblages of cell-wall elements, represented by minus and plus superscripts on the property symbol, were calculated using the series and parallel models. As a result of the complexities of the integrands in Eqs. 2, 3, 9, and 11, we employed the numerical method of integration (30).

In Fig. 8A, the bounds on Young's moduli E_x^+ , E_y^+ , E_x^- , and E_y^- are plotted against the fibril orientation parameter λ . The bounds E_x^+ and E_x^- on the longitudinal modulus increase with increased fibril orientation. The upper bound E_y^+ on the transverse modulus decreases, and the lower bound E_y^- remains almost constant.

Appendix A: Series model

Expressions for Young's and shear moduli

To derive an expression for Young's modulus E_x , consider n cell-wall elements being connected in series along the x axis, as depicted in Fig. 3. These elements are subjected to stress $\sigma_x > 0$ and $\sigma_y = \tau_{xy} = 0$. Equation 1 gives the x -axis strain of element k ,

$$(\epsilon_x)_k = (S_{11}^*)_k \sigma_x \quad (A1)$$

The displacement of element k along the x axis is

$$\Delta u_k = a_k (\epsilon_x)_k = a_k (S_{11}^*)_k \sigma_x \quad (A2)$$

where a_k is the length of element k in the x direction. The total displacement, u , of n elements connected in series can be written as

$$u = \sum_{k=1}^n \Delta u_k = \sum_{k=1}^n a_k (S_{11}^*)_k \sigma_x \quad (A3)$$

The fraction of the microfibrils with orientation θ_k is

$$f(\theta_k) \Delta \theta = a_k / A \quad (A4)$$

where A is the total length of the assemblage given by

$$A = \sum_{k=1}^n a_k \quad (A5)$$

Since the number of cell-wall elements may be assumed to be large, n is a large number. Let $n \rightarrow \infty$, then $a_k \rightarrow da$, and $\Delta \theta \rightarrow d\theta$, and

$$da/A = f(\theta) d\theta \quad (A6)$$

where $f(\theta) d\theta$ is the fraction of fibrils with angles of orientation between θ and $\theta + d\theta$.

The total displacement in the x direction is then

$$\begin{aligned} u &= \lim_{n \rightarrow \infty} \sum_{k=1}^n \Delta u_k \\ &= \lim_{n \rightarrow \infty} \sum_{k=1}^n a_k (S_{11}^*)_k \sigma_x \\ &= A \sigma_x \int_{-\pi/2}^{\pi/2} S_{11}^*(\theta) f(\theta) d\theta \quad (A7) \end{aligned}$$

The overall strain in the x direction is

$$\begin{aligned} \epsilon_x &= \frac{u}{A} \\ &= \sigma_x \int_{-\pi/2}^{\pi/2} S_{11}^*(\theta) f(\theta) d\theta \quad (A8a) \end{aligned}$$

Similarly, the strain in the y direction is

$$\epsilon_y = \sigma_y \int_{-\pi/2}^{\pi/2} S_{22}^*(\theta) f(\theta) d\theta \quad (A8b)$$

In the same vein, the in-plane shear strain is

$$\gamma_{xy} = \tau_{xy} \int_{-\pi/2}^{\pi/2} S_{66}^*(\theta) f(\theta) d\theta \quad (A8c)$$

The effective moduli E_x , E_y and G_{xy} of the cell-wall elements in the series assemblage are defined as stress divided by overall strain, which yields Eqs. 2a–2c. Poisson's ratio is defined by: $\nu_{xy} = -\epsilon_y/\epsilon_x$, with $\sigma_x > 0$ and $\sigma_y = \tau_{xy} = 0$, which yields Eq. 2d.

Moisture expansion coefficients

Consider an element of the cell-wall exposed to moisture. The moisture expansion strains are given by

$$\begin{Bmatrix} e_x \\ e_y \\ e_{xy} \end{Bmatrix} = \Delta M \begin{Bmatrix} \beta_x \\ \beta_y \\ \beta_{xy} \end{Bmatrix} \quad (A9)$$

where β_x , β_y , and β_{xy} are the moisture expansion coefficients in the x – y system of axes, and ΔM is the change in moisture content. The x -axis displacement of element k induced by the moisture change is

$$\Delta u_k = a_k e_x = \Delta M a_k \beta_x \quad (A10)$$

The total displacement, u , of n elements connected in series can be written as

$$u = \sum_{k=1}^n \Delta u_k = \sum_{k=1}^n \Delta M a_k \beta_x \quad (A11)$$

In the limit when $n \rightarrow \infty$

$$u = \Delta M A \int_{-\pi/2}^{\pi/2} \beta_x(\theta) f(\theta) d\theta \quad (A12)$$

The strain in the x direction is

$$\begin{aligned} e_x &= \frac{u}{A} \\ &= \Delta M \int_{-\pi/2}^{\pi/2} \beta_x(\theta) f(\theta) d\theta \quad (A13a) \end{aligned}$$

Similarly, the y axis and shear strains are given by

$$e_y = \Delta M \int_{-\pi/2}^{\pi/2} \beta_y(\theta) f(\theta) d\theta \quad (A13b)$$

$$e_{xy} = \Delta M \int_{-\pi/2}^{\pi/2} \beta_{xy}(\theta) f(\theta) d\theta \quad (A13c)$$

Transformation equations from on-axis (β_1 , β_2) (Appendix B) to off-axis (β_x , β_y , β_{xy}) moisture expansion coefficients are given elsewhere (17).

The upper and lower bounds are far apart for isotropic assemblies ($\lambda = 0$) but tend to converge for highly oriented assemblies ($\lambda \rightarrow 1$).

Figure 8B displays the bounds on the shear modulus G_{xy} versus λ . Both G_{xy}^+ and G_{xy}^- decrease with increased fibril orientation, but G_{xy}^+ decreases much more than does G_{xy}^- .

Figure 8C shows the bounds on Poisson's ratio plotted against λ . Notice here that the series model gives a larger Poisson's ratio than does the parallel model. Both v_{xy}^+ and v_{xy}^- go through maxima close to $\lambda = 0.5$. For highly oriented fibrils ($\lambda \rightarrow 1$), both the upper and lower bounds on the engineering constants approach those of the cell wall: $E_1 = 62.6$ GPa, $E_2 = 13.4$ GPa, $G_{12} = 3.17$ GPa, and $v_{12} = 0.23$.

Influence of moisture content on bounds

Bounds on the elastic constants of the cell-wall assemblages were calculated as a function of moisture content for a constant value of the orientation parameter $\lambda = 0.375$. The range of moisture contents considered corresponds to a range in relative humidity of 0–80%.

Figure 9A shows bounds on the moduli E_x and E_y calculated over the range of moisture contents. The moduli decrease with increasing moisture content because of the softening of hemicellulose and lignin. The softening from moisture absorption becomes more evident when we consider the normalized modulus, $E(\text{wet})/E(\text{dry})$. As **Figure 9B** shows, the fibril-dominated upper bound E_x^+ is least affected, and the lower bound E_y^- on the transverse modulus is most affected by moisture.

Figure 10 shows the bounds on the shear modulus, G_{xy} , and Poisson's ratio, v_{xy} , over the range of moisture contents. Both G_{xy}^+ and G_{xy}^- decrease as a result of moisture absorption. The Poisson's ratio v_{xy}^+ is unaffected by moisture, while v_{xy}^- increases slightly with increasing moisture content.

The moisture expansion strains, e_x and e_y , and the moisture expansion coefficients, β_x and β_y , were calculated from the series and parallel models. The moisture expansion coefficients of the cell-wall material, β_1 and β_2 , were used as input.

Figure 11 shows the bounds on the strains e_x and e_y as a function of moisture content for nearly isotropic ($\lambda = 0.01$) and oriented ($\lambda = 0.375$) assemblages of cell-wall elements. The upper bounds on e_x and e_y almost coincide with the lower bounds. β_x and β_y are respectively the slopes of the plots of e_x and e_y vs. moisture content. Since the strains in **Fig. 12** change linearly with moisture content, β_x and β_y are constants. For the isotropic sheet, β equals 0.2. For the oriented sheet, β_x equals 0.13, and β_y is 0.26.

Figure 12 displays β_x and β_y versus the orientation parameter λ . β_x decreases linearly with λ , and β_y increases linearly with λ . When $\lambda \rightarrow 1$, β_x and β_y approach the principal moisture expansion coefficients of the cell wall, β_1 and β_2 .

Conclusions

This micro model of paper is based on a composite model of the fiber cell wall. Predictions of single-fiber modulus were consistent with experimental data. This outcome indicates that the composite model of the cell wall can be applied.

Bounds on the in-plane engineering constants E_x , E_y , G_{xy} , and v_{xy} of cell-wall assemblages were calculated as functions of the fibril orientation parameter λ . The lower and upper bounds on the elastic moduli were found to be quite far apart. Therefore, modeling of paper based on the upper bound estimate of the elastic moduli should produce results that are not conservative.

With increased alignment of the microfibrils, the upper and lower bounds, E_x^+ and E_y^- , on the longitudinal modulus increased. At the same time, the upper bound on the transverse modulus, E_y^+ , decreased, and

the lower bound, E_y^+ , was unchanged. Both bounds on the shear modulus, G_{xy}^+ and G_{xy}^- , decreased with increased fibril orientation. For highly aligned fibrils, the bounds on the engineering constants of the assemblages of cell-wall elements approached the corresponding constants of the cell wall.

With increasing moisture content, the elastic and shear moduli decreased. The transverse modulus decreased more rapidly than the longitudinal modulus. The moisture expansion coefficients were found to be constant over the range of humidities studied, and the upper and lower bounds on the moisture expansion coefficients were found to be almost identical. ■

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Appendix B: Calculation of moisture expansion coefficients of the cell wall

Schapery's micromechanical analysis (27) is used to calculate the moisture expansion strains of the cell wall.

$$e_1 = \frac{E_m e_m V_m}{E_m V_m + E_{1,f} V_f} \quad (B1a)$$

$$e_2 = (1 + v_m) e_m V_m - e_1 \bar{v} \quad (B1b)$$

where

$$V_m = V_{lig} + V_{hemi} \quad (B2a)$$

$$\bar{v} = v_m V_m + v_{12,f} V_f \quad (B2b)$$

In these equations, e_m is the moisture expansion strain of the matrix, and e_1 and e_2 are the expansion strains in the principal directions of the composite cell-wall layer.

Assuming that volume is additive and that swelling is isotropic,

$$e_m = (1/V_w)^{1/3} - 1 \quad (B3)$$

where V_w , the volume fraction of the matrix (hemicellulose and lignin) in the mixture of water and matrix, is given by Eq. B4 (22):

$$V_w = \{1 + [(m_{hemi} V_{hemi} \rho_{hemi} + m_{lig} V_{lig} \rho_{lig}) / \rho_{water}]\}^{-1} \quad (B4)$$

where m_{hemi} and m_{lig} are the moisture ratios of hemicellulose and lignin. ρ_{hemi} , ρ_{lig} , and ρ_{water} are the densities of hemicellulose, lignin, and water. The moisture content is given by

$$M = \frac{m_{lig} V_{lig} + m_{hemi} V_{hemi}}{1 + m_{lig} V_{lig} + m_{hemi} V_{hemi}} \quad (B5)$$

Finally, the moisture expansion coefficients of the cell wall are defined by

$$\beta_1 = e_1/M$$

$$\beta_2 = e_2/M \quad (B6)$$

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Equations

$$\begin{Bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{Bmatrix} = \begin{bmatrix} S_{11}^* & S_{12}^* & S_{16}^* \\ S_{12}^* & S_{22}^* & S_{26}^* \\ S_{16}^* & S_{26}^* & S_{66}^* \end{bmatrix} \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix}$$

EQUATION (1)

$$\begin{Bmatrix} N_x \\ N_y \\ N_{xy} \end{Bmatrix} + \begin{Bmatrix} F_x \\ F_y \\ F_{xy} \end{Bmatrix} = \begin{bmatrix} A_{11}^* & A_{12}^* & A_{16}^* \\ A_{12}^* & A_{22}^* & A_{26}^* \\ A_{16}^* & A_{26}^* & A_{66}^* \end{bmatrix} \begin{Bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{Bmatrix}$$

EQUATION (5)

$$\begin{Bmatrix} F_x \\ F_y \\ F_{xy} \end{Bmatrix} = \Delta M H \int_{-\pi/2}^{\pi/2} [\bar{Q}(\theta)] [\bar{\beta}(\theta)] f(\theta) d\theta$$

EQUATION (11)

$$\begin{bmatrix} \beta_x \\ \beta_y \end{bmatrix} = \frac{1}{\Delta M \begin{pmatrix} A_{11}^* A_{22}^* - A_{12}^*{}^2 \end{pmatrix}} \begin{bmatrix} A_{22}^* & -A_{12}^* \\ -A_{12}^* & A_{11}^* \end{bmatrix} \begin{bmatrix} F_x \\ F_y \end{bmatrix}$$

EQUATION (12)