JOURNAL OF MATERIALS SCIENCE 37 (2002) 151 – 156

Cell wall properties and their effects on the mechanical properties of fibers

A. BERGANDER, L. SALMÉN
Swedish Pulp and Paper Research Institute (STFI), Sweden
E-mail: Lennart.Salmen@stfi.se

The properties of the cell wall are determined by its structure and by the properties of the wood polymers. In this study, the influence of the elastic constants of the three wood polymers on the elastic modulus of the cell wall was investigated. Cellulose was found to dominate the properties in the longitudinal direction. In the transverse direction, the effect of the properties of hemicellulose was more pronounced. The results show that it is possible to reduce the discrepancy between experimental and modeled values of the transverse modulus to a large extent by lowering the assumed values of the elastic constants of hemicellulose and lignin. The thickness and fibril angles of the S_1- and S_3-layers were also found to be important parameters for the transverse properties of the fiber wall. These two layers should not be neglected when transverse elastic properties are related to cell wall structure.

1. Introduction

Mathematical models of wood and its fibers play an increasingly important role in the understanding of the behavior of wood in different processes. The development of powerful computers has increased the possibility of making models in accordance with the native wood structure [1–3]. The input parameters in these models are usually the elastic constants for the three major wood polymers: cellulose, hemicellulose and lignin, of which only the longitudinal elastic properties of the cellulose have been obtained from measurements on a native material (ramie fibers) [4]. The good agreement between the mathematical models and experimental results in the longitudinal direction of the fibers is mainly due to the fact that reliable data exist for the longitudinal elastic properties of cellulose and to the strong parallel orientation of the cellulose fibrils in the fiber. The elastic constants used for hemicellulose and lignin are derived indirectly from the properties of materials extracted from the wood cell wall. Lignin is assumed in models of wood and wood fibers to be an isotropic material (e.g. [3, 5]). This is perhaps true for the extracted material but there is strong evidence that lignin has an oriented structure within the cell wall [6]. This lack of knowledge of the elastic properties of hemicellulose and lignin may not be a great disadvantage in the direction parallel to the fiber axis but it may be a great problem in the transverse direction.

The arrangement of the wood polymers also influences the stiffness properties of the cell wall. It is clear that the lignin is arranged in more or less tangential lamellae in the cell wall [7, 8]. However, whether lignin is to be considered to exist in separate layers or as a mixture with the hemicelluloses is still under debate. Some evidence clearly suggests that some of the hemicelluloses must be allocated to the cellulose [9] i.e. that hemicelluloses act as a matrix material for the cellulose.

Another feature of importance for the elasticity of the cell wall is the fibril angle of the different layers, particularly those in the secondary wall. The influence of the fibril angle of the S_2-layer in the longitudinal direction is well known [10, 11]. The fibril angle and thickneses of the S_1- and S_3-layers are believed to be of significance in the transverse direction [12, 13] but experimental data are scarce.

This paper focuses on the elastic constants of hemicellulose and lignin and their influence on the elastic modulus in the longitudinal and the transverse direction of the native wood cell wall. Furthermore, the influence and magnitude of structural variations in wood fibers, i.e. fibril angles and layer thickness is discussed in terms of a laminate model of the cell wall. Both the case where hemicelluloses act as a matrix material for the cellulose with separate lignin lamellae and the case of a combined hemicellulose-lignin matrix are considered.

2. Experimental

Two analytical models were used in which the double cell wall of the native wood structure was modeled as a layered laminate (Fig. 1). Both models contained nine layers (S_3, S_2, S_1, P, M, P, S_1, S_2, and S_3) where the middle lamella (M) consisted of a layer of a lignin-hemicellulose matrix.

In Model 1, each of the nine layers was considered to be a composite material with the cellulose fibrils embedded in a matrix of hemicellulose and lignin. This matrix was modeled as a 50/50 mixture of serial and

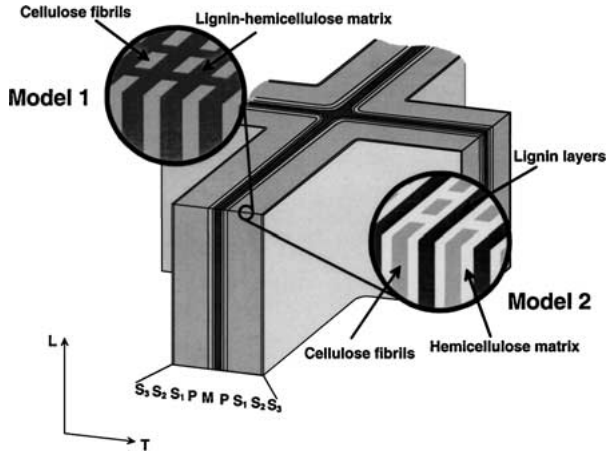

Figure 1 A schematic description of the nine-layer structure of the double cell wall in wood and the difference between the two laminate models.

parallel aligned hemicellulose and lignin. This is considered to be a reasonably good approximation in view of the lack of knowledge of the real structural arrangement. The matrix and the cellulose fibrils were coupled using the Halpin-Tsai equations [14] and the nine different layers were joined to one unit by classic lamination theory [15].

In Model 2, each of the eight layers of the primary (P) and secondary wall (S) was subdivided into separate layers of polysaccharides and lignin. The polysaccharide layers were modeled as composite materials where the cellulose fibrils were embedded in a matrix of hemicellulose. Layers of pure lignin were placed between the polysaccharide layers.

The different sets of elastic constants at a moisture content of 12% used for the three different wood polymers and the structural and chemical properties of the cell wall are shown in Tables I and II respectively. Two groups of lignin constants were used; the measured isotropic lignin A and the estimated orthotropic lignin B. In the latter case an orthotropic ratio of 2 was assumed between the longitudinal and transverse elastic properties of lignin.

TABLE I The different cases of mechanical property data at 12% moisture content for the cell wall polymers used in the two laminate models

	A		B		C	
Lignin						
E_x (GPa)	2.0	[16]	2.0	[16]		
E_y (GPa)	2.0	[16]	1.0	(Est.)		
G (GPa)	0.8	[17]	0.6	(Est.)		
ν	0.3	[17]	0.3	[17]		
Hemicellulose						
E_x (GPa)	7.0	[18]	7.0	[18]	4.0	(Est.)
E_y (GPa)	3.5	(Est.)	1.4	(Est.)	0.8	(Est.)
G (GPa)	1.8	(Est.)	1.8	(Est.)	1.0	(Est.)
ν	0.2	(Est.)	0.2	(Est.)	0.2	(Est.)
Cellulose						
E_x (GPa)	167.5	[19]	134	[4]		
E_y (GPa)	30.5	[19]	27.2	[20]		
G (GPa)	3.0	[19]	4.4	[20]		
ν	0.1	[20]	0.1	[20]		
l/d	5000	(Est.)	5000	(Est.)		

TABLE II The structural and chemical properties of the cell wall layers of an earlywood fiber

Layer	Thickness (μm)	Fibril angle degrees	Cellulose (%)	Hemicellulose (%)	Lignin (%)
S_3	0.03	70	48	36	16
S_2	1.6	10	50	31	19
S_1	0.15	−70, +70	28	31	41
P	0.1	unordered	15	33	52
M	0.3	–	0	44	56
Total	2.18		40	33	27

The measured elastic properties of an extracted hemicellulose [18] were taken as the basis for hemicellulose A. The orthotropic ratio between the longitudinal and transverse elastic properties of hemicellulose was assumed to be 2 in hemicellulose A and 5 in hemicellulose B. This change was made so that the properties should resemble the orthotropic ratio of cellulose, since cellulose and hemicellulose are closely related to each other in the secondary wall [21]. It is probable that hemicellulose extracted from the cell wall crystallizes and has a higher modulus than the material in its native state. Kalichevsky *et al*. [22] have measured the elastic modulus of amorphous amylopectin to be 4.5 GPa at a moisture content of 12%. Even though the structure of amylopectin differs from that of wood hemicellulose, its elastic modulus indicates that it is possible that wood hemicellulose in the cell wall has a lower modulus than extracted hemicellulose [18]. The elastic constants of hemicellulose C were therefore lowered to the same level as amorphous amylopectin with the same orthotropic ratio as in hemicellulose B.

Two different sets of properties of cellulose were compared; Cellulose A with molecularly modeled elastic constants of cellulose [19] and cellulose B in which the elastic constants in the longitudinal direction were taken from measured data for crystalline ramie fibrils [4] and the transverse modulus was taken from molecular modeling data [20].

For an anti-symmetric laminate the longitudinal (ε_1) and transverse strain (ε_2) are given by:

$$\begin{aligned} \varepsilon_1 &= A^*_{11}N_1 + A^*_{12}N_2 + B^*_{16}K_6 \\ \varepsilon_2 &= A^*_{12}N_1 + A^*_{22}N_2 + B^*_{26}K_6 \end{aligned} \tag{1}$$

where A^*_{11}, A^*_{12}, A^*_{22}, B^*_{16}, B^*_{26} are the stiffness components for the laminate in the respective directions, ε_1 and ε_2 are the strains in the normal directions, and N_1, N_2 and K_6 are the normal forces of the laminate and the twisting component respectively. If twisting is restricted and only longitudinal or transverse forces are applied, the engineering moduli of the fiber wall can be derived as:

$$\begin{aligned} E_1 &= N_1/\varepsilon_1 t = 1\big/A^*_{11}t \\ E_t &= N_2/\varepsilon_2 t = 1\big/A^*_{22}t \end{aligned} \tag{2}$$

where E_1 is the longitudinal modulus of the fiber wall, E_t is the transverse modulus of the fiber wall and t is the thickness of the laminate.

The sensitivities of the elastic constants of the fiber wall to the elastic constants of cellulose, hemicellulose and lignin were analyzed by a three-factor multilinear regression model, Modde v5.0 (Umetrics AB, Sweden), using the input parameters of Table I. The regression model took account of the quadratic and interaction terms of the three factors: hemicellulose (h), cellulose (c) and lignin (l):

$$E = \beta_0 + \beta_h X_h + \beta_l X_l + \beta_c X_c + \beta_{hh} X_h^2 + \beta_{ll} X_l^2 + \beta_{cc} X_c^2 + \beta_{hl} X_h X_l + \beta_{hc} X_h X_c + \beta_{lc} X_l X_c + \varepsilon \quad (3)$$

where E is the elastic modulus obtained from the regression model, β_j, β_{jj} and β_{jk} are the coefficients of the linear, quadratic and interactions terms respectively, X_j is the factor concerned and ε is the residual error of the regression.

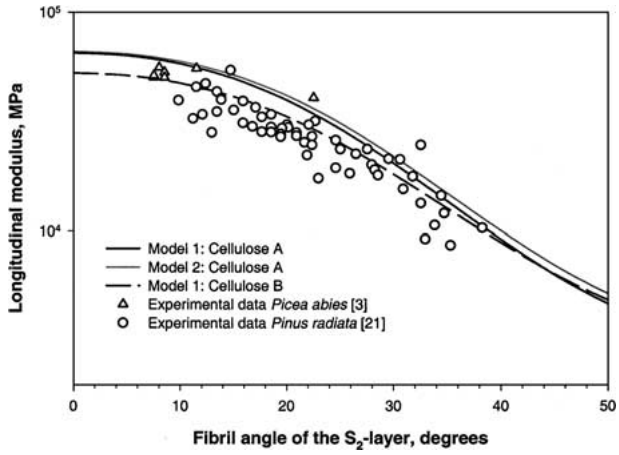

Figure 3 The influence of the elastic properties of cellulose on the longitudinal elastic modulus of the cell wall. The properties of hemicellulose and lignin were held constant using hemicellulose C and lignin B.

3. Results and discussion

3.1. Longitudinal direction

The longitudinal modulus of the cell wall was not affected by variations in either the hemicellulose or the lignin modulus (Fig. 2). Nor was there any substantial difference between the Models 1 and 2 in these calculations. At fibril angles above 30°, there is a tendency for the experimental values [3, 23] to deviate more from the model. Cell walls with a high fibril angle are usually compression wood fibers, and these tend to have a morphology and chemical composition different from those of normal cell walls. For example, the S_1- and S_2-layers are thicker in compression wood fibers and the compositions and structures of cellulose, hemicellulose and lignin are also different [24]. An increase in the thickness of the S_1- and S_2-layers did not reduce the deviation between modeled and experimental values at angles above 30°. This behavior suggests that the differences in the composition and structure of the wood polymers in these fibers are more important for the properties in the longitudinal direction. Since the lignin and hemicellulose have a very small influence on the elastic properties in this direction, it is probably the properties of cellulose that vary and influence the longitudinal elasticity. The elastic properties of this type of compression wood cellulose are unfortunately unknown. In the present calculations, the only measured values of cellulose are from measurements on crystals of cellulose fibrils in ramie fibers [4] obtained by x-ray diffraction. The validity of applying such values to the modulus of fibers with not entirely crystalline fibrils of cellulose is somewhat doubtful. No measurements have been made in the transverse direction. Instead modeled values of the cellulose structure and its hydrogen bonding are used in this direction in models of the wood fiber material.

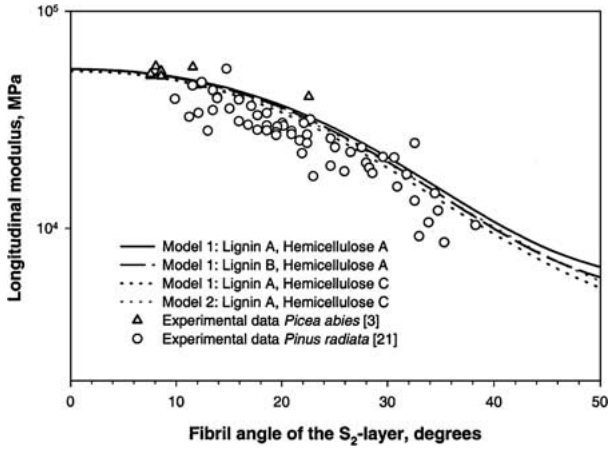

Figure 2 The influence of changes in the hemicellulose and lignin moduli on the longitudinal elastic modulus of the cell wall. The properties of the cellulose were held constant using cellulose B.

Fig. 3 shows the influence of the S_2 fibril angle on the longitudinal modulus of the cell wall using cellulose A and B in Models 1 and 2. The higher values for the constants in cellulose A give a curve parallel to the highest experimental values obtained on wood by Cave [23] and Persson [3]. However, molecular mechanics calculations by Kroon-Batenburg *et al*. [25] points to the unrealistically high values of the longitudinal elastic constant of cellulose A. The value of 136 ± 6 GPa obtained by Kroon-Batenburg *et al*. [25] fits instead excellent to the experimental data of cellulose B. The small number of high experimental values could come from parts of the wood with a chemical composition different from that of the rest of the wood, and this could explain the deviation from the majority of the experimental values. If the chemical composition is the same, the magnitude and variation of the experimental and modeled elastic properties of cellulose need to be further investigated.

3.2. Transverse direction

The influences of the elastic properties of lignin and hemicellulose respectively on the transverse modulus of the cell wall are shown for Model 1 and 2 in Figs 4 and 5. It is clear that the properties of hemicellulose have a greater influence on the transverse modulus than the orthotropy of lignin (lignin B). The difference between the two models was more pronounced using isotropic lignin (lignin A) and the higher values for hemicellulose (hemicellulose A and B).

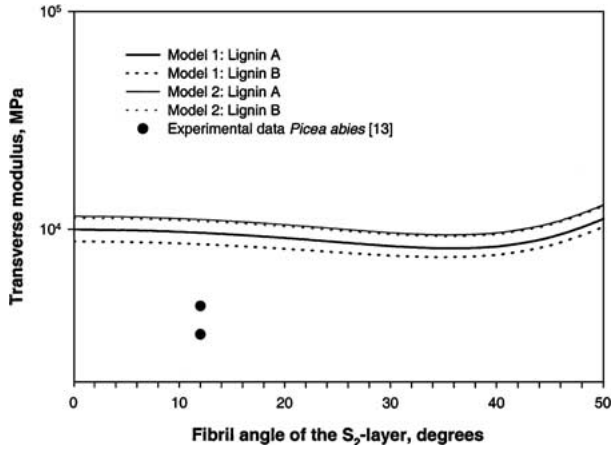

Figure 4 The difference between the effects of lignin A (isotropic) and lignin B (orthotropic) on the transverse elastic modulus in Models 1 and 2. The properties of cellulose and hemicellulose was held constant using cellulose B and hemicellulose A.

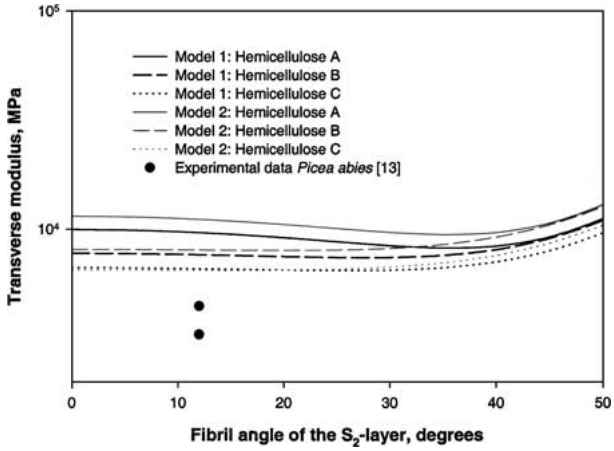

Figure 5 The influence of changes in the hemicellulose constants on the transverse elastic modulus in Models 1 and 2. The properties of cellulose and lignin were held constant cellulose B and lignin A.

For fibril angles of the S_2-layer between 10° and 20°, a change from lignin A to lignin B, i.e. from isotropic to orthotropic lignin, resulted in a lowering of the transverse modulus by 11% and 2% for Models 1 and 2 respectively (Fig. 4). Compared with hemicellulose A, the more orthotropic hemicellulose B led to a decrease in modulus of 20% for Model 1 and 26% for Model 2 (Fig. 5). These differences between the two models show that, if lignin or hemicellulose make up a part of the matrix material that surrounds the cellulose fibrils, their influence on the transverse modulus will be greater. The orthotropy of lignin has no major influence on the modulus in Model 2 where the lignin lies in separate layers.

The sensitivity of the transverse modulus to the elastic properties of hemicellulose was also analyzed (Fig. 5). A change from hemicellulose B to hemicellulose C resulted in a reduction in the transverse modulus by 14% and 19% in Models 1 and 2 respectively. The lower reduction in Model 1 indicates that lignin in the lignin-hemicellulose matrix has a moderating effect.

The total reduction in modulus achieved by reducing the elastic constants of hemicellulose (hemicellulose A to hemicellulose C) and introducing orthotropy of lignin (lignin A to lignin B) was 37% for Model 1 and

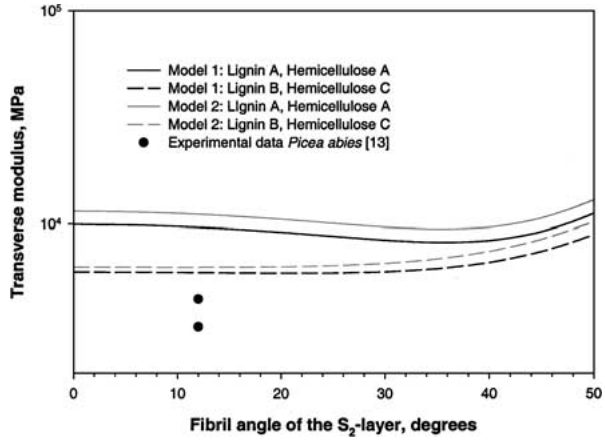

Figure 6 The transverse elastic modulus as a function of the fibril angle of the S_2-layer. The properties of cellulose were held constant using cellulose B.

42% for Model 2 (Fig. 6). This also diminished the discrepancy between the two models. Thus, with a high degree of orthotropy and lower moduli of hemicellulose and lignin, the build up of the matrix surrounding the cellulose fibrils plays a less important role for the laminate structure. Using these values of the elastic properties of lignin and hemicellulose, the discrepancy between the modeled transverse cell wall moduli and the experimental elastic modulus measured on wood fiber walls was reduced [13]. This also confirmed the merits of assuming a 50/50 mixture of parallel and serial alignment between the lignin and the hemicellulose in fiber wall layers of model 1 and of the middle lamella layer.

3.3. Relative influences of the wood polymers

In order to estimate the relative influences of the three wood polymers on the modeled elastic properties of the fiber in different directions, a multilinear regression model was developed. The significant coefficients from the regression model of the results from calculations of transverse and longitudinal moduli respectively using Models 1 and 2 are shown in Figs 7 and 8. The analysis

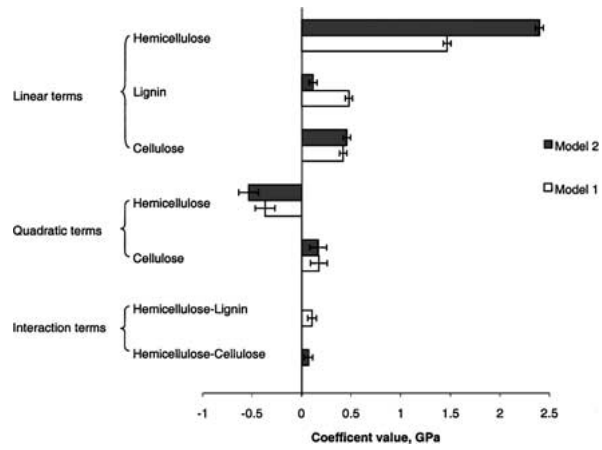

Figure 7 The significant coefficients and their 95% confidence intervals obtained for a multilinear regression model of the transverse elastic modulus in Models 1 and 2 using the different groups of elastic constants of hemicellulose, cellulose and lignin in Table I.

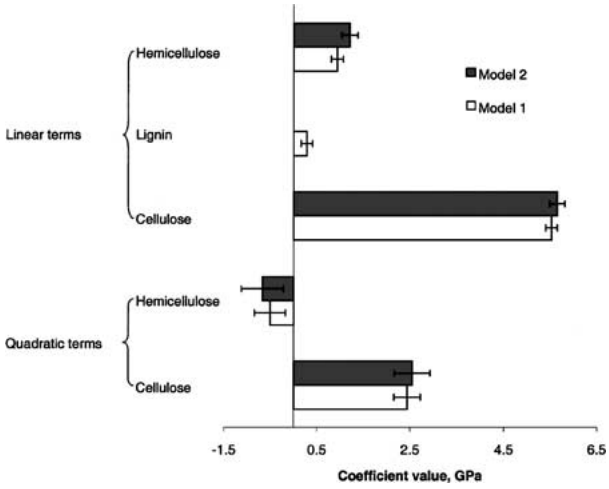

Figure 8 The significant coefficients and their 95% confidence intervals obtained for a multilinear regression model of the longitudinal elastic modulus in Models 1 and 2 using the different groups of elastic constants of hemicellulose, cellulose and lignin in Table I.

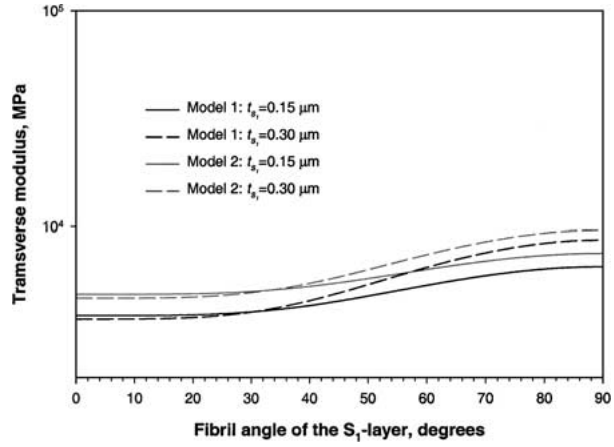

Figure 9 The influence of thickness of the S_1-layer on the transverse elastic modulus of the cell wall as a function of the S_1 fibril angle. The properties of cellulose, hemicellulose and lignin were held constant using cellulose B, lignin B and hemicellulose C. The fibril angles of the S_2- and S_3-layers were held constant at 10° and 70° respectively.

showed that the properties of the hemicellulose had the greatest influence on the transverse modulus (Fig. 7), while the properties of cellulose dominated in the longitudinal direction (Fig. 8). The difference between the two laminate models was insignificant in the longitudinal direction. In the transverse direction, the coefficients relating to lignin and hemicellulose differed in that the hemicellulose properties were much more important in Model 2 than in Model 1 while lignin properties influenced only Model 1.

3.4. Layer thickness and fibril angles of the S_1- and S_3-layer

The S_1- and S_3-layers of the secondary wall are sometimes neglected in models since they are known to have only a minor effect on the properties in the longitudinal direction of the cell wall. In the transverse direction, however, their influence is larger and can explain differences between the moduli of early- and latewood fibers [13]. The influences of the thickness and fibril angle of the S_1-layer are shown in Fig. 9.

When the thickness of the S_1-layer was doubled at a fibril angle of 70°, the modulus was increased by 20% and a change in fibril angle of the S_1-layer from 60 to 80° increased the transverse modulus by 15%, regardless of the model used. These increases show the importance of the cell wall morphology and structure of the wood fiber material for its mechanical properties in the transverse direction.

Abe *et al*. [26] have measured the variation in the S_3 fibril angle from the lumen side and have found large variations in fibril angle of the last deposited layer of cellulose fibrils. Since the S_3-layer is very thin compared to the S_1-layer, its influence on the properties in the transverse direction should be smaller than that of the S_1-layer. A change in fibril angle of the S_3-layer from 50° to 80° resulted in a 9% increase in the transverse modulus in the two analytical models. This increase is the same as the influence of the S_2-layer at fibril angles between 0° and 25° (Fig. 6). The influence of the S_3-layer in the transverse direction can therefore be regarded as being of the same magnitude as that of the S_2-layer.

4. Conclusions

Based on the model analysis it was concluded that:

- The elastic constants of cellulose are almost exclusively determining the elastic properties in the longitudinal direction of the cell wall. There is a surprisingly good agreement between the modeled and the experimental values considering that the elastic constants for purely crystalline cellulose are used which may not be representative of the semicrystalline fibril structure in the cell wall. However, if even better modeling prediction is needed in the longitudinal direction, a more accurate knowledge of the elastic constants and structure of the cellulose is necessary.
- For the transverse cell wall modulus the properties of the hemicellulose are dominating. The use of orthotropic elastic constants of both hemicellulose and lignin gave a much better fit to experimental data suggesting this to be a more representative structure. Surprisingly, the arrangement of the matrix polymers had no major influence on the transverse properties.
- Although the S_2-layer is the dominant part of the cell wall, the S_1-layer is an important parameter for the properties in the transverse direction. Knowledge regarding the variation in both its thickness and fibril angle is of great importance to improve the modeled properties of cell walls in the transverse direction.

Acknowledgments

Financial support from the graduate school Wood and Wood Fibre sponsored by the Swedish Council of Forestry and Agricultural Research is gratefully acknowledged.

References

1. R. J. ASTLEY, J. J. HARRINGTON and K. A. STOL, in Proceedings of IPENZ Conference, Dunedin, February 9–13 (1996) p. 402.
2. S. KOPONEN, T. TORATTI and P. KANERVA, *Wood Sci. Technol.* **25** (1991) 25.
3. K. PERSSON, Lic. thesis, Lund University/Lund Institute of Technology, 1997.
4. I. SAKURADA, Y. NUKUSHIMA and T. ITO, *J. Polym. Sci.* **57** (1962) 651.
5. S. KOPONEN, T. TORATTI and P. KANERVA, *Wood Sci. Technol.* **23** (1989) 55.
6. R. H. ATALLA and U. P. AGARWAL, *Science* **227** (1985) 636.
7. J. E. STONE, A. M. SCALLAN and P. A. V. AHLGREN, *Tappi* **54** (1971) 1527.
8. A. J. KERR and D. A. I. GORING, *Cell. Chem. Technol.* **9** (1975) 563.
9. L. SALMÉN and A.-M. OLSSON, *J. Pulp Paper Sci.* **24** (1998) 99.
10. R. D. PRESTON, "The Physical Biology of Plant Cell Walls" (Chapman and Hall, London, 1974).
11. B. G. BUTTERFIELD, "Microfibril Angle in Wood" (University of Canterbury, Westport, 1998).
12. R. E. MARK, in "Theory and Design of Wood and Fiber Composite Materials," edited by B. A. Jayne (Syracuse University Press, Syracuse, 1972) p. 49.
13. A. BERGANDER and L. SALMÉN, *Holzforschung* **54** (2000) 654.
14. J. C. HALPIN and J. L. KARDOS, *Polym. Eng. Sci.* **16** (1976) 344.
15. S. W. TSAI and H. T. HAHN, "Introduction to Composite Materials" (Technomic Publishing Company, Westport, 1980).
16. W. J. COUSINS, *Wood Sci. Technol.* **10** (1976) 9.
17. J. BODIG and B. A. JAYNE, "Mechanics of Wood and Wood Composites" (Van Nostrand Reinhold, New York, 1982).
18. W. J. COUSINS, *Wood Sci. Technol.* **12** (1978) 161.
19. K. TASHIRO and M. KOBAYASHI, *Polymer* **32** (1991) 1516.
20. R. E. MARK, "Cell Wall Mechanics of Tracheids" (Yale University Press, New Haven, London, 1967).
21. C. Y. LIANG, K. H. BASSETT, E. A. MCGINNES and R. H. MARCHESSAULT, *Tappi* **43** (1960) 1017.
22. M. T. KALICHEVSKY, E. M. JAROSZKIEWICZ, S. ABLETT, J. M. V. BLANSHARD and P. J. LILLFORD, *Carbohydrate Polymers* **18** (1992) 77.
23. I. D. CAVE, *Wood Sci. Technol.* **3** (1969) 40.
24. T. E. TIMELL, "Compression Wood in Gymnosperms" (Springer-Verlag, Berlin, 1986).
25. L. M. J. KROON-BATTENBURG, J. KROON and M. G. NORTHOLT, *Polym. Comm.* **27** (1986) 290.
26. H. ABE, J. OHTANI and K. FUKUZAWA, *IAWA* **13** (1992) 411.

Received 8 September 2000
and accepted 16 January 2001