J Wood Sci (2005) 51:118–123
DOI 10.1007/s10086-004-0630-6

ORIGINAL ARTICLE

Petri P. Kärenlampi · Pekka Tynjälä · Pasi Ström

Phase transformations of wood cell wall water

Received: January 14, 2004 / Accepted: March 15, 2004

Abstract The amount of apparently nonfreezing water per dry mass unit significantly differs between earlywood and latewood, and drying changes the nonfreezing water content of earlywood cell walls in a time-dependent manner. However, the equilibrium moisture content of spruce wood is not affected by drying and rewetting. The results indicate that different mechanisms govern these two types of phase transformations of cell wall water. The nonfreezing water content, as determined using differential scanning calorimetry, appears to be a nonequilibrium property. It is hypothesized that the measured changes in nonfreezing water content mostly reflect changes in the porous cell wall structure, on a scale well above the molecular scale, rather than the abundance of chemical adsorption sites.

Key words Differential scanning calorimetry · Nonfreezing water · Water sorption · Drying · Rewetting

Introduction

In heterogeneous hydrated systems, the amount of water with depressed melting temperature is detectable using differential scanning calorimetry (DSC).[1–3] The depressed melting temperature can be interpreted either as a consequence of some material constituents being partially solubilized or the material being microporous in such a way that surface tension of pure water depresses the melting temperature of water, due to the small pore radius.[4] The latter interpretation enables porosity investigation in terms of thermoposimetry.[4–6]

It is known that water in pores of nanometer scale does not freeze at all. This can also be explained in a variety of ways. One of the simplest explanations is that in a space of size close to that of a molecule, there is not much room for molecular motion. Thus, the matter appears solid-like, regardless of the temperature, and no thermal transition between solid and liquid is recognized.[7] Molecular mobility may also be reduced due to adsorption to sites like ionic groups, ultimately forming a polymer gel.[8–10] Alternatively, one might explain the existence of nonfreezing water in terms of slowness of diffusion at low temperature and in small capillaries.[11]

The porosity of the wood fiber cell wall increases along with decreasing yield of pulp in the course of chemical pulping,[4,12–14] and increases in the course of mechanical pulping and chemical pulp beating.[4,13–15] It has been recently shown that the cell wall porosity significantly evolves along with wood basic density, as a function of position within an annual ring.[16]

Like most organic materials, wood is hygroscopic and it is able to absorb and desorb moisture, therefore having a measurable moisture content. The moisture content depends on the temperature and humidity of the surrounding air. The interaction between water and a hydrophilic surface is important for many physical properties of any cellulosic material. Water molecules may interact with different kinds of polar surface groups such as hydroxyl groups, carboxylic acid groups, and sulfonic acid groups.[8–9]

This article clarifies the nature of cell wall water . In particular, we investigate whether nonfreezing water is related to the existence of chemical adsorption sites within the molecular structure, or to the porous cell wall structure in a larger scale of pores and cavities. We investigate how the nonfreezing water content in wood cell walls is affected by drying and rewetting. We also investigate the effect of freezing time on the nonfreezing water content. Furthermore, we hope to gain additional understanding of the character of cell wall water by investigating the effect of drying and rewetting on sorption isotherms.

P.P. Kärenlampi (✉) · P. Tynjälä · P. Ström
Faculty of Forestry, University of Joensuu, PO BOX 111, FIN-80101 Joensuu, Finland
Tel. +358-13-251-4009; Fax +358-13-251-3590
e-mail: petri.karenlampi@joensuu.fi

Experimental procedure

Specimens of relatively fast-grown spruce sapwood were acquired at Joensuu, province of North Carelia, Finland. For the DSC measurements, specimens of 200 μm thickness and dry mass in the order to 5 mg were prepared using a sliding microtome. Before drying, the specimens were soaked in deionized water for 2 days. The specimens were oven-dried at 103°C and rewetted according the procedure shown in Table 1: the drying times varied between 1 day and 8 days, and the rewetting times varied between 1 and 64 days.

The above procedure was carried out for both earlywood and latewood as well as for both heartwood and sapwood.

Water-soaked wood specimens, along with 5–20 mg of deionized water, in a 40-μl aluminum pan, were placed into a Mettler Toledo differential scanning calorimeter. The specimen was frozen by a dynamic temperature ramp down to −45°C at a rate of 10°C/min. The specimen was thawed by a dynamic temperature ramp up to 25°C at a rate of 5°C/min. The latent heat of melting, which was assumed to be directly proportional to the mass of melting water, was measured.

Wood specimens generally contain water that does not freeze in the temperature range covered in the experiment. The total amount of water was determined as the difference between total mass and the dry specimen mass. Then, the amount of nonfreezing water (NFW) was determined as the difference between the total mass of water and the mass of melted water, the latter determined through the melting enthalpy measurements.

The effect of freezing time on the NFW content of earlywood was studied. Specimens were frozen with a dynamic temperature ramp down to −45°C at a rate of 10°C/min and the specimens were held at −45°C for 6 h. In the reference analysis, the specimens were held at −45°C for 0 min. Specimens were thawed with a ramp up to 25°C with a rate of 5°C/min.

For the sorption experiments, 12 sets of specimens were prepared, each set containing microtome slices corresponding to a dry weight of approximately 50 mg. Two earlywood and two latewood specimen sets corresponding to a native (green) state were placed in water directly after preparation. Two earlywood and two latewood specimen sets were oven-dried at 103°C for 1 day, followed by rewetting for 1 day before the sorption experiment. Two earlywood and two latewood specimen sets were oven-dried at 103°C for 3 days, followed by rewetting for 1 day before the sorption experiment. The preparation procedure was carried out for both heartwood and sapwood. The determination of the sorption isotherms was conducted at 25°C by varying the relative humidity (RH) of the air-conditioned room and by monitoring the masses of the specimens twice a day. The specimens were kept at each RH level for 2 days, or until the equilibrium weights were reached. In the experiment, the following cycling procedure for relative air humidity was used:

RH%: 90 –70 – 50 – 30 – 50 – 70 – 90 – 70 – 50 – 30 – 50 – 70 – 90 – 70 – 50 – 30 – 50 – 70 – 90

After the cycling, the moisture contents of the specimens were determined by oven drying at 103°C.

Table 1. Rewetting times in days for samples after drying

Drying time (days)			
1	2	4	8
1	1	1	1
2	2	2	2
4	4	4	4
8	8	8	8
	16	16	16
		32	32
			64

Results

Calorimetric results

The NFW contents of native earlywood and latewood were 0.17–0.22 g/g and 0.32–0.35 g/g, respectively, as shown in Figs. 1 and 2.

The NFW content of earlywood increased significantly in the course of drying (Figs. 1 and 2). As seen particularly in

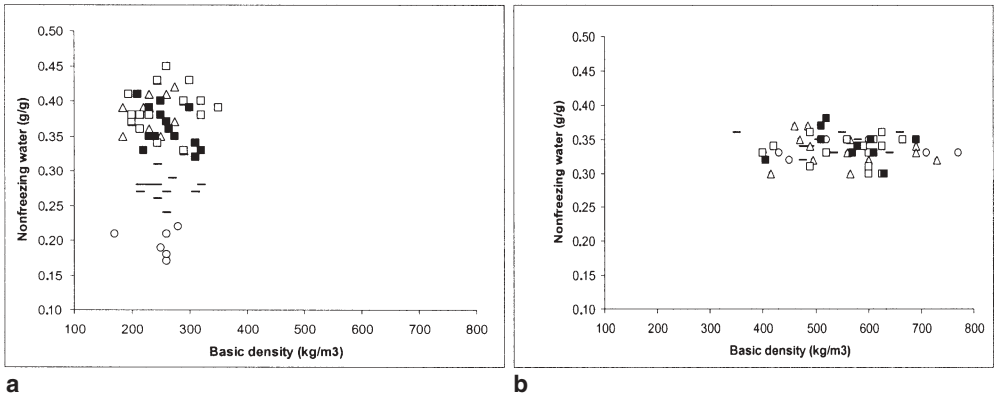

Fig. 1. The nonfreezing water content of earlywood (**a**) and latewood (**b**) of heartwood. *Circles*, *lines*, *triangles*, *empty squares*, and *filled squares* represent native specimens, specimens dried for 1 day, specimens dried for 2 days, specimens dried for 4 days, and specimens dried for 8 days, respectively

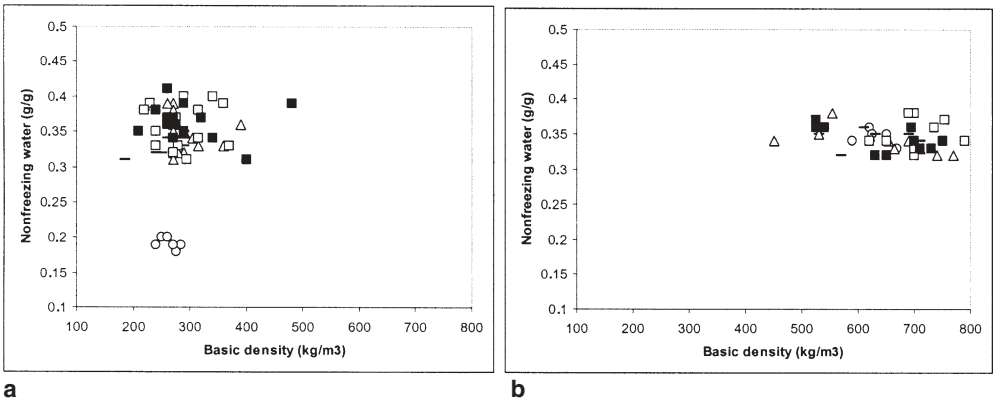

Fig. 2. The nonfreezing water content of earlywood (**a**) and latewood (**b**) of sapwood. *Circles*, *lines*, *triangles*, *empty squares*, and *filled squares* represent native specimens, specimens dried for 1 day, specimens dried for 2 days, specimens dried for 4 days, and specimens dried for 8 days, respectively

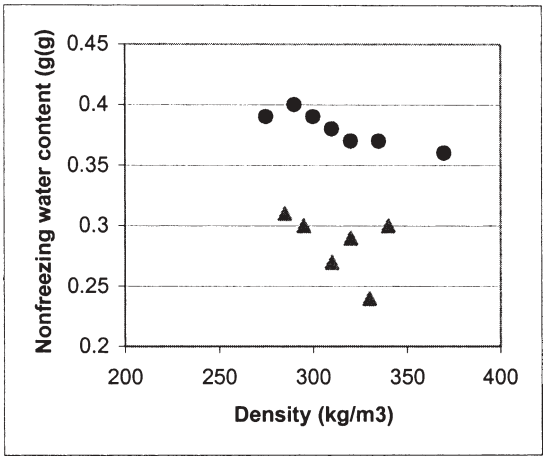

Fig. 3. The effect of freezing time on the nonfreezing water content of earlywood. *Circles* and *triangles* represent nonfreezing water levels in specimens kept at −45°C for 0 h and 6 h, respectively

case of heartwood, the magnitude of the increment clearly appears to be a function of drying time. In the case of latewood, oven drying and rewetting appeared to have no effect on the amount of NFW.

During rewetting, the NFW content of all specimens remained at the level measured after the drying. Not even rewetting for 64 days sufficed to convert the NFW content back to that of the native state. Thus, the changes induced by drying appeared to be irreversible.

The effect of freezing time on the amount of NFW was studied by prolonging the time the specimens were held at −45°C from 0 to 6 h. The prolonged freezing time resulted in a decrease of the NFW content of earlywood of 0.36–0.40 g/g down to 0.24–0.31 g/g, as shown in Fig. 3. Figure 3, which includes both heartwood and sapwood specimens, shows that the NFW content of earlywood appears to significantly depend on freezing time.

Sorption results

Equilibrium moisture contents for heartwood and sapwood during the cycling procedure are shown in Figs. 4 and 5, respectively.

The equilibrium moisture content of latewood at any relative air humidity appears to be slightly higher than that of earlywood (Figs. 4 and 5). The equilibrium moisture content at any RH level appeared not to be sensitive to drying and rewetting. This result does differ from the calorimetric data, which showed a significant increase of NFW level in oven-dried earlywood (Figs. 1 and 2).

Discussion

According to the sorption results (Figs. 4 and 5), the equilibrium moisture content at any RH level is not sensitive to drying and rewetting. Thus, the equilibrium moisture content may depend on the number of available bonding sites, in accordance with the site adsorption theory.

The NFW content of earlywood increases along with drying (Figs. 1 and 2). It has been proposed that such a phenomenon could be explained by interpreting the cell wall as a cross-laminated structure where each lamina experiences anisotropic drying shrinkage.[16] Internal drying stresses obviously appear at the crossing regions of the lamina.[17] Such internal stresses appearing in cross-laminated fibrillar structures may open new cavities of nanometer scale, resulting in an increase of NFW. Spruce latewood predominantly consists of fibrillar structures with a uniform orientation of fibrils,[18–22] thus explaining the different behavior in comparison with earlywood.

Significant dependency of NFW content of earlywood on freezing time was found (Fig. 3). Thus, the NFW content, as generally determined using DSC, appears to be a nonequilibrium property. An explanation to this may be found in the kinetic nature of freezing. The diffusivity of water has been reported to be a steep function of concentration and temperature.[11] The diffusion coefficient decreases steeply with decreasing concentration as well as with decreasing temperature. Therefore, the decrease of temperature slows down or even inhibits the transport of water from tiny cell wall pores into larger cavities where crystallization may take place.

Because the NFW content of wood, as determined using conventional DSC, is obviously not at equilibrium, some caution should be exercised when interpreting earlier

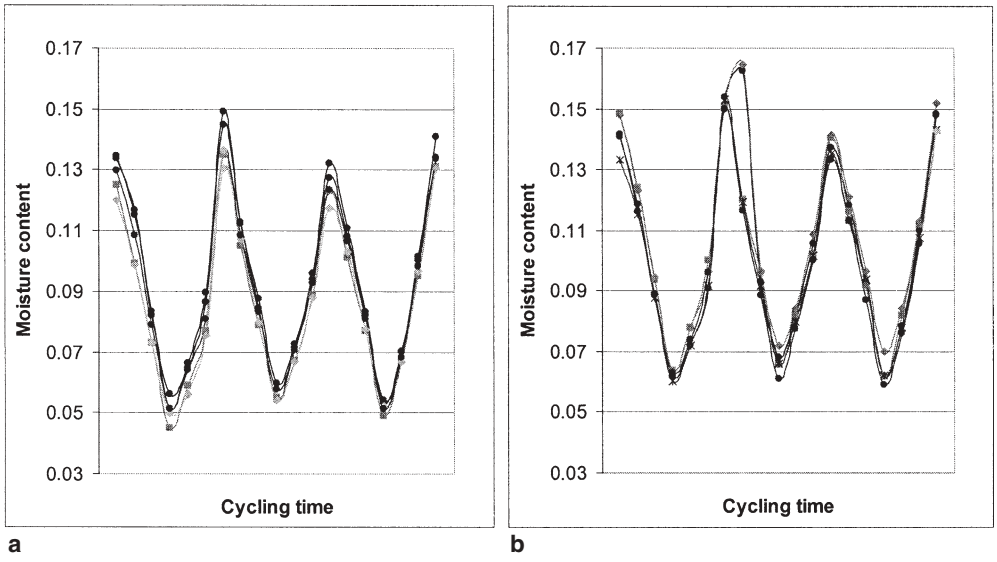

Fig. 4. Equilibrium moisture contents of earlywood (**a**) and latewood (**b**) of heartwood specimens as a function of sorption cycling. *Circles*, *squares*, and *diamonds* correspond to native specimens, specimens dried for 1 day, and specimens dried for 3 days, respectively

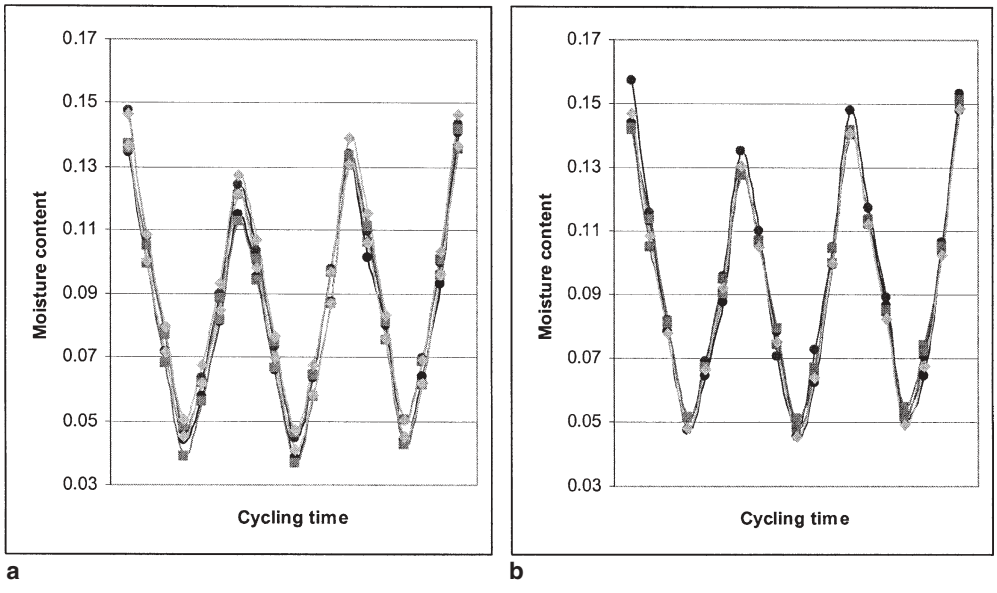

Fig. 5. Equilibrium moisture contents of earlywood (**a**) and latewood (**b**) of sapwood specimens as a function of sorption cycling. *Circles*, *squares*, and *diamonds* correspond to native specimens, specimens dried for 1 day, and specimens dried for 3 days, respectively

reported results of relatively rapid calorimetric experiments.[4,5,8,10,16] Interpretation of the present results also requires a thorough discussion of the time-dependent freezing behavior of cell wall water.

In order to clarify the effect of time-dependent freezing on the results of calorimetric experiments, let us discuss the freezing of cell wall water in terms of a simple phenomenological model. It is not known how freezing of cell wall water proceeds with time. For simplicity, it will be described as a simple exponential. Given a finite freezing time t, the NFW content per dry mass unit is modeled as

$$\mathrm{NFW}_t = \mathrm{NFW}_\infty + \exp\left(-\frac{t}{\tau}\right)\mathrm{FBW}_\infty \qquad (1)$$

where NFW_∞ is the nonfreezing water content that is approached at infinite freezing time, FBW_∞ is the freezing bound water content approached at infinite freezing time, and τ is a time constant for freezing. The sum of NFW_∞ and FBW_∞ is assumed to equal the total amount of bound cell wall water per dry mass unit, bound water here referring to water with thermodynamic properties differing from free water.

Equation 1 is schematically illustrated as the solid line in Fig. 6. With the freezing of cell wall water being a time-dependent process, at the limit of zero freezing time, the apparently nonfreezing water corresponds to all the bound cell wall water. In other words, $\mathrm{NFW}_0 = \mathrm{NFW}_\infty + \mathrm{FBW}_\infty$. On the other hand, at the limit of infinite freezing time, the NFW content tends to NFW_∞. Between these well-defined extremes, the experimentally measurable NFW content is arbitrarily addressed using the exponential of normalized time $\frac{t}{\tau}$.

We find from Eq. 1 that the NFW content, determined in an experiment with finite duration, in addition to the time t, will depend on three variables: NFW_∞, FBW_∞, and τ. The principle of effect of any of these variables on the experi-

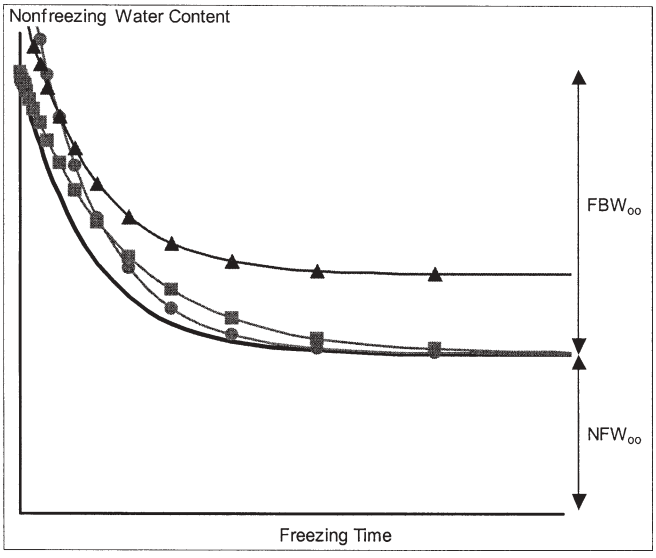

Fig. 6. Apparent nonfreezing water (NFW) content as a function of freezing time, with reference to NFW_∞ shown on the right (solid line). Line with *triangles* corresponds to 50% increased NFW_∞. Line with *circles* corresponds to 50% increased freezing bound water FBW_∞. Line with *squares* corresponds to 50% increased time constant τ

mentally determined NFW is demonstrated in Fig. 6. We find that the effect of increased NFW_∞ increases apparent NFW at relatively long freezing times, where the contribution of NFW_∞ is greatest according to Eq. 1. The effect of increased FBW_∞ increases apparent NFW at relatively short freezing times, where the contribution of FBW_∞ is greatest according to Eq. 1. Increased value of the time constant τ extends the time required for the freezing of the FBW_∞.

The value of any of the three variables NFW_∞, FBW_∞, and τ certainly depends on moisture content. It appears reasonable to assume that NFW_∞ may relate to the site adsorption theory. However, it is possible that in addition to chemical bonding sites, water exists in pores small enough to be permanently nonfreezing.[7] Furthermore, it seems reasonable to assume that FBW_∞ depends on the cell wall microstructure: the greater the volume of pores that are small enough to make the thermodynamic behavior of pore water differ from that of free water, the greater is FBW_∞ in a water-saturated cell wall.

Assuming that the time delay in the freezing of cell wall water, evident in Fig. 5, can be associated with the transport of water from tiny cell wall pores into larger cavities where there is enough space for crystallization, the time constant of cell wall water freezing τ can be viewed as characteristic to cell wall transport properties. Such transport properties obviously depend on temperature, moisture content, and cell wall microstructure.[11] The dependency on moisture content and microstructure mean that τ is hardly independent of FBW_∞. It appears reasonable to assume that increased cell wall porosity, resulting in increasing FBW_∞, might improve cell wall transport capability, corresponding to a decreased value of the time constant τ.

Another question of significance is how results of previously conducted experiments should be interpreted, considering the nonequilibrium nature of the NFW measurements. In the present study, it was found that the NFW content in fresh spruce earlywood is less than in latewood, and that the NFW content in earlywood irreversibly increases with drying (Figs. 1, 2). Other recent studies have shown that the NFW content of spruce earlywood may significantly increase with compressive fatigue loading.[23,24]

As is obvious from the above discussion, based on Fig. 3 and the tentative Eq. 1, there are basically three alternatives for the interpretation of changes in such a measured nonequilibrium property. Any change in measured NFW content may reflect a change in the equilibrium NFW content NFW_∞, the freezing bound water content FBW_∞, or the time scale of reaching equilibrium τ. Even if any of these three variables may be affected, microscopic observations regarding the effect of drying have shown significantly changed cell wall pore structure.[25,26] Microscopically observable pores are likely to contain freezing bound water. Creation of such pores may also affect transport properties, but because the apparent NFW content of earlywood increases with drying (Figs. 1, 2), the increase of FBW_∞ is likely to be the dominating mechanism.

It is not known what is the dominating mechanism of apparent NFW increase in the case of compressive fatigue loading.[23,24] However, it is quite possible that repeated large-strain compression of wet wood forces water from the lumens into the cell walls. Thus, the authors hypothesize that increase of freezing cell wall water FBW_∞ might be the dominating mechanism of apparent NFW increase, also in the case of mechanical loading.

References

1. Rennie GK, Clifford J (1997) Melting of ice in porous solids. J Chem Soc F1 73:680–689
2. Homshaw LG (1981) Calorimetric determination of porosity and pore size distribution (PSD): effect of heat on porosity, pore form, and PSD in water-saturated polyacrylonitrile fibers. J Colloid Interface Sci 84:127–140
3. Iskiriyama K, Todoki M (1995) Pore size distribution measurements of silica gels by means of differential scanning calorimetry. Colloid Interface Sci 171:103–111
4. Maloney TC, Paulapuro H (1999) The formation of pores in the cell wall. J Pulp Paper Sci 25:430–436
5. Maloney TC, Paulapuro H, Stenius P (1998) Hydration and swelling of pulp fibers measured with differential scanning calorimetry. Nordic Pulp Paper Res J 13:31–36
6. Maloney TC, Paulapuro H (2001) Thermoporosimetry of pulp fibers. 12th Fundamental Research Symposium, Keble College, Oxford, England, September 17–21, 2001, pp 897–926
7. Berlin E, Kliman P, Pallansch MJ (1970) Changes in state of water in proteinaceous systems. J Colloid Interface Sci 34:488–494
8. Berthold J, Despiéres J, Rinaudo M, Salmén L (1994) Types of absorbed water in relation to the ionic groups and their counterions for some cellulose derivatives. Polymer 35:5729–5736
9. Berthold J, Rinaudo M, Salmén L (1995) Association of water to polar groups; estimations by an adsorption model for lignocellulosic materials. Eighth International Symposium on Wood and Pulping Chemistry, Helsinki, Finland, June 6–9, 1995, pp 575–580
10. Salmén L, Berthold J (1997) The swelling ability of pulp fibers. 11th Fundamental Research Symposium, Cambridge, England, September 21–26, 1997, pp 683–701

11. Pouchlý J, Biroš J, Beneš S (1979) Heat capacities of water swollen hydrophilic polymers above and below 0°C. Macromol Chem 180:745–760
12. Stone JE, Scallan AM (1967) The effect of component removal upon the porous structure of the cell wall of wood II. Swelling in water and the fibre saturation point. TAPPI 50:496–501
13. Stone JE, Scallan AM, Abrahamson B (1968) Influence of beating on the cell wall swelling and internal fibrillation Sven Papperstidn 71:687–694
14. Scallan AM (1977) The accommodation of water within pulp fibers. Sixth fundamental Research Symposium, 1977, (Fiber-Water Interactions in Papermaking), London 1978, pp 9–29
15. Salmén L, Tigerström A, Fellers C (1985) Fatigue of wood-characterization of mechanical defibration. J Pulp Paper Sci 11:J68–73
16. Tynjälä P, Kärenlampi PP (2001) Cell wall porosity in spruce wood – variation within annual ring and drying response. First International Conference of the European Society of Wood Mechanics, April 19–21, 2001, Lausanne, Switzerland, pp 55–58
17. Van den Akker JA (1961) Some theoretical considerations on the mechanical properties of fibrous structures. In: Bolam F (ed) Formation and structure of paper. Vol I. Symposium transactions. Oxford, 1961. Technical section of the British Paper and Board Maker's Association, London, pp 205–241
18. Bailey IW, Vestal MR (1937) The orientation of cellulose in the secondary wall of woody cells. J Arnold Arbor 18:185–195, Pls 209–208
19. Preston RD (1946) The fine structure of the walls of the conifer tracheid. I. The X-ray diagram of conifer wood. Proc Roy Soc Lond B Bio 133:327–348
20. Preston RD (1947) The fine structure of the walls of the conifer tracheid. II. Optical properties of dissected walls in *Pinus insignis*. Proc Roy Soc Lond B Bio 134:202–218
21. Abe H, Ohtani J, Fukazawa K (1991) FE-SEM observations on the microfibrillar orientation in the secondary wall of tracheids. IAWA Bull 12:431–438
22. Fengel D, Stoll M (1973) On the variation of the cell cross area, the thickness of the cell wall, and of the wall layers of sprucewood tracheids within an annual ring. Holzforschung 27:1–7
23. Kärenlampi PP, Tynjälä P, Ström P (2003) Molecular reorganization in wood. Mechanics of materials 35:1149–1159
24. Kärenlampi PP, Tynjälä P, Ström P (2003) Molecular fatigue in streamed wood. Int J Fatigue 25:489–497
25. Wallström L, Lindberg KAH (2000) Distribution of added chemicals in the cell of high temperature dried and green wood of Swedish pine, *Pinus sylvestris*. Wood Sci Tech 34:327–336
26. Wallström L, Lindberg KAH (2000) The diffusion, size, and location of added silver grains in the cell walls of Swedish pine, *Pinus sylvestris*. Wood Sci Tech 34:403–415

The publication of this article was made possible by an Emachu Research Fund. The author is greatful for the fund.