

Le Xuan Phuong · Satoshi Shida · Yukie Saito

Effects of heat treatment on brittleness of *Styrax tonkinensis* wood

Received: December 26, 2005 / Accepted: August 23, 2006 / Published online: December 21, 2006

Abstract A new approach is proposed for the evaluation of the brittleness of heat-treated *Styrax tonkinensis* wood. Heat treatment made wood more brittle when wood was heated at a higher temperature or for a longer time. The brittleness increased to four times that of the control when wood was heated at 200°C for 12 h. For treatment at 160°C, the increase in brittleness without any change in weight is thought to be possibly caused by the relocation of lignin molecules. At higher temperatures, loss of amorphous polysaccharides due to degradation is thought to become the main factor affecting brittleness. The crystallites that were newly formed after 2 h of treatment showed brittleness that was different from that of the inherent crystallites remaining after 12 h of heat treatment. This inherent crystalline cellulose possibly plays a role in brittleness. There is also the possibility of using color to predict the brittleness of heat-treated wood.

Key words Heat treatment · Brittleness · Crystallinity · Lignin · Color

Introduction

Brittleness is one of the mechanical properties of wood, which is characterized by sudden breaking at relatively small deflection across the grain. Because of its danger, high attention should be paid to preventing possible accidents while loading. Although Koehler¹ noted this phenomenon a long time ago, there is still no method to measure brittleness other than toughness. From the view of material mechanics, wood is considered to be an elastoplastic material and brittleness can be interpreted as the elastic region in

wood. However, by using toughness, with the energy (work) required to cause rapid complete failure in a centrally loaded bending specimen,² it is not only difficult to clarify the ratio between elastic and plastic regions, which is regarded as its brittle character (see Fig. 1), but it is also difficult to evaluate the brittleness in such cases as that of the same toughness but with different deformation.

Toughness changes after heat treatment for a short time in air or at less than 120°C as discussed elsewhere.^{1,3,4} Kubojima et al.⁵ have also reported in detail on the toughness of Sitka spruce heated at 160°C in N₂ gas. However, the brittleness of heat-treated wood and its main factors have not been fully studied so far.

The structural properties of wood are reported to change as a result of heat treatment.^{6,7} With the role of providing a rigid frame for wood strength, changes in crystallinity may contribute to its brittleness. In addition, brown rotted wood is customarily brittle,⁸ which also suggests that lignin plays some role in its brittleness.

The decay resistance of the low-durability wood of *Styrax tonkinensis* was improved by heat treatment,⁹ but we still do not know whether it is safe to use in structural housing because of the danger of its brittleness. This study investigated the brittleness of wood heated in N₂ gas from 160° to 200°C for 2–12 h. Structural changes, lignin content, and color were examined to elucidate the effect of heat treatment on the brittleness of *S. tonkinensis* wood.

Materials and methods

Materials

Twelve-year-old *Styrax tonkinensis* logs were sawn and kiln-dried at a maximum temperature of 70°C to a moisture content of 10% ± 2%, and then were cut to the board dimensions of 25 (tangential, T) × 700 mm (longitudinal, L), with variation in the radial (R) direction of 110–180 mm. The specimens for the brittleness test were carefully cut to the dimensions of 10 (R) × 10 (T) × 200 mm (L). Further-

L.X. Phuong (✉) · S. Shida · Y. Saito
Biomaterial Sciences Department, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan
Tel. +81-3-5841-5249; Fax +81-3-5684-0299
e-mail: lexuanphuongfuv@yahoo.com

more, specimens with dimensions of 25 (R) × 2 (T) × 40 mm (L) were prepared for X-ray measurements. To standardize the specimens, we selected the radial boards from clear wood with the same annual ring width of about 1 cm from the 8th ring to the 12th ring.

Heat treatment

To prevent oxidation from occurring during the heating process (e.g., weight loss of the wood powder by thermal degradation was about 20% in air compared with 13% in N₂ gas in our thermogravimetry pretest), heat treatments were performed in N₂ gas using the same procedures as described in our previous report.⁹ The heating times were 2, 4, 8, and 12 h at 160°, 180°, and 200°C, respectively.

Brittleness test

From the load–deflection curve of static bending (Fig. 1), brittleness was calculated by using the ratio (%) of the work absorbed in the elastic region to the total work absorbed to maximum load, as shown in Eq. 1:

$$\text{Brittleness} = \frac{\text{Area 1}}{\text{Area 1} + \text{Area 2}} \times 100(\%) \quad (1)$$

The proportional limit was decided by drawing a linear correlation curve using data from 0% load to the limit value (correlation coefficient $R^2 = 0.999$). The static bending test was performed using center-point loading over a 140-mm span with the load applied in the tangential direction. The cross-head speed was 1 mm/min. All tests were conducted using an Instron 4202 testing machine. For each heating condition, we used ten specimens that were equilibrated in a room conditioned at 20°C and 65% relative humidity for 1 month before testing. Untreated *Cryptomeria japonica* was used as a reference species because of its wide use as a construction material in Japan.

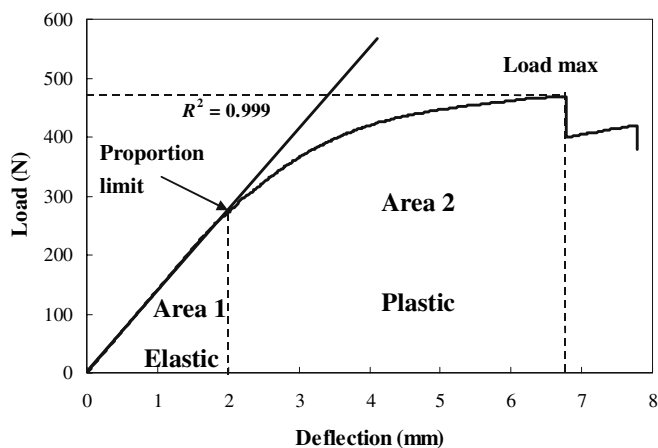


Fig. 1. Relationship between load and deflection

Weight loss by heat treatment

The weight loss was calculated based on the dried weight of the bending test samples before (m_{01}) and after (m_{02}) heat treatment as shown in Eq. 2:

$$\text{Weight loss} = \frac{m_{01} - m_{02}}{m_{01}} \times 100(\%) \quad (2)$$

where m_{01} is the dried weight of specimen before heating calculated based on its weight and the equilibrium moisture content (EMC), and m_{02} is the oven-dried (105°C for 2 days) weight of the heat-treated specimen after the bending test.

X-Ray diffractometry

X-Ray diffractometry was achieved by the symmetrical reflection method using a Rigaku RINT diffractometer with CuK α rays generated by 30 kV and 40 mA. The sampling time was 20 s with a step angle of 0.1°. The crystallinity index was calculated by the ratio of the integral intensity of the crystalline portions (planes: $\bar{1}\bar{1}0$, 110, 200, and 004) to the total intensity of the sample over the range $2\theta = 10^\circ$ to 40° . The crystallite size, that is, the mean dimension of the crystallites perpendicular to the planes (200), was calculated by Scherrer's equation.¹⁰ Five specimens of each condition were equilibrated in the conditioning room for 6 months before the X-ray test.

After X-ray measurements, specimens were oven-dried at 105°C for 2 days to determine the moisture content. This value was considered as the EMC of heat-treated wood in this study. Prior to the X-ray measurements, we investigated the effect of moisture content on crystallinity index. Ten untreated *S. tonkinensis* specimens were equilibrated at 20°C in a relative humidity of 65% and then 35%, which corresponds to EMC values of 9.2% and 7%, respectively. A minor increase in the crystallinity index (about 0.006 in absolute value or equivalent to 2% in relative value) was observed. EMC values ranged from 9.2% for the control to as low as 4.2% for heat-treated wood (see Table 1). This 5% difference in moisture content is not large enough to substantially affect the crystallinity index. Therefore, we are still able to use the crystallinity index of heat-treated wood with different EMC values for comparison purposes.

Lignin content determination

Lignin content was determined by the Klason method with a slightly modified procedure as described in our previous report.⁹ Lignin content is the sum of acid-insoluble Klason lignin and acid-soluble lignin, calculated based on the oven-dried weight of wood.

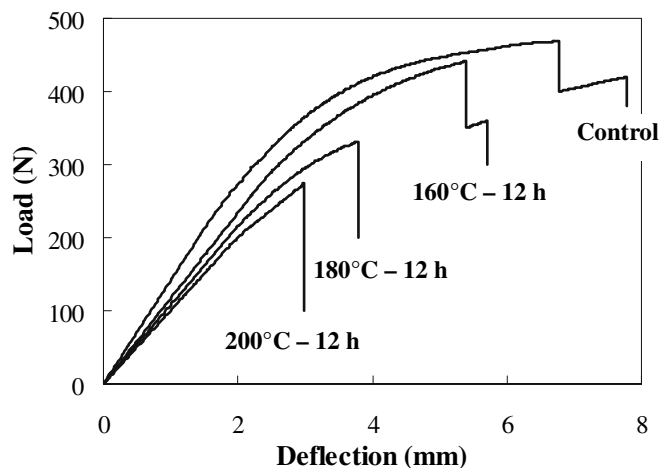


Fig. 2. Changes in load and deflection during the bending test. Heat treatments were carried out for 12 h

Color test

The color test (CIE Lab, JIS Z 8729) was carried out using a Topscan TC-1800 color analyzer and dried wood powder in tablet form. The 2-cm-diameter tablets were made using 0.5 g of dried wood powder (63 μm particle size) loaded by 2 tons for 3 min.

Results and discussion

Brittleness

The relationships between load and deflection while bending of untreated wood and wood treated at 160°, 180°, and 200°C for 12 h are shown in Fig. 2. Brittleness was significantly changed after heat treatment. With larger specimen size and a loading speed that was one quarter of that in the work of Kubojima et al.,⁵ the elastic region was more clearly distinguished. The work absorbed in the elastic region at 160°C was increased slightly, but for most cases this value seemed to be unchanged compared with the control. Figure 3 shows the effects of heat treatment conditions on brittleness. Untreated *Styrax tonkinensis* and *Cryptomeria japonica* had similar values of brittleness. However, heat-treated *S. tonkinensis* wood became more brittle depending closely on the heating conditions. Davis and Thompson³ found the decrease in toughness even in short-duration treatment of less than 1 h in air. However, in our study, brittleness increase was not clearly observed because the decrease of toughness may have contributed to higher degradation in the presence of oxygen in the air. Wood became more brittle after exposure for a longer time or to higher temperatures. Brittleness could reach 60% or equivalent to four times higher than untreated wood for the most severe conditions of 200°C and 12 h. The tendency of increasing brittleness at 160°C follows the change of brittleness calculated from the data of Kubojima et al.⁵

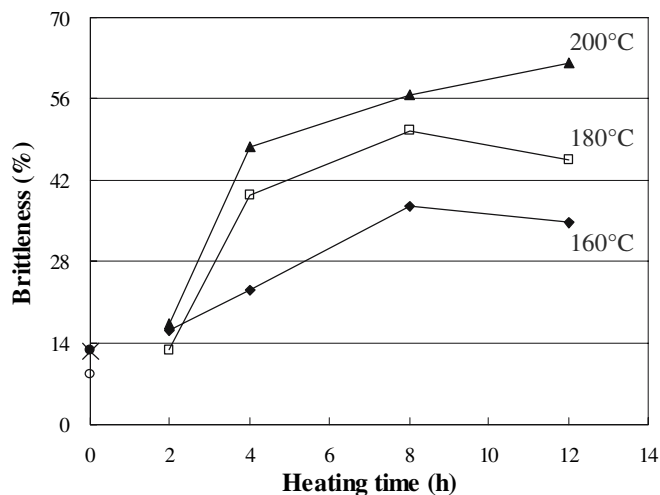


Fig. 3. Changes in brittleness of *Styrax tonkinensis* due to heat treatment. Cross, untreated sample; open circle, *Cryptomeria japonica* sapwood; filled circle, *C. japonica* heartwood

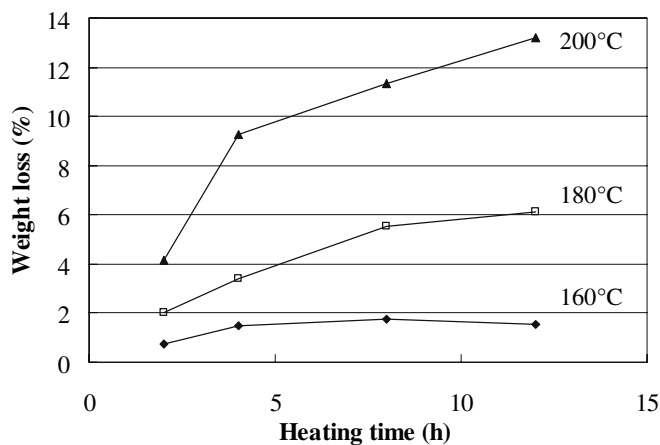


Fig. 4. Changes in weight loss due to heat treatment

Weight loss by heat treatment

Figure 4 shows the weight loss caused by thermal degradation. Both treatment temperature and treatment time apparently affected the weight loss. Figure 5 shows a close relationship between weight loss and brittleness ($R^2 > 0.78$). At 160°C, brittleness increases steadily with little change in weight loss. The reason for the increase in the brittleness at this relatively low temperature could be due to the degradation and loss of amorphous polysaccharides, which are responsible for tight combination of cellulosic fibers and the amorphous matrix including lignin. We can also suggest the possibility of lignin relocation. It is reported that the glass transition temperatures (broad transition, α_1) of Sitka spruce and sugar maple appear at 80° and 100°C, respectively, as determined by dynamic mechanical spectra,¹¹ at a moisture content of 10% (the same as our specimens before heating). In addition, Hatakeyama et al.¹² reported that the glass transition temperature of lignin was about 400K (126°C), although the lignin was dried dioxane lignin iso-

lated from Japanese cypress, which might be different from protolignin. Thus, treatment at 160°C is probably enough to cause lignin molecules located between the fibril aggregates¹³ to change their position and damage the adhesive linkage of lignin with cellulose fibrils. These changes are thought to be major factors contributing to the increase in brittleness at 160°C. On the other hand, at higher temperatures, weight loss contributed to further brittleness, which clearly means that degradation of amorphous polysaccharides becomes the main reason.

Changes in crystallinity

Figure 6 shows the X-ray diffractograms for the control and for samples treated at 160°C for 2 h and 200°C for 12 h. Increases in the height of peaks $\bar{1}\bar{1}0$, 110 and 200 can be clearly observed. This leads to the increase in crystallinity index and crystallite size as shown in Table 1. The increase in crystallinity index over 2 h of treatment is considered to be caused by the change from a semicrystalline region to a

crystalline region. These additional crystallites are “newly formed” crystallites. However, when treated for a longer time, the crystallinity index decreases again, probably due to the degradation of newly formed crystallite. Thus, after such longer treatment, it is possible that only the inherent crystallites remain. The decrease in the amorphous region in wood after heat treatment results in increased crystallinity index. The same tendency was also observed by Andersson et al.⁷ The increase in the size of cellulose crystallites and the degradation of the amorphous part are the main structural changes in wood during heat treatment. The relationship between crystallinity index and brittleness is shown in Fig. 7. There are two different trends observed between the samples treated for 2 h and those treated for longer times. This means, from the view of brittleness, newly formed crystalline cellulose (in the 2-h-treated sample) may demonstrate a different strength from inherent crystalline cellulose (in the samples treated for longer times). The inherent crystalline cellulose possibly plays a role in brittleness ($R^2 = 0.64$), but the newly formed crystalline cellulose does not appear to do so ($R^2 = 0.13$).

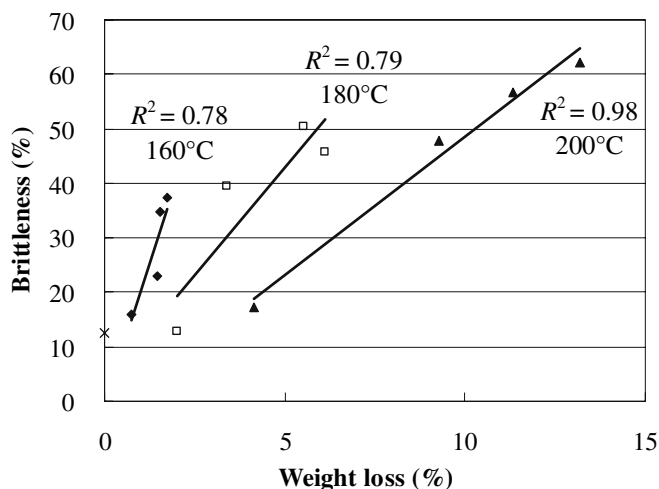


Fig. 5. Relationship between weight loss and brittleness. *Solid lines* are trend lines

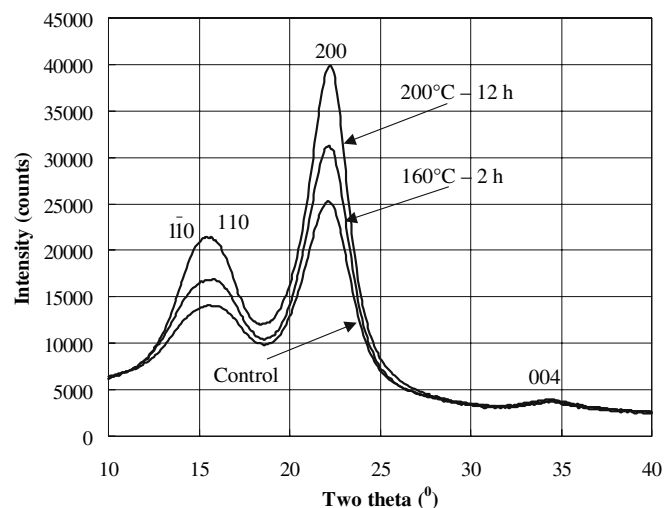


Fig. 6. X-Ray diffractograms of control and heat-treated samples

Table 1. Changes in equilibrium moisture content (EMC), color, crystallinity, and lignin content due to heat treatment

Temperature (°C)	Time (h)	EMC (%)	Color			Crystallinity index	Crystallite size (Å)	Lignin content	
			(L*)	(a*)	(b*)			Insoluble	Acid soluble
Control	0	9.2	84.6	0.8	14.8	0.31	29.8	24.4	1.9
160	2	7.3	72.3	2.8	19.6	0.36	31.2	24.7	1.7
	4	6.9	68.5	4.1	20.8	0.33	30.4	24.2	2.1
	8	6.5	65.6	4.8	20.9	0.33	30.3	24.6	2.0
	12	6.1	64.8	4.8	21.8	0.35	30.5	24.6	1.8
180	2	6.1	63.6	4.9	20.8	0.37	32.2	24.5	1.5
	4	5.7	53.8	6.7	19.7	0.34	30.7	25.1	1.8
	8	5.4	43.2	7.3	17.1	0.39	31.8	25.5	2.1
	12	5.4	47.9	7.3	18.8	0.40	34.1	25.4	1.7
200	2	4.9	49.7	6.8	19.3	0.37	32.4	24.4	1.3
	4	4.4	36.3	6.7	14.6	0.35	31.7	28.4	1.6
	8	4.4	37.3	6.9	15.0	0.36	31.3	27.7	1.7
	12	4.2	33.5	6.6	13.7	0.39	32.9	31.1	1.6

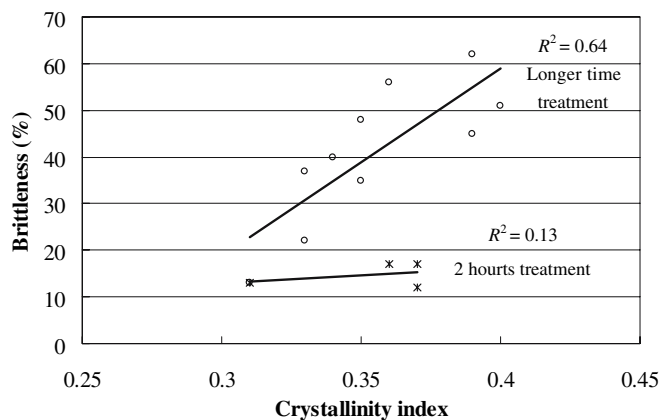


Fig. 7. Relationship between crystallinity index and brittleness. *Solid lines* are trend lines

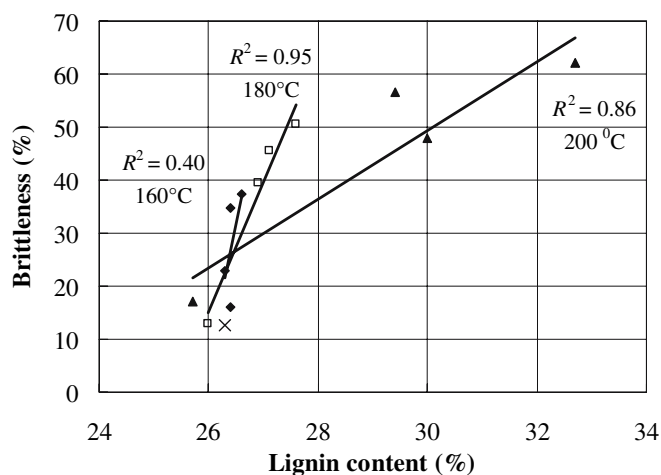


Fig. 8. Relationship between lignin content and brittleness. *Solid lines* are trend lines. Symbols are defined in Fig. 3

Changes in lignin content

Lignin contents of heat-treated wood are shown in Table 1. An apparent increase in lignin content was observed during heat treatment. Figure 8 shows the relationship between lignin content and brittleness. The lignin content seems to affect the brittleness when wood is heated at higher temperatures.

During heat treatment, the increase in crystallinity index in line with lignin content shows that thermal degradations mainly occurred in the amorphous region of wood that contains materials such as extractives, hemicellulose, and amorphous cellulose. This idea is supported by the decrease in neutral sugars in wood found in our previous report.⁷ Because the degradation of amorphous parts breaks or weakens the fiber matrix interaction (cohesive force), this degradation causes an increase in brittleness.

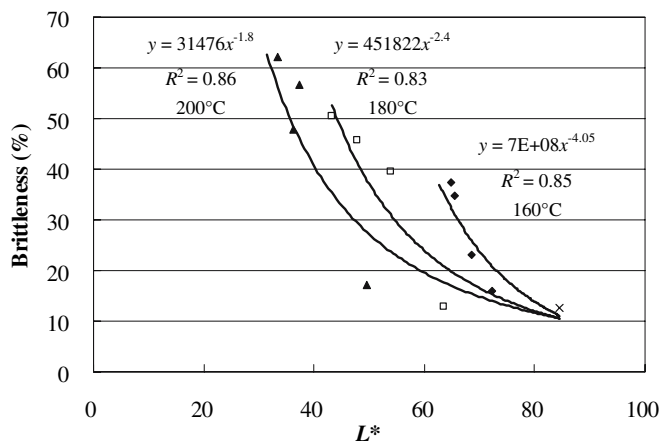


Fig. 9. Relationship between L^* and brittleness. *Solid curves* are trend lines

Changes in color due to heat treatment

Colors of heat-treated wood are shown in Table 1. At 160°C, lightness (L^*) was slightly decreased, while at higher temperatures, a significant decrease of L^* was observed. Wood became darker and browner during heat treatment. The relationship between L^* and brittleness is shown in Fig. 9. The relationship shows that if we know the heating temperature, we can predict the brittleness using the L^* value ($R^2 > 0.94$).

Conclusions

This study investigated the brittleness of *Styrax tonkinensis* wood heated in N_2 gas from 160° to 200°C for 2–12 h. The respective relationships between the brittleness of wood and structural changes, lignin content, and color were examined. The findings of the study are summarized as follows:

1. The brittleness of *S. tonkinensis* wood heat-treated in N_2 gas from 160° to 200°C was estimated by using the load-deflection curve of static bending. The brittleness increased significantly after heat treatment. Under the most severe heat treatment conditions, brittleness could be increased by as much as four times that of the original brittleness.
2. Lignin relocation was suggested as the cause of brittleness at relatively low temperature around 160°C, in addition to the thermal degradation of amorphous parts. At higher temperature, loss of amorphous polysaccharides due to degradation is thought to become the main factor affecting brittleness.
3. Crystallites that were newly formed after 2 h of treatment possessed different brittleness compared with the inherent crystallites that remained after 12 h of heat treatment. The inherent crystalline cellulose possibly plays a role in brittleness, but the newly formed crystallites do not appear to do so.

4. There is the possibility of using color to predict the brittleness of heat-treated wood.

References

1. Koehler A (1933) Causes of brashness in wood. USDA FPL Technical bulletin 342
2. Forest Products Laboratory (1999) Wood handbook – wood as an engineering material. Forest Products Laboratory, USDA Forest Service, Madison, WI
3. Davis WH, Thompson WS (1964) Influence of thermal treatments of short duration on the toughness and chemical composition of wood. *Forest Prod J* 14:350–356
4. Sumi H (1982) High-temperature drying of wood III. Influence of temperature and heating treatment time on types of static-bending failure of Western hemlock (in Japanese). *Mokuzai Gakkaishi* 28:489–494
5. Kubojima Y, Okano T, Ohta M (2000) Bending strength and toughness of heat-treated wood. *J Wood Sci* 46:8–15
6. Kubojima Y (1998) Improvement of vibrational properties of wood for musical instruments. Ph.D. thesis, The University of Tokyo
7. Andersson S, Serimaa R, Vaananen T, Paakkari T, Jamsa S, Viitaniemi P (2005) X-ray scattering studies of thermally modified Scots pine (*Pinus sylvestris* L.). *Holzforschung* 59: 422–427
8. Eriksson K, Blanchette RA, Ander P (1990) Microbial and enzymatic dégradation of wood and wood components. Springer, Berlin Heidelberg New York London, p 407
9. Phuong LX, Shida S, Saito Y, Momohara I (2006) Effect of heat treatment on bending strength and decay resistance of *Styrax tonkinensis* wood. *Wood Preserv* 32:7–12
10. Alexander LE (1979) X-Ray diffraction methods in polymer science. Krieger, New York, pp 423–424
11. Kelly SS, Rials TG, Glasser WG (1987) Relaxation behaviour of the amorphous components of wood. *J Mater Sci* 22:617–624
12. Hatakeyama T, Nakamura K, Hatakeyama H (1982) Studies on heat capacity of cellulose and lignin by differential scanning calorimetry. *Polymer* 23:1801–1804
13. Salmén L (2004) Micromechanical understanding of the cell-wall structure. *Comptes Rendus Biologies* 327:873–880