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Vibrational properties of Sitka spruce heat-treated in nitrogen gas*

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Abstract Sitka spruce (*Picea sitchensis* Carr.) wood was heated for 0.5–16.0h at temperatures of 120°–200°C in nitrogen gas or air. The values for Young's modulus, shear modulus, and loss tangent were measured by free–free flexural vibration tests. X-ray diffractometry was carried out to estimate the crystallinity index and crystallite width. The results obtained are as follows: (1) Density decreased at higher temperatures and longer heating times. The specific Young's modulus, specific shear modulus, crystallinity index, and crystallite width increased during the initial stage and were constant after this stage at 120°C and 160°C, whereas they increased during the initial stage and decreased later when the temperature was high. Loss tangent in the longitudinal direction increased under all conditions, whereas that in the radial direction increased at 120°C and decreased at 160°C and 200°C. (2) From the relation between Young's modulus and moisture content, it can be safely said that Young's modulus is increased by the crystallization and the decrement in equilibrium moisture content, and that crystallization (rather than degradation) is predominant at the initial stage of the heat treatment, whereas the latter is predominant as the heating time increases. (3) It is implied that the specific Young's modulus, specific shear modulus, crystallinity index, and crystallite width decreased more in air than in nitrogen gas because of oxidation in air.

Key words Heat treatment · Vibrational properties · Crystallization · Atmospheric condition · Temperature–time condition

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Introduction

When wood is heat-treated, it is known that Young's modulus increases during the initial stage of the reaction and then decreases with time when the temperature is lower, whereas it decreases monotonically with heating time at high temperatures.[1–3] This phenomenon is ascribed to the superiority of the crystallization of the cellulose or the degradation of wood components during the heat treatment because the crystallinity index has a tendency similar to that of Young's modulus.[3,4] Taniguchi and Nakato[5] reported that rearrangement of cellulose molecules at 110°C brought the increase in the crystallinity index and that cellulose crystallites began to degrade at 210°C.

The effect of heat treatment is influenced by the atmosphere as well as the heating temperature and time. The antishrink efficiency of wood heated in molten metal is better than that in air,[6] and the degree of polymerization of cellulose heated in oxygen is less than that heated in nitrogen gas.[7]

The objective of this study was to investigate the effect of oxidation in during heat treatment of wood. Sitka spruce wood was heated in nitrogen gas or air under several temperature and time conditions. The heating temperatures were from 120°C to 200°C because residual Young's modulus of Hinoki (*Chamaecyparis obtusa* Sieb. and Zucc.) has a maximum in the curve versus the heating time up to 200°C.[3] We then investigated the effect of heat treatment on the vibrational properties and crystallinity indexes measured by X-ray diffractometry.

Experiment

Specimen

Sitka spruce (*Picea sitchensis* Carr.) lumber kiln-dried for piano soundboard was used. The wood was stored in a room at 20°C and 65% relative humidity (RH) for more than a half-year and was conditioned to a uniform moisture

content. Longitudinal (L)- and radial (R)-direction specimens for the vibration tests were carefully cut to the dimensions of 180mm (L) × 25mm (R) × 8mm (tangential, T) and 110mm (R) × 25mm (L) × 8mm (T), respectively. Furthermore, specimens with a dimension of 40mm (L) × 25mm (R) × 2mm (T) were prepared for the X-ray measurements. For every heat treatment condition, three specimens were used for the vibration tests and four for the X-ray measurements.

Specimens were conditioned at 20°C and 65% RH before and during the tests.

Vibration tests

Free–free flexural vibration tests were conducted to obtain Young's modulus, the shear modulus, and the loss tangent. Each specimen was suspended by threads at the nodal positions of free–free vibration corresponding to each resonance mode. The lateral vibration was excited by hitting one end of the specimen in the thickness direction with a small hammer. The motion of the specimen was detected by a microphone at the other end. The signal was then processed by an fast fourier transform (FFT) signal analyzer to yield resonance frequencies.

Young's modulus and the shear modulus were calculated by Goens-Hearmon regression[8,9] based on Timoshenko's bending theory.[10] The resonance modes used for the calculation were the first to the third for the L-direction specimens and the first to the fourth ones for the R-direction specimens. In the case of specimens with the length/depth ratio mentioned above, the obtained shear moduli have proved to be adequate.[11]

Using the amplitude of vibration corresponding to the first cycle (A_1) and that of vibration corresponding to the 10th cycle (A_{10}), on a free vibration curve of the first mode the logarithmic decrement (λ) was calculated from the following equation

$$\lambda = \frac{1}{10} \ln \frac{A_1}{A_{10}}$$

The loss tangent (tanδ) was then obtained by dividing λ by π.

X-ray diffractometry

To estimate the crystallinity index (Cr) and the mean dimension of the crystallites perpendicular to the planes (200), (L), X-ray diffractometry was undertaken using a symmetrical reflection method. Table 1 shows the conditions of the X-ray diffraction technique.

The crystallinity index was determined by the ratio of the integral intensity of the crystalline portion to the total intensity of the sample over the range $2\theta = 10°–30°$. The mean dimension of the crystallites perpendicular to the planes (200) was calculated by Sherrer's equation.[12]

Table 1. Conditions of X-ray diffractometry

X-ray: CuK_α, 30kV, 40mA
Divergence slit: 0.5°
Scattering slit: 0.5°
Receiving slit: 0.15mm
Sampling time: 20s
Step angle: 0.1°
Scan area: $10° \leq 2\theta \leq 30°$

Heat treatment

The specimens were encapsulated in a pressure-resistant stainless steel potable reactor with nitrogen gas or air. The gases in the potable reactors were not refreshed during the heat treatment. The reactor was then heated in a constant-temperature oven. The heating temperatures were 120°, 160°, and 200°C. The heating times were 0.5, 1, 2, 4, 8, 12, and 16h. The heat treatments were done accumulatively. After the heat treatment, the specimens were left at 20°C and 65% RH for a week and then were tested. For example, after the 0.5-h treatment and conditioning in 20°C and 65% RH for a week, the vibration tests were done, and then the specimens were heated for 0.5h. This step is called the 1-h treatment in this study.

Results

Density

Figure 1 shows the change of density (ϱ) due to the heat treatment. The density decreased rapidly during the initial

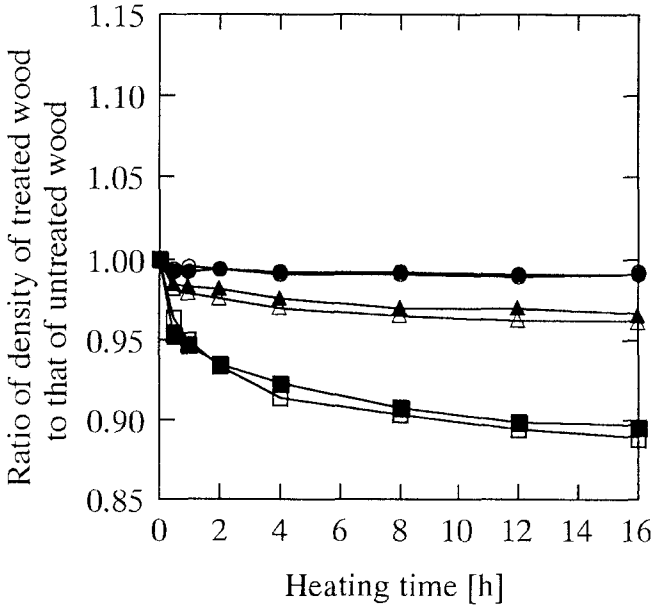


Fig. 1. Change of density due to heat treatment. *Filled symbols* represent the average of the results by the heat treatment in nitrogen gas at 120°C (*circles*), 160°C (*triangles*), and 200°C (*squares*). *Open symbols* represent the average of the results by the heat treatment in air at 120°C (*circles*), 160°C (*triangles*), and 200°C (*squares*)

half-hour and then even more with the increased heating temperature and heating time. There was no difference in the atmospheres at 120°C, whereas at 160°C and 200°C the density became lower in air than in nitrogen gas.

Specific Young's modulus

Figure 2 shows the change in specific Young's modulus due to the heat treatment. The specific Young's modulus in the L-direction (E_L/ϱ) and the specific Young's modulus in the R-direction (E_R/ϱ) increased during the initial stage and stayed constant at 120°C and 160°C. At 200°C, it increased during the initial stage and then decreased with the increased heating time. The difference in the atmosphere was not clear at 120°C and 160°C, but the specific Young's modulus was lower in air than in nitrogen gas at 200°C. It is possible that the specific Young's modulus would decrease with longer treatment at 120°C and 160°C.

Specific shear modulus

Figure 3 shows the change in specific shear modulus due to heat treatment. At 120°C in nitrogen gas, the specific shear modulus of the LT plane (G_{LT}/ϱ) increased during the initial stage and remained constant. At 120°C in air, it increased more gradually than in nitrogen gas. At 160°C in nitrogen gas, it increased during the initial stage and remained constant. At 160°C in air, it increased during the initial stage and then decreased with the increased heating time. At 200°C in both nitrogen gas and air, it increased during the initial stage and then decreased with the increased heating time; it decreased more in air than in nitrogen gas. The specific shear modulus of the RT plane (G_{RT}/ϱ) had a tendency similar to that of G_{LT}/ϱ. It is possible that the specific shear modulus would decrease with longer treatment at 120°C and 160°C.

Loss tangent

Figure 4 shows the change of loss tangent due to heat treatment. The loss tangent in the L-direction ($\tan\delta_L$) increased with every condition. The value of $\tan\delta_L$ increased during the early stage of the treatment and then became constant. There was no difference with different atmospheres, either nitrogen gas or air. Regarding the loss tangent in the R-direction ($\tan\delta_R$) a general tendency emerged: At 120°C the $\tan\delta_R$ increased during the early stage of treatment and then became constant in nitrogen gas, whereas in air $\tan\delta_R$ increased and then decreased. At 160°C $\tan\delta_R$ decreased after 0.5 h and then became constant in both nitrogen gas and air. At 200°C, $\tan\delta_R$ decreased after 0.5 h and then became constant in both nitrogen gas and air, as at 160°C; however, there was a difference in the atmospheres in that $\tan\delta_R$ decreased more in nitrogen gas than in air.

Crystallinity index

Figure 5 shows the change in the crystallinity index. There was a general tendency for the value of *Cr* to increase. At 120°C the *Cr* was nearly equal in nitrogen gas and air. At 200°C it increased initially and then decreased with the increased heating time. There was a difference in the atmospheres in that *Cr* decreased more in air than in nitrogen gas.

Crystallite width

Figure 6 shows the change in crystallite width due to heat treatment. The value of *L* increased during an early stage of the treatment and then became constant under most conditions. At 200°C in air it increased initially and then decreased.

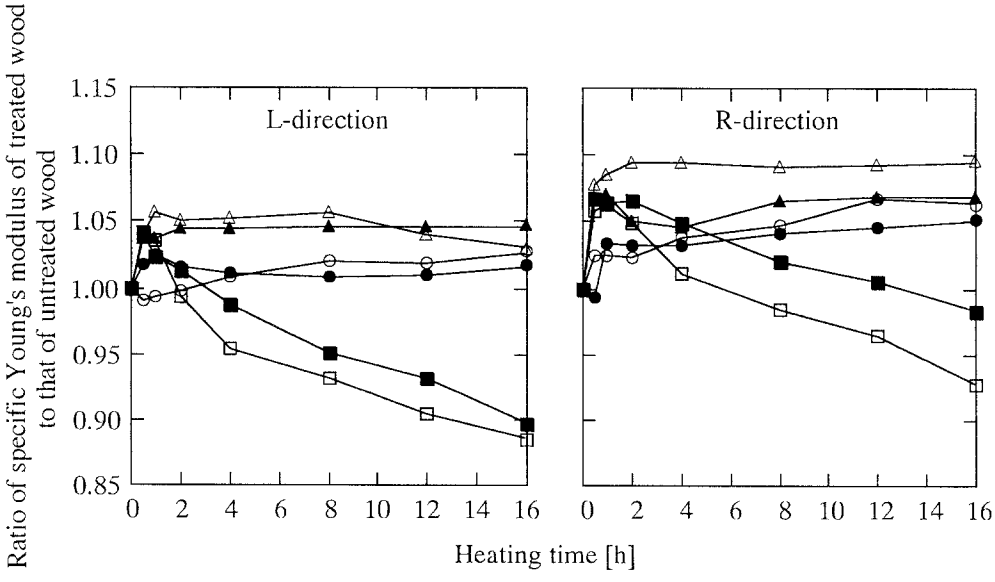


Fig. 2. Change of specific Young's modulus due to heat treatment
Symbols: Refer to Fig. 1

Fig. 3. Change of specific shear modulus due to heat treatment
Symbols: Refer to Fig. 1

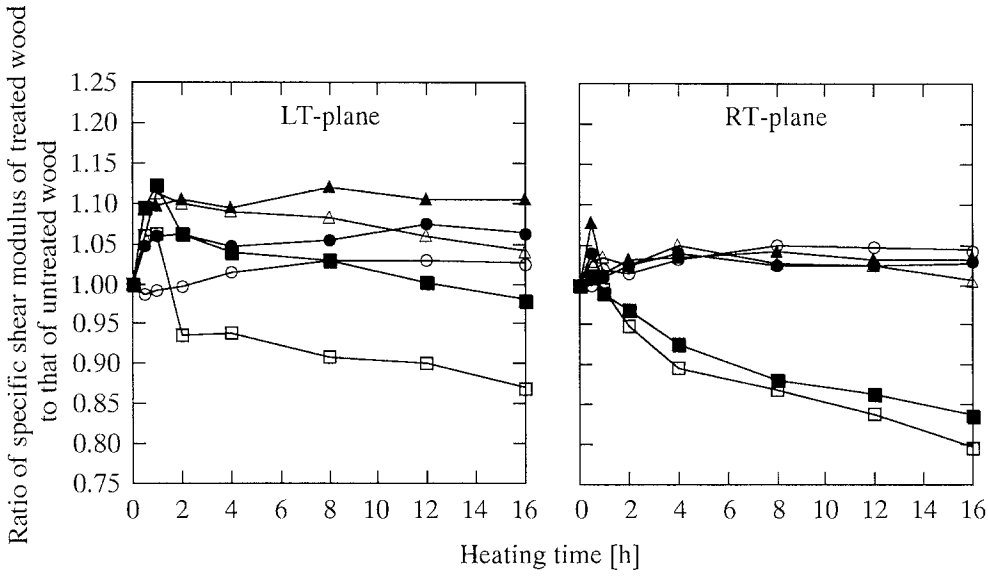
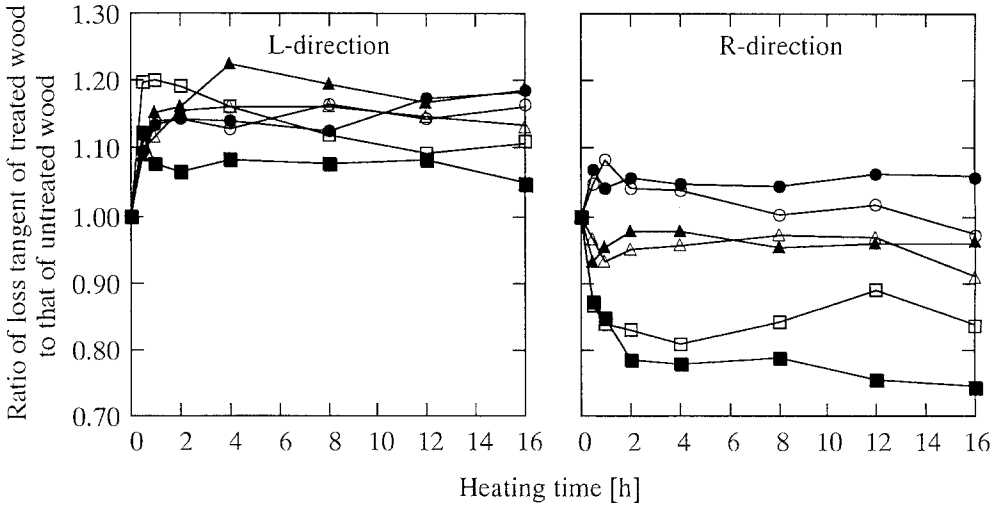


Fig. 4. Change of loss tangent due to heat treatment
Symbols: Refer to Fig. 1



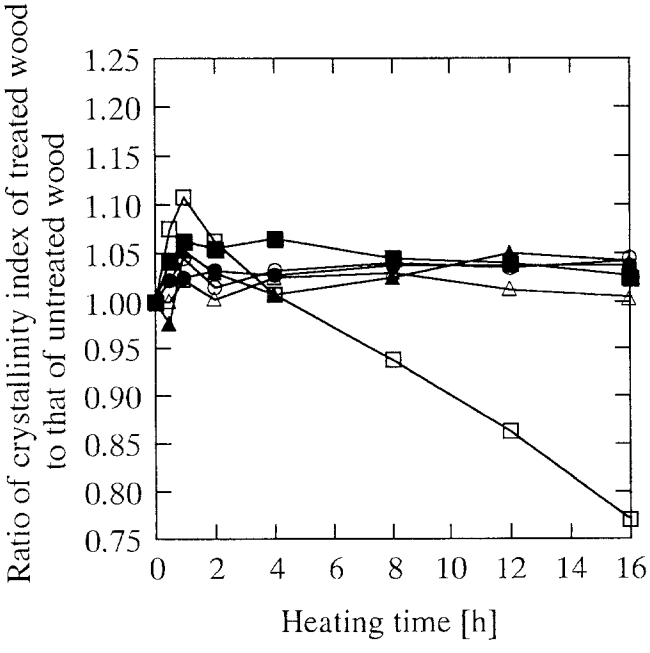


Fig. 5. Change of crystallinity index due to heat treatment
Symbols: Refer to Fig. 1

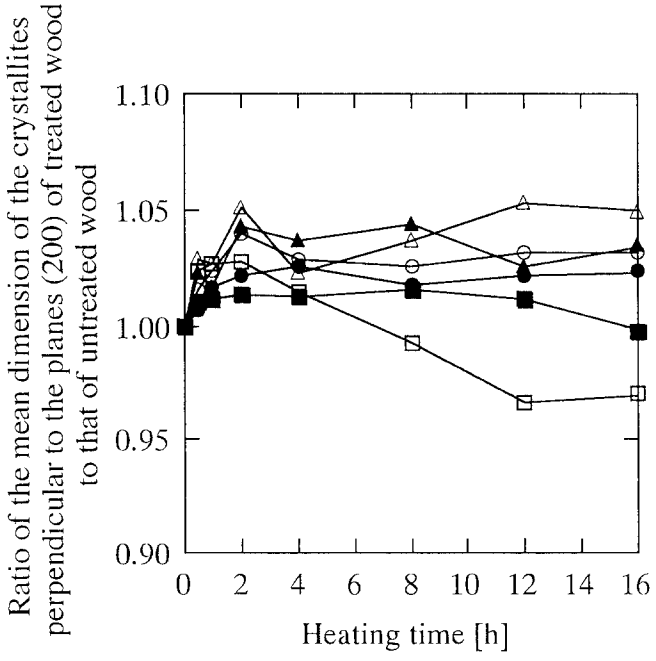


Fig. 6. Change of crystallite width due to heat treatment
Symbols: Refer to Fig. 1

Discussion

The moisture contents when the vibrational tests were done were not constant in this study. It then becomes necessary to investigate the effect of the change in moisture content on the change in vibrational properties. As did Hirai et al.,[3] we have discussed this subject using the relation between Young's modulus and moisture content; that is, Young's modulus is constant or has a peak value in the range 0%–10% moisture content and decreases monotonically in the range 10%–30% moisture content.

If Young's modulus is decreased, the decrement must be caused by the thermal degradation of wood because the equilibrium moisture content was lowered by the heat treatment less than the initial moisture content (about 10%). On the other hand, when Young's modulus is increased by the heat treatment, it may be because of the decrease of the moisture content and crystallization. Hence, we investigated the results of a 0.5-h treatment where the thermal degradation is minimal at each heating temperature. The relative value of Young's modulus after heat treatment and at the initial state (E_u/E_i) are shown in Table 2. The relation between E_u/E_i and moisture content was linear in the range 0%–10% moisture content (Kubojima, unpublished data); E_u/E_i at u% moisture content was then calculated by substituting u into the linear equation. The experimental values of E_u/E_i are larger than the calculated values with one exception. Moreover, the crystallinity index increased. Hence, it is safe to say that Young's modulus is increased by crystallization as well as by the decreased equilibrium moisture content, and that the crystallization is more predominant than the degradation during the initial stage of the heat treatment, whereas the latter is predominant as the heating time increases.

We investigated whether oxidation in air influenced the vibrational and fine structural properties. As mentioned above, there were clear differences in the changes of wood properties between the atmospheres at 200°C: E/ϱ, G/ϱ, Cr, and L decreased more in air than in nitrogen gas after the initial stage. It is notable that moisture content may not be equal at the same heating time for the two atmospheres. The calculated maximum differences in the range of 0%–10% moisture content of E_L and E_R are 0.012 point and 0.029 point, respectively, whereas the average of the differences are 0.023 point and 0.041 point, respectively. It is implied that E/ϱ, G/ϱ, Cr, and L decreased more in air than in nitrogen gas because of oxidation in air.

Table 2. Effect of equilibrium moisture content on the change of Young's modulus by 0.5-h treatment

Temperature (°C)	u (%)	E_{Lu}/E_{Li}		E_{Ru}/E_{Ri}	
		Calc.	Exp.	Calc.	Exp.
120	7.6	1.002	1.007	1.006	1.024
160	6.4	1.004	1.022	1.010	1.048
200	1.3	1.010	1.017	1.026	1.021

u, equilibrium moisture content; L, R, longitudinal and radial directions, respectively; E_i, Young's modulus at initial state; E_u, Young's modulus at u% moisture content; Calc.: calculated data based on the relation between Young's modulus and moisture content; Exp., experimental data.

Conclusions

Sitka spruce intended for use as piano soundlboards was heated in nitrogen gas or air at temperatures of 120°–200°C for periods of 0.5 to 16.0 h. The following results were obtained.

1. The value of ϱ decreased at higher temperatures and longer heating times. Specific Young's modulus (E_L/ϱ and E_R/ϱ), specific shear modulus (G_{LT}/ϱ and G_{RT}/ϱ), Cr, and L increased initially and remained constant after this stage at 120°C and 160°C, whereas they increased initially and decreased later at 200°C. The loss tangent ($\tan\delta_L$) increased under all conditions, whereas $\tan\delta_R$ increased at 120°C and decreased at 160°C and 200°C.
2. From the investigation of E_u/E_i, it is safe to say that Young's modulus is increased by crystallization as well as the decrease in equilibrium moisture content, and that crystallization is predominant, rather than degradation, at the initial stage of the heat treatment; the latter is predominant as the heating time increases.
3. It is implied that E/ϱ, G/ϱ, Cr, and L decrease more in air than in nitrogen gas because of oxidation in air.

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