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Effects of heating humidity on the physical properties of hydrothermally treated spruce wood

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Abstract

To clarify the effects of humidity during heating on the physical properties of hydrothermally treated wood, Sitka spruce wood was heated in an autoclave at 120°C and different heating humidity (HRH), and their equilibrium moisture content (EMC), specific dynamic Young's modulus (E'/ρ), and mechanical loss tangent ($\tan\delta$) were measured at 25°C and 60% RH before and after the hydrothermal treatment. Higher values of HRH resulted in greater loss in weight (WL) because of the acceleration of thermal degradation in the presence of moisture. The time–humidity superposition was applicable to the changes in WL. The EMC was minimized by heating at intermediate HRH (60%), but it recovered significantly after the wood was moistened at 100% RH. This fact suggested that the reduction in hygroscopicity due to hydrothermal treatment included both reversible and irreversible effects. The reversible effect was not observed when the wood was heated at 92% HRH or above. After the moistening, the EMC value of hydrothermally treated wood decreased monotonically with increasing HRH and WL. An irreversible chemical change such as decomposition of hemicelluloses was responsible for the irreversible effect, whereas the reversible effect may have resulted from the annealing of amorphous wood polymers. After hydrothermal treatment at 80% HRH or lower, E'/ρ increased and $\tan\delta$ decreased mainly because of the reduction in EMC. On the other hand, high-humidity heating (92% HRH) resulted in significant decrease in E'/ρ and remarkable increase in $\tan\delta$ probably because of the depolymerization of hemicelluloses. The color of wood was darkened by the hydrothermal treatment, and the CIELAB color parameters of hydrothermally treated wood were closely connected to the WL.

Introduction

Hydrothermal treatment is well known as an effective method of wood modification. It reduces the hygroscopicity of wood, which directly improves the dimensional stability and indirectly stabilizes the mechanical properties depending on the moisture content. The hydrothermal treatment is also an important process to fix the shape of compressed and bent wood. The basic characteristics and recent applications of hydrothermally treated wood were reviewed by Sandberg et al. (2013).

Another important aspect of hydrothermal treatment is the acceleration of ageing, because various chemical changes involved in long-term ageing are more or less accelerated by elevating temperatures. In fact, the characteristics of aged wood, such as enhanced rigidity, improved stability, reduced ductility, and darkened color, are qualitatively reproduced by heating at high temperature (Obataya 2010, Matsuo et al. 2011).

Accelerated ageing has been an interest of artisans making wooden musical instruments because the acoustic quality of wood is thought to be improved by long-term ageing. In fact, old lumber is often priced higher than recently cut timber for making the soundboards and bass bars of stringed instruments. In addition, a recent investigation has implied that the acoustic quality of red pine wood was improved by long term ageing (Noguchi et al. 2012). If such effects of ageing can be artificially reproduced by hydrothermal treatment, it may allow the efficient production of quality lumber for musical instruments.

Quality musical instruments require appropriate mechanical and vibrational properties as well as color that dominate the aesthetic value of the instruments. Although the mechanical properties and color of hydrothermally treated wood have been studied extensively (Millett and Gerhards 1972, Kubojima et al. 2000, Borrega and Kärenlampi 2008, Tolvaj et al. 2012), little information is available on their vibrational, i.e., dynamic mechanical properties. According to Kubojima et al. (1998), the E'/ρ value of Sitka spruce wood can be enhanced by heating it in dry nitrogen gas, but its acoustic quality is reduced by the significant increase in tanδ. This indicates that it is still uncertain whether hydrothermal treatment is an effective method to improve the acoustic quality of wood.

It should be remembered that natural ageing proceeds at intermediate relative humidity, and the moisture affects much of the thermal degradation of wood polymers as well as the thermally activated crystallization of cellulose (Bhuiyan et al. 2000, Tjeerdsma and Militz 2005). Therefore, when we try to reproduce the effects of ageing by hydrothermal treatment, we need to clarify the effects of heating humidity (relative humidity during heating, HRH) on the physical properties of wood. However, hydrothermal treatments are usually conducted in the absence of moisture (oven heating, 0% HRH) or in saturated water vapor (steaming, 100% HRH), and only a few investigations have focused on the effects of HRH (Borrega and Kärenlampi 2007, 2008).

The effects of hydrothermal treatment have so far been explained by irreversible chemical changes such as decomposition, cross-linking, and recrystallization of wood constituents (Sandberg et al. 2013). However, it has been suggested that the reduced hygroscopicity of oven-heated wood was reasonably recovered once it was exposed to high humidity (Obataya and Tomita 2002). This finding requires us to reconsider the recoverable i.e., temporary change in hygroscopicity, due to the hydrothermal treatment.

This study aims to evaluate the effects of HRH on the hygroscopicity, vibrational properties, and color properties of wood in terms of a valued material for making musical instruments. The temporary effects of the treatment on the properties were also considered. The results will contribute to the acoustically and aesthetically precise imitation of aged wood for musical instruments.

Materials and methods

Wood specimens

A Sitka spruce lumber selected for use as harp soundboard was cut into strips with dimensions of 1.6 mm (tangential) × 15 mm (radial) × 120 mm (longitudinal). The average air-dry density was 408 kg/m^3 with a standard deviation of 25 kg/m^3. To remove the effects of the hygroscopic history during seasoning, the specimens were previously moistened at 25°C and 100% RH for at least 5 days, followed by vacuum drying on P_2O_5 at room temperature for a week. The specimens were then conditioned at 25°C and 60% RH for more than 1 month to determine their equilibrium moisture content (EMC) and vibrational properties. Some specimens showing irregular vibrational properties were eliminated and finally 168 specimens were selected. Those selected specimens were then divided into 21 groups as the average values of vibrational properties of each group to be almost the same.

Next, the specimens were conditioned at 25°C and 0%, 30%, 60%, 80%, or 100% RH before they were subjected to the hydrothermal treatment. Five groups i.e. 40 specimens were used for each conditioning humidity.

Hydrothermal treatment

An autoclave equipped with a thermocouple and pressure sensor (PHS-B-500KP, Kyowa Dengyo Co.) was used for the hydrothermal treatment of the wood specimens. The apparatus is illustrated in Figure 1. The inner dimensions of the autoclave were 200 mm × 150 mm × 80 mm. According to Chédeville et al. (2012), the chemical reactions induced by heating at 150°C or higher are qualitatively different from those at 130°C or lower. Therefore, we employed 120°C as the treatment temperature because our final goal was the reproduction of naturally aged wood. The wood specimens previously conditioned at different values of RH were placed in the autoclave with a certain amount of water depending on the expected HRH. The autoclave was then tightly closed and heated to 120°C. Eight specimens including 3 spare specimens were used for each treatment condition. The temperature and pressure in the autoclave reached the expected levels within 1 h. After the heat treatments, which lasted for 1, 2, 4 and 7 days, the specimens were removed from the autoclave, immediately cooled to room temperature, and vacuum-dried on P_2O_5 at room temperature for a week to determine their absolutely dry weight. Finally, the specimens were conditioned at 25°C and 60% RH to determine their EMC and vibrational properties.

Vibration test

The specific dynamic Young's modulus (E'/ρ) and mechanical loss tangent ($\tan\delta$) of the wood specimens were determined by the free–free flexural vibration method (Obataya et al. 2000). The value of E'/ρ was calculated from the resonant frequency of the first mode of vibration, and the value of $\tan\delta$ was calculated from the half width of the resonance curve. The vibration test was conducted in a chamber where the temperature and humidity were kept at precisely 25°C and 60% RH, respectively.

Moistening

Both the unmodified and hydrothermally treated wood specimens were conditioned at 25°C and 100% RH for at least 5 days. This process is referred to as "moistening" in this paper. After the moistening, the specimens were air-dried under ambient conditions for a few days, completely vacuum-dried on P_2O_5 at room temperature for a week, and then conditioned at 25°C and 60% RH to measure their EMC and vibrational properties. It was confirmed that the moistening did not affect the absolutely dry weights of the specimens.

Color measurement

The CIELAB color parameters (L^*, a^*, b^*) were used to evaluate the color of the wood specimens. The color of the edge-grain surface of the untreated and hydrothermally treated wood specimens was measured with a spectrophotometer (UV-3100PC, Shimadzu Co.) using a D65 light source and an observation angle of 10°. The rectangular sensor head of the spectrophotometer had dimensions of 13 mm × 30 mm. Five specimens were tested for each treatment condition, and measurements were obtained at three locations in each specimen. The average values and standard deviations were calculated from 15 sets of data measured for each treatment condition.

Results and discussion

Fluctuation in temperature and humidity during hydrothermal treatment

In this paper, the average relative humidity in the autoclave is referred to as HRH, which is distinguished from RH where the wood specimens were conditioned and moistened at room temperature. HRH is defined as P/P_0, where P is the pressure inside the autoclave excluding that of air, and P_0 is the pressure of saturated water vapor at a given temperature. Figure 2 shows the changes in the heating temperature (T) and HRH at the beginning of hydrothermal treatment. Both T and HRH reached the expected values within 1 h, after which T remained constant. Hereafter, the time for the elevation of temperature (1 h) is neglected and the duration of each specimen's treatment at constant T is regarded as the heating duration (t). Since we used a closed system, HRH fluctuated to some extent probably because of the moisture sorption of modified wood specimens as well as the vaporization of decomposed wood constituents. However, such a fluctuation in HRH (average fluctuation: ± 5%) was not large enough to mask the effects of HRH ranging from 0 to 95%. As an exception, the value of HRH is regarded as 0% when a wood specimen is heated in the absence of moisture, while the vaporization of decomposition products resulted in non-zero values of P.

Loss in weight due to the hydrothermal treatment

As a part of the wood constituents was depolymerized and lost by heating, the loss in weight (WL) of an absolutely dried specimen is an indication of the degree of thermal degradation. Actually, various physical properties such as EMC and strength of heat-treated wood can be expressed as functions of WL irrespective of heating temperature (Millett and Gerhards 1972, Obataya et al. 2002, 2006, Borrega and Kärenlampi 2008). The WL values at different HRH are listed in Table 1, and

Figure 3 shows the changes in WL with the elapse of heating time. Longer heating at higher HRH resulted in greater WL, and the value of WL was approximated by the following empirical equation:

$$\text{WL (\%)} = k_{\text{H}}\, t^{\,b}, \quad (1)$$

where the factors k_{H} and b represent the effects of HRH on the rate of thermal degradation. The factors k_{H} and b are plotted against HRH in Figure 4. The k_{H} value strongly depended on that of HRH, while the b value was independent of the HRH value. The HRH dependency of k_{H} was not sigmoid-shaped, but similar to the sorption isotherm of dissolved or multi-layered water, implying that the amount of dissolved water, rather than that of hydrated water, was responsible for the acceleration of thermal degradation with respect to WL.

Here we define the shift factor a_{H} as

$$a_{\text{H}} \equiv \frac{t_{\text{H}}}{t_{\text{ref}}}, \quad (2)$$

where t_{ref} is the test time at a reference HRH, and t_{H} is the time required to give the same response at the test HRH. When the b value is almost constant (≈ 0.756), the shift factors at different HRH can be calculated from the k values as follows:

$$a_{\text{H}} = \left(\frac{k_{\text{ref}}}{k_{\text{H}}}\right)^{\frac{1}{b}}, \quad (3)$$

where k_{ref} is the k value at a reference HRH and k_{H} is that at the test HRH. Here we choose 0% as the reference HRH, and the result of the time–humidity superposition is exhibited in Figure 5. The different curves in Figure 3 are well superposed into a single curve. Since the time–humidity equivalence has not been proved yet, the physical meaning of the shift factor a_{H} is still unclear. However, such a time–humidity superposition may be practically useful to predict the degree of thermal degradation at different HRH.

Reversible and irreversible changes in hygroscopicity

The most promising feature of hydrothermally treated wood is reduced hygroscopicity. The hygroscopicity of wood is usually evaluated by measuring the value of EMC under ambient conditions. Table 1 lists the EMC values of hydrothermally treated wood specimens at 25°C and 60% RH, and those values are plotted against the WL in Figure 6a. The standard deviation within groups is not represented because it was small enough to be ignored. The lowest EMC was achieved by heating the specimens at intermediate HRH (35–62%). Similar results have already been reported by Borrega et al. for the hydrothermal treatment of Norway spruce: the EMC value of wood that was treated at intermediate humidity (50% HRH) was lower than that treated at 0 or 100% HRH at the same WL (Borrega and Kärenlampi 2007). Such a particular effect of intermediate HRH seems remarkable for the effective dimensional stabilization of wood, but it should be remembered that the reduced EMC of the hydrothermally treated wood is partly recoverable (Obataya and Tomita 2002). As shown in Figure 6b, the value of EMC of hydrothermally treated wood was considerably recovered by moistening, and the plots of EMC *vs.* WL lie on a single curve regardless of the value of HRH. In Figure 7, the EMC values of wood heated for 2 days are plotted against the HRH values. The largest reduction in EMC was achieved at 60% HRH, but most of it was reversed by the moistening. Consequently the EMC value showed monotonic decrease with increasing HRH after the moistening. Similar trend was recognized in the other wood specimens heated for 4 days or longer. Those results indicate that the EMC value of wood was temporarily reduced by the hydrothermal treatment, particularly when the wood was heated at intermediate HRH.

The recovery in EMC due to the moistening did not result from insufficient conditioning because the wood specimens were conditioned for more than one month and their mass was confirmed to be completely equilibrated prior to the determination of EMC. Hygroscopic hysteresis did not account for the recovery in EMC because the EMC values were always determined from an adsorption process: the wood specimens were always vacuum-dried and then conditioned at 25°C and 60% RH prior to the determination of EMC.

Borrega and co-researchers explained the particular effect of intermediate HRH by hornification (Borrega and Kärenlampi 2007). They speculated that the accessibility of wood is reduced by the dehydration of amorphous wood polymers during or after the heating. In our study, however, the EMC was recovered considerably by the moistening, whereas the term hornification is generally used for the irreversible reduction in accessibility and mobility of polymers due to drying (Kato and Cameron 1999). Therefore, the hornification is excluded from the present discussion.

Any irreversible changes such as hydrolysis, condensation, and crystallization of wood constituents cannot explain the significant recovery of EMC. We speculate that physical ageing or annealing of amorphous wood polymers was responsible for the temporary reduction in EMC due to the hydrothermal treatment. When wood is dried from its natural green state, certain stress or strain remains in the amorphous region because its shrinkage is restricted by the rigid and hydrophobic crystalline part. Such distortion is similar to that in quenched polymers, and it remains unrecovered unless the wood polymers are plasticized with moisture under humid conditions. Upon heating, the remaining stress is relaxed with the thermal activation of amorphous polymers. Such an annealed structure reduces the mobility of wood polymers to restrict the moisture sorption at room temperature. On the other hand, the annealed wood polymers recover their initial or natural conformation when they are well plasticized with moisture at 100% RH, and therefore, the wood recovers its original hygroscopicity after the moistening.

Higher HRH must involve faster relaxation of internal stress, but the temporary reduction in EMC is slighter at higher HRH because lesser internal (drying) stress remains in the wood. The internal stress is maximized in absolutely dry condition, but the temporary reduction in EMC is not maximized at 0% HRH, because the amorphous wood polymers are not mobile enough to relax completely in the absence of moisture. At intermediate HRH, the internal stress is not maximized, but the annealing of amorphous wood polymers is easier than that in absolutely dry condition because a certain amount of moisture acts as a plasticizer to accelerate the rearrangement of wood polymers. Consequently, the annealing effect i.e. temporary reduction in EMC is maximized at intermediate HRH.

Although it is difficult to experimentally prove that hypothesis, dynamic infrared analysis will be a useful method to observe the slight conformational changes in amorphous wood polymers (Åkerholm and Salmén 2001). X-ray diffractometry may also give useful information on the distortion of amorphous wood polymers, as it can detect the deformation of cellulose crystals accompanied by the shrinkage and swelling of amorphous wood polymers (Abe and Yamamoto 2006).

Another potential mechanism underlying the temporary reduction in hygroscopicity by hydrothermal treatment is the closure of micropores. Kojiro et al. (2008a) determined the presence of micropores smaller than 0.6 nm in oven-heated cypress wood by CO_2-adsorption measurements. The micropores decreased in number with heating, but increased after rewetting and drying. Similar reversible changes in micropores were also recognized in wood that was aged for over a thousand years (Kojiro et al. 2008b). This coincides with the temporary reduction in EMC from hydrothermal treatment and its recovery by moistening, and it was possibly responsible for the enhanced rigidity of aged and hydrothermally treated wood, as well as the reduction in hygroscopicity by repeated humidity cycling (Esteban et al. 2005).

From a practical point of view, the temporary effect of heating should be taken into consideration when we evaluate the dimensional stability and moisture-dependent mechanical properties of hydrothermally treated wood. When the hygroscopicity of hydrothermally treated wood is evaluated just after the treatment, its performance is possibly overestimated.

After the moistening, the EMC of hydrothermally treated wood was still lower than that of unmodified wood, and it decreased monotonically with increasing HRH, as shown in Figure 7. The unrecoverable i.e., irreversible reduction in EMC reflects the irreversible chemical changes in wood constituents, such as the loss of extractives and hygroscopic hemicelluloses, crystallization of cellulose, and cross-linking of lignin (Wikberg and Maunu 2004, Tjeerdsma and Militz 2005).

The value of EMC decreased with increasing WL irrespective of HRH, but it increased instead after WL reached 5%, as shown in Figure 6b. This slight increase in EMC is speculated to be due to the moisture sorption of low-molecular-weight sugars generated by the hydrolysis of hemicelluloses.

Irreversible changes in vibrational properties

The parameters E'/ρ and $\tan\delta$ are important factors determining the acoustic conversion efficiency (ACE). The ACE is defined as $\sqrt{E'/\rho^3}/\tan\delta$, and when the ρ does not vary within a species, the ACE is dominated by the E'/ρ and $\tan\delta$ of wood, depending on the microstructure of the wood cell wall (Obataya et al. 2000). It has been proved theoretically (Yano and Matsuhisa 1991) and experimentally (Ono 1996) that higher ACE gives greater amplitude of sound radiation. The vibrational properties of 105 unmodified wood specimens are listed in Table 2. Although the E'/ρ and $\tan\delta$ values of unmodified wood specimens varied to some extent, changes in those values due to hydrothermal treatment did not vary widely. Therefore, the average values of five specimens are exhibited in Figures 8–10. Figure 8 shows the changes in E'/ρ and $\tan\delta$ values due to hydrothermal treatment at 62% HRH for over 7 days. The significant increase in E'/ρ and decrease in $\tan\delta$ indicate that the acoustic quality of wood could be improved by the hydrothermal treatment at intermediate HRH. However, the effect was diminished after the moistening treatment involving the recovery of hygroscopicity. Thus, the temporary effects had to be eliminated by the moistening treatment otherwise the acoustic quality of hydrothermally treated wood was overestimated. It also required us to reconfirm the past results for which the temporary effects were not taken into consideration.

In Figure 9, the changes in E'/ρ and $\tan\delta$ due to the hydrothermal treatment are plotted against WL. Note that those changes reflect only the irreversible effects of hydrothermal treatment because the wood specimens were moistened before the vibration test. There were two different trends depending on the value of HRH. After the hydrothermal treatment at 80% HRH or lower, E'/ρ increased and $\tan\delta$ decreased slightly or remained unchanged. Those changes were dominated by the reduction in EMC, as described later. On the other hand, high-humidity heating (92% HRH) induced a remarkable reduction in E'/ρ and a steep increase in $\tan\delta$, mainly due to the depolymerization of hemicelluloses. The hemicelluloses are an important constituent for maintaining the fiber-reinforced structure of the wood cell wall (Åkerholm and Salmén 2001), but those polysaccharides are readily depolymerized by heating under moist conditions (Tjeerdsma and Militz 2005). Since we used a closed system, a part of the decomposition residue such as acetic acid may have accelerated further acid-catalyzed degradation (Tjeerdsma et al. 1998). A part of the hemicelluloses remained in the wood cell wall, but it would have hardly contributed to the rigidity of wood. Low-molecular-weight sugars generated by the decomposition of hemicelluloses were possibly responsible for the extraordinarily high $\tan\delta$ of the hydrothermally treated wood (Obataya and Norimoto 1999).

Figure 10 shows the changes in E'/ρ and $\tan\delta$ values due to the hydrothermal treatment plotted against the EMC. When the value of HRH was 80% or lower, the E'/ρ and $\tan\delta$ values of the hydrothermally treated wood exhibited moisture dependencies close to those of unmodified wood, as shown by the crosses and broken lines in the plots. This indicates that the slight increase in E'/ρ and decrease in $\tan\delta$ due to the hydrothermal treatment resulted mainly from the reduction in EMC. Since the value of E'/ρ of the treated wood was slightly higher than that of untreated wood at the same EMC, the crystallization of cellulose might have been involved as a minor effect. On the other hand, the value of E'/ρ was considerably reduced and the value of $\tan\delta$ was remarkably enhanced by high-humidity heating (92% HRH), whereas the value of EMC was not effectively reduced. As described above, such adverse effects of high-humidity heating are attributed to the depolymerization of hemicelluloses.

From a practical point of view, an intermediate HRH is advisable for the quality enhancement of wooden soundboards. By heating at an intermediate HRH, the hygroscopic stability of wood is improved with the least heating time, while its acoustic quality is not degraded or slightly improved. When wood is always used under dry conditions, as is the case for musical instruments, hydrothermally treated wood can be used without moistening treatment. In that case, the acoustic quality of wood is expected to be significantly improved, as exhibited in Figure 8.

Changes in color

The color of wood specimens was evaluated by lightness (L^*) and color coordinates (a^* and b^*) based on the CIELAB color parameters. Through both oven heating and steaming, the color of wood is generally darkened, which is expressed by decreasing L^* value. The change in chromatic parameters (a^* and b^*) varies depending on the wood species. The light color of some softwood such as spruce and Japanese cypress becomes redder (expressed by increasing a^* value) and more yellow (increasing b^* value) at the beginning of the treatment, and then those colors are gradually lost (decreasing a^* and b^* values) (Brischke et al. 2007, Matsuo et al. 2010, Tolvaj et al. 2012).

Figure 11 shows the values of L^* of hydrothermally treated wood plotted against WL. With increasing WL, L^* decreased monotonically and the plots obtained at different values of HRH overlap to form a single curve. This suggests that the loss in weight and darkening of color were apparently dominated by the same chemical reaction, and that reaction was simply accelerated by elevating HRH. In Figure 12a, the L^* values are plotted against the elapse of heating time, and the result of time–humidity superposition using the shift factor a_H was exhibited in Figure 12b. Since L^* and WL were tightly connected, the values of the shift factor a_H calculated from WL are applicable to the changes in L^* due to the hydrothermal treatment.

Figure 13 shows a^* and b^* values of hydrothermally treated wood as functions of WL. Those parameters increased at the beginning and then decreased, which coincided with previous studies of oven-heated and steamed wood. In contrast to L^*, the values of a^* and b^* had wide variations even at the same WL and were not simple functions of WL, presumably because the chemical reactions dominating the changes in a^* and b^* were complicated and different from those responsible for the changes in L^*. However, because the variations in each color parameter were small enough in terms of sensory perception, this type of hydrothermal treatment with appropriate treatment duration would enable us to modify the wood color or to imitate the antique appearance of aged wood. Furthermore, the color parameters could be an index of the degradation of other properties that coincided with treatment intensity (Brischke et al. 2007). This would help us roughly and quickly monitor the changes of other properties during hydrothermal treatment.

Conclusions

Sitka spruce wood was hydrothermally treated in a closed autoclave at 120°C and various values of relative humidity (HRH) for 1–7 days. Higher HRH resulted in greater loss in weight. The EMC of wood was minimized by heating at intermediate HRH, but it was sufficiently recovered after moistening. The temporary reduction in hygroscopicity was attributed to the annealing-like effects of hydrothermal treatment. After moistening, the value of EMC of the hydrothermally treated wood showed monotonic decrease with increasing HRH. After hydrothermal treatment at low and intermediate HRH followed by moistening treatment, the value of E'/ρ increased and the value of tanδ decreased slightly or remained unchanged, mainly because of the reduction in EMC. In contrast, hydrothermal treatment at high HRH resulted in marked decrease in E'/ρ and increase in tanδ probably due to the depolymerization of hemicelluloses. The color change due to the hydrothermal treatment was tightly connected to the loss in weight.

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Table 1 Average values of weight loss (WL) and equilibrium moisture content at 25°C and 60% RH (EMC) of wood specimens hydrothermally treated at different heating relative humidity (HRH).

Heating duration (day)	HRH (%)		WL (%)	EMC (%)[a]		
	Average			Unmodified	After hydrothermal treatment	After moistening treatment
1	0	0	0.2	11.4	10.3	11.3
2		0	0.3	11.1	9.5	10.7
4		0	0.4	11.3	9.6	10.6
7		0	0.7	11.0	8.9	10.3
1	35	39	0.3	11.3	8.7	11.0
2		39	0.7	11.3	8.2	10.7
4		29	0.9	11.3	7.8	10.3
7		33	1.6	11.3	7.1	10.1
1	62	64	0.6	11.5	8.3	10.8
2		64	0.9	11.1	7.4	10.1
4		63	1.8	11.3	7.2	10.0
7		57	2.1	11.0	6.7	9.4
1	80	81	0.9	11.4	8.8	10.4
2		81	1.4	11.3	8.2	9.9
4		82	2.6	11.1	7.8	9.4
7		77	3.8	11.3	7.2	9.0
1	92	95	1.8	11.6	9.8	10.0
2		93	2.9	11.2	9.2	9.4
4		90	5.5	11.3	9.1	9.5
7		89	7.9	11.0	9.7	9.7

a, The EMC values were always determined in adsorption process: the wood samples were vacuum dried on P_2O_5 at room temperature and then conditioned at 25°C and 60% RH to determine their EMC values.

Table 2 Average values of density (ρ), equilibrium moisture content (EMC), dynamic Young's modulus (E'), specific dynamic Young's modulus (E'/ρ), and mechanical loss tangent ($\tan\delta$) of 105 unmodified spruce wood specimens tested at 25°C and 60% RH.

ρ (kg/m^3)	EMC (%)	E' (GPa)	E'/ρ ($\times 10^{-6}$ m^2/s^2)	$\tan\delta$ ($\times 10^4$)
408 (25)	11.3 (0.2)	11.0 (1.2)	26.9 (3.0)	76 (7)

Values in parenthesis indicate standard deviations.

Figure captions

Figure 1 Apparatus for hydrothermal treatment.

a, Wood specimens; b, pressure sensor; c, leak bulb; d, thermocouple; e, stainless steel box; f, insulation foam; g, heater; h, hot plate.

Figure 2 Changes in temperature (*T*) and relative humidity (HRH) inside the autoclave at the beginning of hydrothermal treatment.

Figure 3 Average value of loss in weight (WL) due to hydrothermal treatment at the indicated HRH as a function of treatment time (*t*).

Open circles, treated at 120°C and 0% HRH; *open triangles*, 35% HRH; *open squares*, 62% HRH; *open diamonds*, 80% HRH; *solid circles*, 92% HRH.

Figure 4 Effects of HRH on the reaction parameters.

Filled circles, k_H values; *open circles*, *b* values.

Figure 5 WL due to hydrothermal treatment as a function of superposed heating time (t/a_H).

See Figure 3 for definition of symbols.

Figure 6 Average values of equilibrium moisture content at 25°C and 60% RH (EMC) for hydrothermally treated wood plotted against WL.

a, Before moistening treatment; b, after moistening treatment. See Figure 3 for definition of symbols.

Figure 7 Effects of HRH on EMC of hydrothermally treated wood.

Open circles, hydrothermally treated at 120°C for 2 days; *filled circles*, hydrothermally treated and moistened at 25°C and 100% RH; *cross and dashed line*, EMC value of unmodified wood.

Figure 8 Changes in specific dynamic Young's modulus (E'/ρ) and mechanical loss tangent ($\tan\delta$) due to hydrothermal treatment at 120°C and 62% HRH with the elapse of heating time (*t*).

Squares, changes in E'/ρ; *circles*, changes in $\tan\delta$; *dashed lines*, hydrothermally treated; *solid lines*, hydrothermally treated and moistened.

Figure 9 Changes in E'/ρ and tanδ due to hydrothermal treatment at 120°C as a function of WL

See Figure 3 for definition of symbols. The E'/ρ and tanδ values were determined after moistening treatment: only the irreversible effects are shown.

Figure 10 Changes in E'/ρ and tanδ due to hydrothermal treatment at 120°C plotted against EMC at 25°C and 60% RH.

See Figure 3 for definition of symbols. Crosses and dashed lines indicate the moisture dependencies of unmodified wood.

Figure 11 Relationship between the lightness (L^*) and WL of hydrothermally treated wood.

See Figure 3 for definition of symbols. Bars indicate standard deviations. Dashed line indicates the average L^* value of unmodified wood.

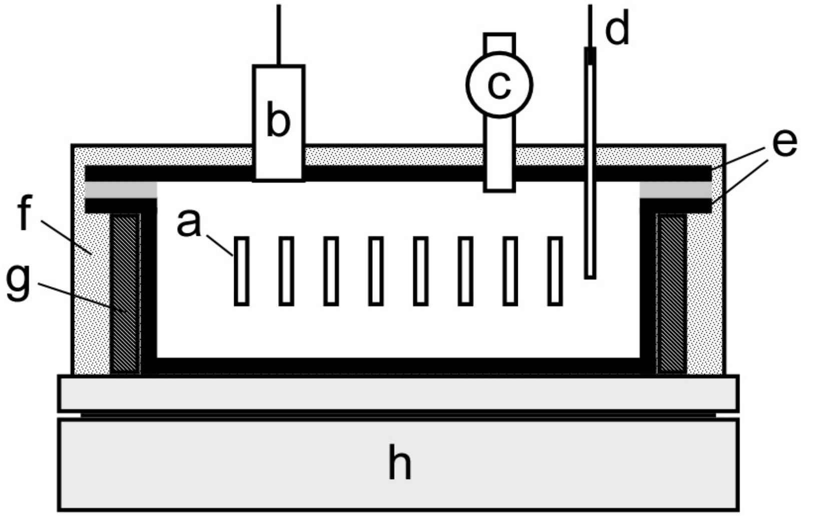
Figure 12 Results of time–humidity superposition using shift factors (a_H) depending on HRH.

See Figure 3 for definition of symbols. Bars indicate standard deviations. Dashed line indicates the average L^* value of unmodified wood.

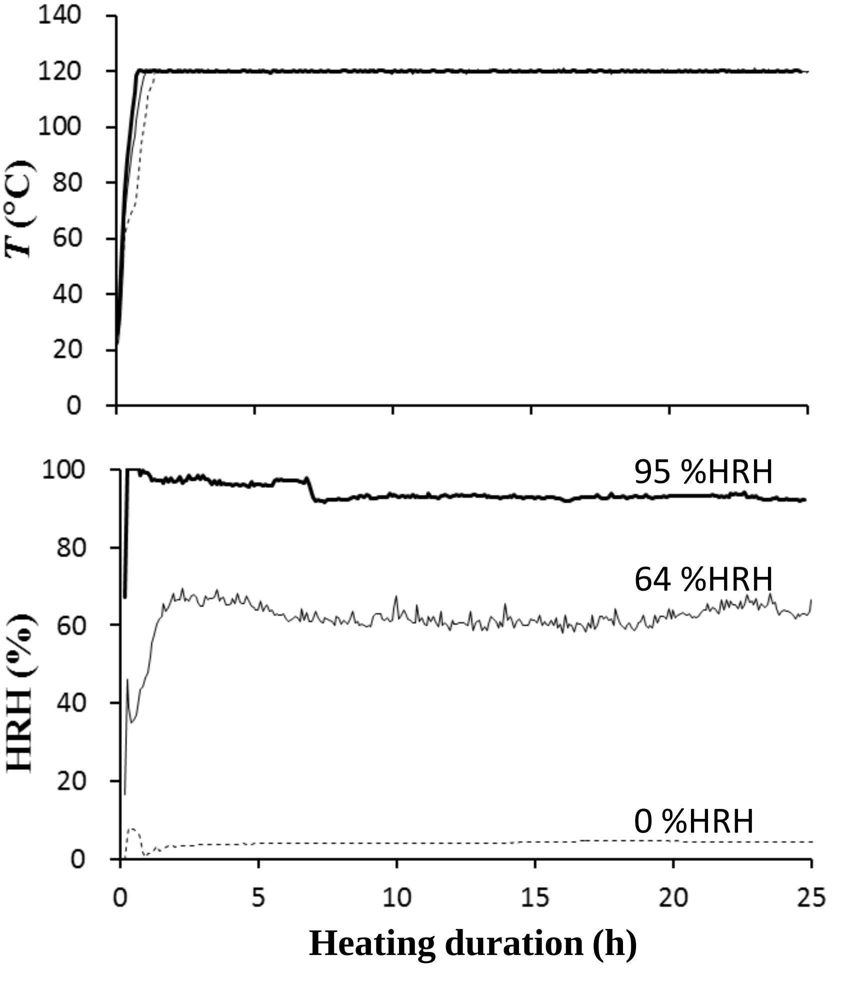
Figure 13 Relationship between the color coordinates (a^* and b^*) of hydrothermally treated wood and WL.

See Figure 3 for definition of symbols. Bars indicate standard deviations. Broken lines indicate the average values of unmodified wood.

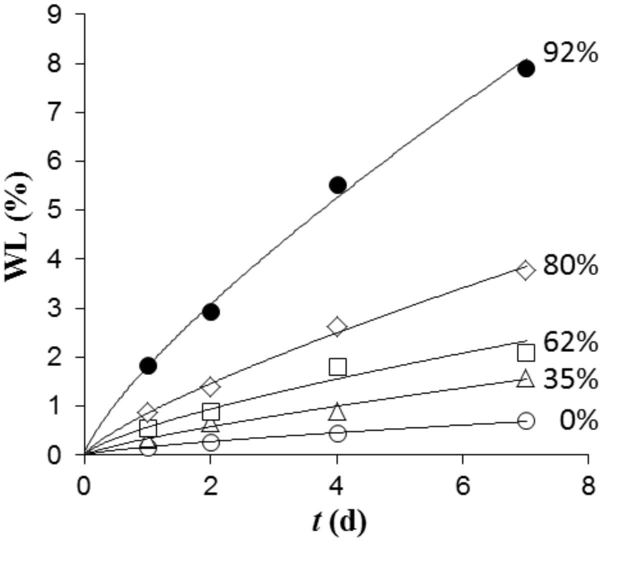
Endo et al. Figure 1



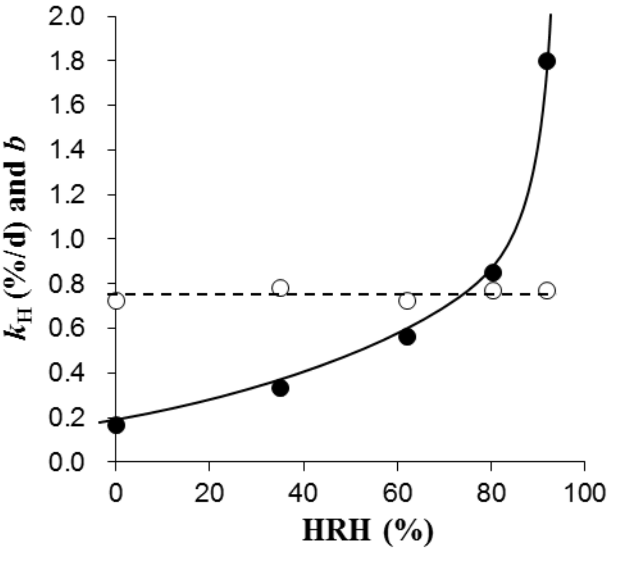
Endo et al. Figure 2



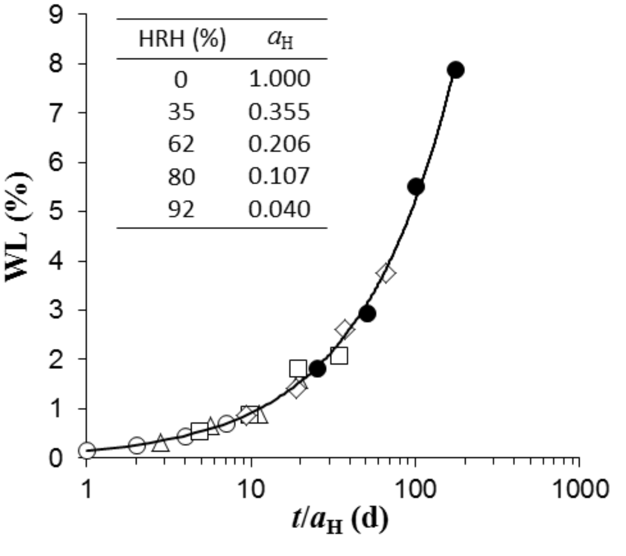
Endo et al. Figure 3



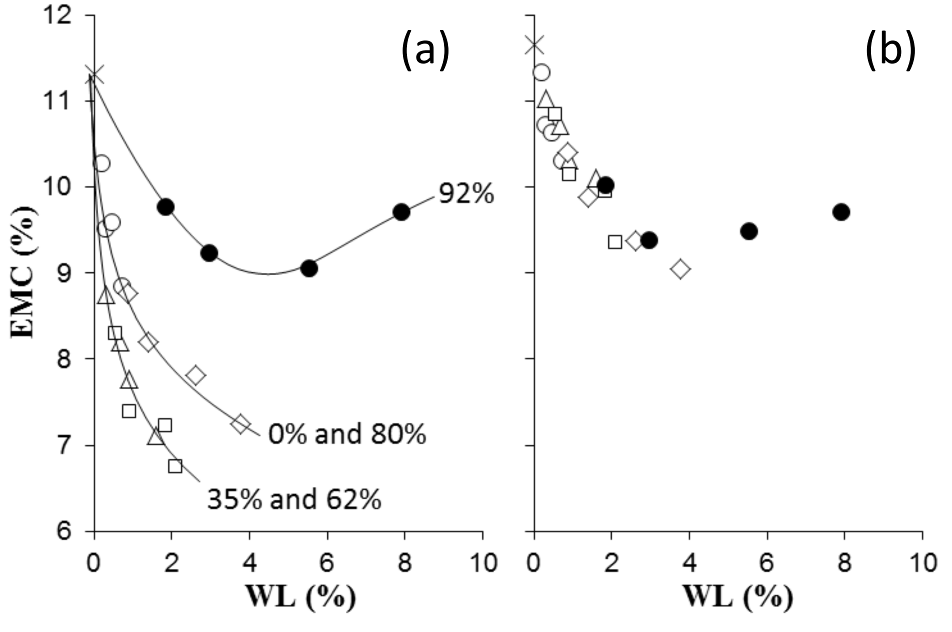
Endo et al. Figure 4



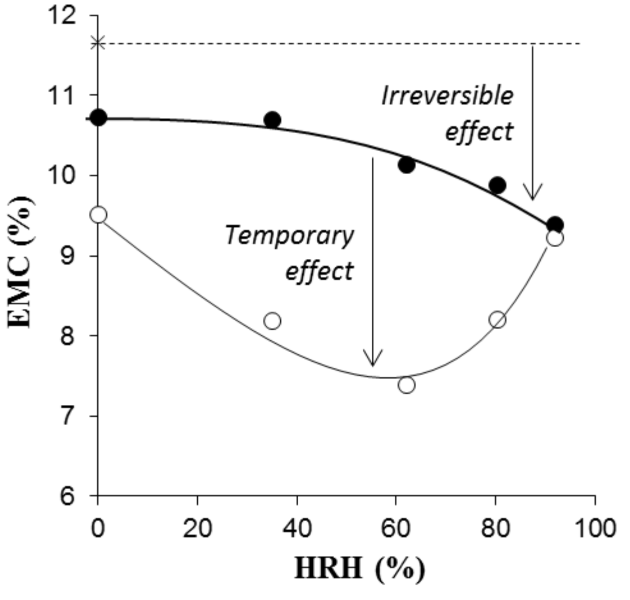
Endo et al. Figure 5



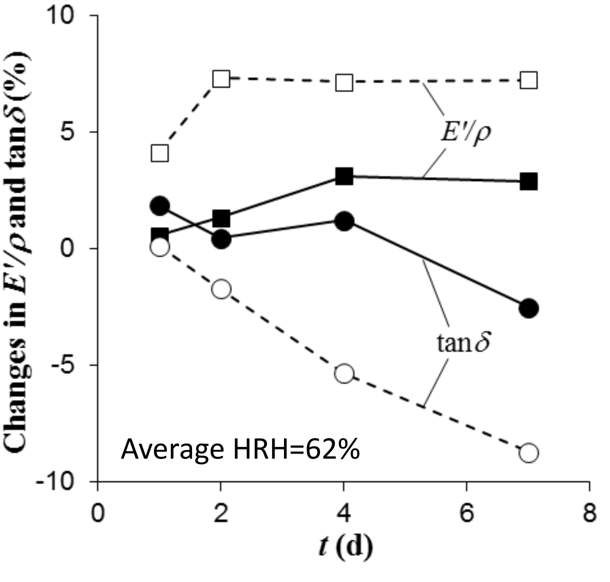
Endo et al. Figure 6



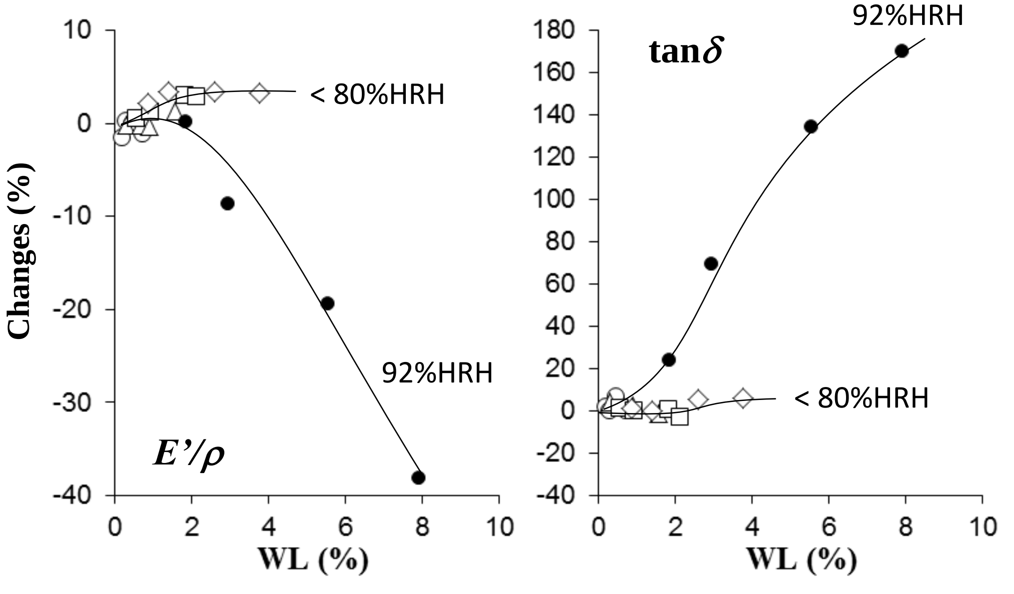
Endo et al. Figure 7



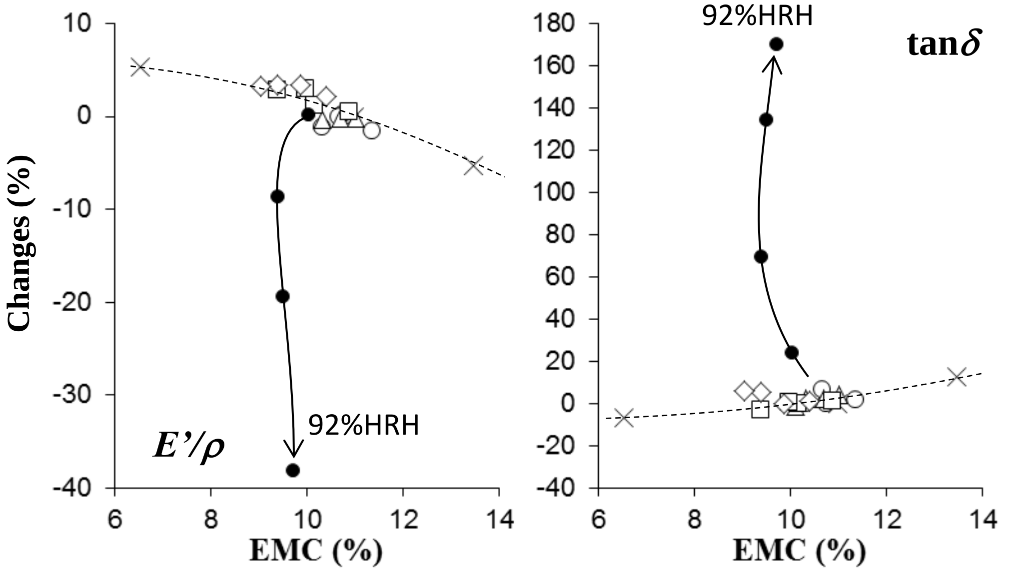
Endo et al. Figure 8



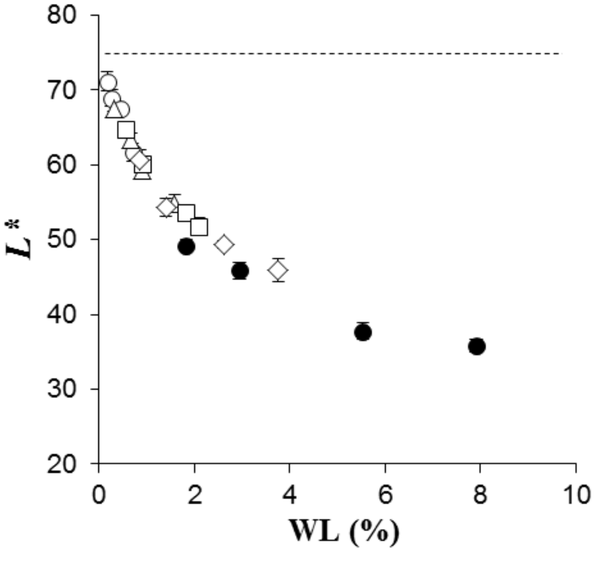
Endo et al. Figure 9



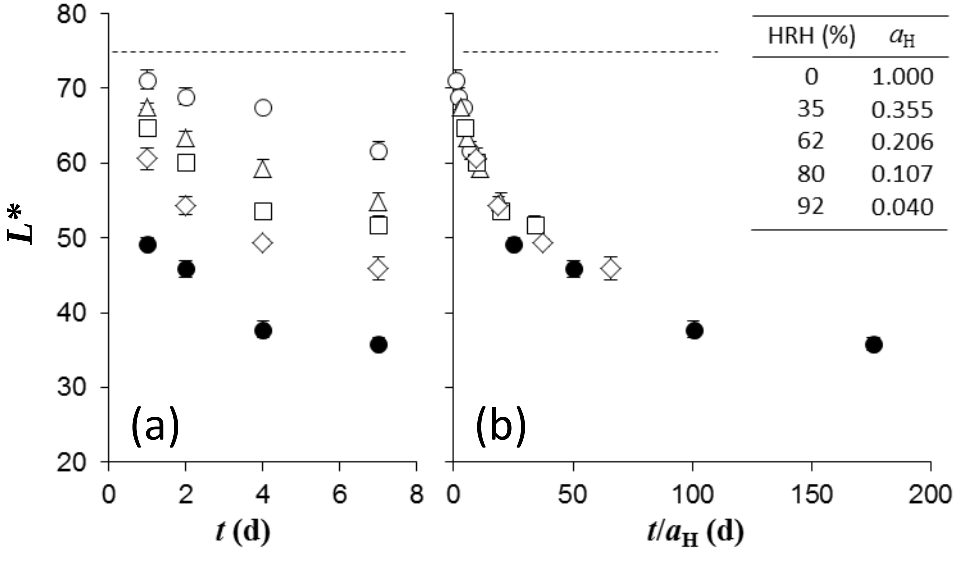
Endo et al. Figure 10



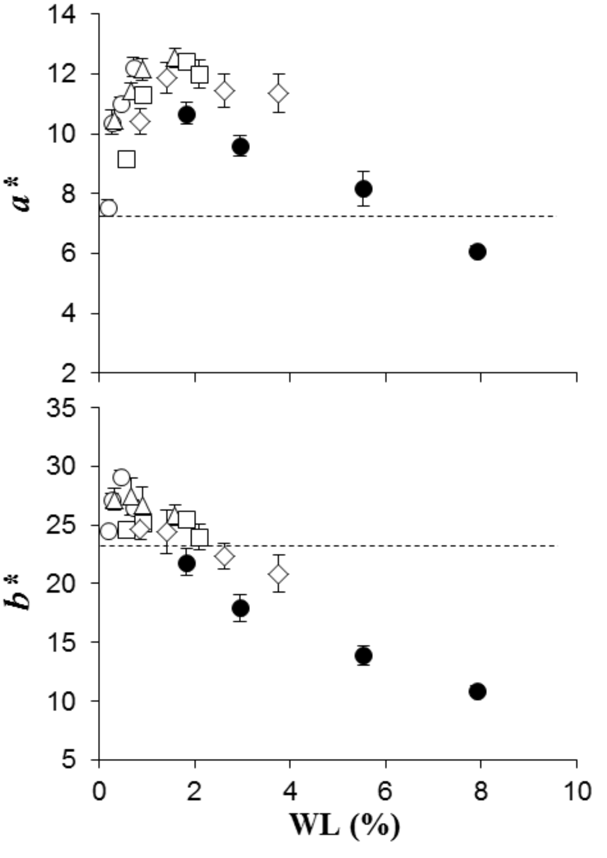
Endo et al. Figure 11



Endo et al. Figure 12



Endo et al. Figure 13



Replies to reviewers' comments for WSAT-D-15-00226

Authors are grateful to all reviewers for their suggestive comments. We have revised our manuscript considering all those comments. Here we reply to each *original comment*. The revised sentences are red-colored in the manuscript.

To Reviewer #1:

* *The term "hydrothermal" is often associated to the presence of liquid water or steam in saturated conditions. Since many of the thermal treatments were here conducted at relative humidities below saturation, I would suggest replacing "hydrothermally" by simply "thermally" in the title.*

In recent articles (e.g. Sandberg et al 2013) “hydrothermal” seems a general term including dry heating as well as steaming, whereas “thermal” is sometimes regarded as “oven heating”. As the present manuscript deals with the effects of steaming (HRH>90%), we would like to use the term “hydrothermal” at this time. I wish the reviewer would accept our decision.

* *Please provide the relative humiditiy values (HRH) of your experiments in the experimental section. Also, be consistent with their use throughout the manuscript. For example, in Fig. 2, the values of 95 and 64% are shown, while in Fig. 3 values of 92 and 62% are shown. Also in the text, sometimes the HRH at about 60% is just referred to as 60%. The use of different values is confusing.*

The actual HRH values for each treatment condition are summarized in Table 1 to prevent any confusions. Unfortunately the HRH value varied to some extent around the target value, because it was technically difficult to achieve a constant HRH over the treatment duration. However, such variations in HRH were not large enough to mask the effects of HRH ranging from 0 to 95%, as mentioned in page 3.

* *Fig. 7 shows the reversible and irreversible effects on EMC for a set of specimens heated at 120°C for 2 days, and therefore with limited weight losses. What was the situation for other specimens, particularly those heated during 7 days and showing a higher weight loss? These needs to be, if not shown, at least mentioned in the text.*

The other specimens also showed significant recovery in EMC by moistening, and the trend was qualitatively the same as that exhibited in Fig.7. We suppose that Fig.6 is enough to show greater reduction and recovery in EMC at larger loss in weight, but for clearer understanding, additional explanation was inserted in the revised manuscript (page 5).

Anyway, we would like to emphasize that **the EMC is reduced significantly and temporarily even when the weight loss is very small**.

* *The speculation of annealing of wood polymers as the main mechanism behind the recovery of hygroscopicity is unclear. Internal stresses within the cell wall structure will be relaxed during*

thermal treatments, and particularly in those with the highest HRH. Specimens heated in dry conditions may have a more rigid structure due to the absence of water as plasticizer; however those specimens do not show the lowest EMC at a given weight loss. Please explain in more detail.

Detailed explanation was inserted in the revised manuscript (page 6).

* *Page 6. Lines 48-54. The weight loss of the specimens shown in Fig. 7 is less than 3%, based on data from Fig. 3. Such small weight losses are probably due, to a large extent, by the loss of extractives.*

Actually the spruce samples used in this study contain 1~2 % extractives. Those extractives might be lost by heating and the loss of extractives possibly affects the slight “irreversible” reduction in EMC (filled plots, in Fig.7). In the revised manuscript (page 7), we briefly mentioned the influence of extractives. In that part, however, we would like to focus on the marked “reversible” change in EMC, rather than the slight “irreversible” change with small loss in weight.

* *The selection of heating temperature 120 °C may be justified by the reproducing of natural aging conditions. However, commercial thermal treatments are mostly conducted at temperatures above 160°C. Since it is also mentioned in the text that, according to Chedeville et al, the chemical reactions induced at below or above 150°C are different, would you expect the results from this study to be translated to wood thermally treated at higher temperatures ?*

This may be a question rather than a comment. As the reviewer #2 supposed, we wish to realize the precise imitation of naturally aged wood, rather than the property enhancement of wood for industrial use. We are sure that the “reversible” change occurs at 160°C or above (Obataya et al 2002, up to 200°C), but considering the Chedeville’s results, the irreversible (chemical) changes at higher temperatures must be qualitatively different from those at 150°C or lower. Therefore, we do not think that the results in the present paper can be simply expanded to higher temperatures.

* *Fig. 9. Replace the ~ symbol by < to indicate those treatments conducted at HRH lower than 80%.*

Thank you for your correction. The wrong symbol “~” was replaced with “<”.

Reviewer #2:

* *A short sentence of introduction (context and objectives) could be inserted in the beginning of the abstract. Line 36-37: "92% HRH" (instead of RH?). "After the re-moistening" (instead of moistening?).*

Thank you for your suggestion and correction. A short sentence was added in the beginning of abstract, and the wrong expression was corrected.

Introduction

The introduction is well-conducted and concise. However, a very high proportion of it is centred on the concept of "artificial aging", although this topic does not appear so clearly to be the main focus of the article (which is of more general interest to the broad field of thermal treatments). Another related comment is that the assumption by authors that "quality of wood is thought (by artisans and instrument makers) to be improved by long term aging" is taken for granted, here, but could it be supported by some references on the topic? Such an opinion may be true for some wood users, but not so much so for some others users…It might be advisable to "soften" this part of text about putative "end-users" purposes, to the benefit of adding a bit more background on the different types of hydrothermal treatments? This is only a suggestion.

As we agree with reviewer #2 suggesting that the effects of ageing is still questionable, we tried to “shorten” this section and “soften” the expression as possible, in the revised manuscript.

On the other hand, it is true that aged wood is priced higher than recently cut one for making stringed instruments. Although the empirical knowledge of artisans are not recorded in “scientific” journals, that is a fact. At least, there is no literature suggesting the “degradation in acoustic quality” due to long term ageing, whereas higher acoustic quality of “some” aged wood has already been reported (Noguchi et al 2012).

The effects of ageing must depend strongly on the environmental humidity. That is what we really want to clarify. Considering the variability in wood properties, only limited information is given by comparing new wood and aged wood. However, the hydrothermal treatment i.e. accelerated ageing allows precise and reproducible results required for detailed discussion on the effects of humidity. We predict that “some” aged wood shows improved acoustic quality while “some other” aged wood will show degraded quality due to long term exposure to high humidity. Such variations will be reported in a following article and explained by the results presented in this manuscript.

Materials and methods

Wood specimens: Did all the specimens come from one same tree, or from different trees? What was the total number of specimens tested? How were they distributed in different groups for the different kinds of treatments? (some of these questions are answered later in the manuscript, but some precision as soon as in this "material" section would be useful).

We added those information in “Material and Methods” section.

Hydrothermal treatment: it might be useful to insert a synthetic graphic/flow chart, or at least a simple explanation in the text, of how many different modalities of treatment were applied throughout the experimental work.

Additional table (Table 1) was inserted for clearer understanding of different treatment modalities. We expect that the table also enables to understand the flow of experiments, especially the timing of moistening, without additional flow diagram.

Results and discussion

Page 4: The equations and modelling of the rate of modification are very interesting… However, it would make the reading smoother if 1-2 sentences of introduction would precede these paragraphs (i.e. to explain why these calculations are done, the underlying hypotheses and the search for an equivalence between time and humidity…).

The empirical time–humidity "superposition" must be practically useful to predict the effects of heating humidity, but frankly speaking, we have no evidence for the time–humidity "equivalence". Those facts are frankly described in the revised manuscript (page 4).

Page 4, l.52-54: "The variation in values were smaller than the size of plot"?? Does this mean that the standard deviation within groups is not represented because it was small enough to be ignored? This could be made a bit more clear.

The sentences were improved according to your suggestion (page 4). Thank you.

Bottom part of page 6: the discussion about the underlying chemical effects is very interesting. However, wouldn't it be possible that there is also some kind of effect coming from cross-linking of lignins?

Yes, it is possible. That possibility is mentioned in the revised version, citing some articles suggesting the cross-linking of lignin due to thermal treatment (page 7). Thank you for your suggestion.

Page 7, line 9-10: "the acoustic conversion efficiency" = it would be useful to give a definition of this parameter (its physical meaning, how it is calculated and used for what purpose?).

We inserted the definition of acoustic conversion efficiency (ACE) with references suggesting that higher ACE gives greater amplitude of sound radiation (page 7).

Page 7, lines 32-36: the note in the text indicates that, in Figure 9, only the irreversible effects are shown. This should probably appear also directly in the figure caption of Figure 9.

That note was added in the caption of Fig.9.

Page 8, changes in color: The discussion about the increase of a and b* in the beginning of the treatment, followed by a decrease of these parameters, should take into account that such evolution is not primarily due to the treatment itself, but to the inhomogeneity of the CIELab colour space: in this space, for both high and low values of L* (lightness) it's nearly impossible to have high values of a* and b*. These 2 last parameters therefore have a maximum around the median values of L*. For high L*, a* and b* always decrease, and similarly for low L* values.*

I agree that the CIELab color system has a distorted color sphere. However, I guess there is still enough space in the sphere outer than color values of the present study, because we could measure high *a** and *b** with high *L** for a red or yellow object, for example. I would like you to see a supplementary document (suppliment.pdf) showing the results of color measurement of colored papers by using the same spectrophotometer and measuring condition employed in the present study.

Page 0, lines 17-18: "the variations were small enough in terms of sensory perception" **->** *this sounds interesting, however, the sentence is not straightforward to understand: which variations were "small enough"?*

The sentence was corrected to clarify which variations were small enough (page 9). Thank you.

Conclusion

Line 43: "After treatment at intermediate HRH" ("followed by re-moistening" to be inserted here to make the conclusion more clear for the reader?)

That phrase was inserted. Thank you for your suggestion.

Reviewer #3:

Page 0, line 34: acoustic conversion efficiency... for those being not familiar with acoustics please define this term or give references for further reading.

That problem is also pointed out by the reviewer #2. We added the definition of acoustic converting efficiency with references suggesting its meaning (page 7).

Discussion:

The attempt to widely explain reversible and irreversible parts of the treatment is appreciated, it may offer hypothesis for further investigations. The part regarding color changes is short but shows a relationship with the ageing, which needs to be deepened in the future.

Thank you for your encouragements. The color is also an important factor affecting the practical quality of wood, particularly used for musical instruments. We will try to do in the future.

Thank you again for your kind, detailed and suggestive comments.

Eiichi OBATAYA

Corresponding author

CIELAB color parameters of high *L**, *a**, and *b**

color	*L**	*a**	*b**
	92.80	-2.66	18.87
	91.35	-1.55	39.80
	87.15	6.64	45.67
	88.67	4.47	47.48
	86.57	6.17	67.70
	82.88	15.18	52.98
	71.16	38.58	51.62
	68.47	45.06	36.35
	62.00	49.50	38.48
	87.26	12.36	19.82
	80.41	23.74	15.81
	84.22	21.19	5.09
	84.07	20.93	-2.26
	80.44	24.83	-2.82
	73.10	39.69	-10.90
	71.75	42.37	-11.66

Spectrophotometer:
UV-3100PC, Shimadzu Co.

light source: D65
view angle: 10°
sensor head: 13 mm x 30 mm

Material:
Colored paper