RECENT PROGRESS IN WOOD SCIENCE AROUND NATURAL AGING AND ARTIFICIAL AGING

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1. INTRODUCTION

Wood has long been the most important construction material in Japan. In fact, 45% of the common houses in the country are constructed by using wood. The Horyu-ji temple, built in A.D. 607, is the oldest wooden construction of the world (Fig. 1a), and its dark-colored wooden frame is regarded as a venerable object reminiscent of its long history. The well-preserved construction proves that aged wood remains incredibly durable when appropriately maintained and protected from weathering and biological attacks.

Musicians and artisans also usually prefer instruments made of aged wood (Fig. 1b) over those made from recent wood, as aging is believed to improve the stability and acoustic quality of the instruments. In this case, aging is not a negative senescence but a positive "treatment" that improves the quality of wooden products.

At the same time, researchers generally accept that a few hundred years of aging slightly improves the stiffness and hardness of wood but significantly reduces the shear strength and toughness (Kohara, 1952, 1954a; Hirashima *et al.*, 2004a, 2004b, 2005; Yokoyama *et al.*, 2009). The mechanism of wood aging is still under debate: the improved performance of the aged wood has not been convincingly explained, though its brittleness can be explained by the degradation of polysaccharides and the crosslinking of lignin (Yokoyama *et al.*, 2009). The improved quality of old musical instruments is also questionable, because of the limited information about the acoustic or vibrational properties of the aged wood.

Artificial aging is an important topic in wood engineering. This process allows for the reliable lifetime prediction of wooden structures and it may enable us to fabricate quality musical instruments without waiting for hundreds years. Various thermal treatments have been proposed to accelerate aging, but complete reproduction of naturally aged wood has not yet been realized. In this paper, the recent progress in wood aging and the unanswered questions related to this process are introduced to stimulate further detailed discussions on this topic.



Figure 1. Horyu-ji temple built in 607 (a) and an old Italian violin (b).

2. BASIC STRUCTURE AND PROPERTIES OF WOOD

2.1 Structure of wood

Here, we focus on the structure and properties of coniferous wood as it is widely used in construction and to fabricate soundboards of musical instruments. Figure 2 illustrates the structure of typical coniferous wood in different scales. The coniferous wood has a honeycomb structure in which the tubular tracheid cells are aligned in the longitudinal (L) direction (Fig. 2b). Each cell wall has a multilayered structure (Fig. 2c) in which the oriented cellulose fibers (microfibrils) are embedded in an amorphous matrix comprising substances such as hemicelluloses and lignin (Fig. 2d). Such a multilayered

and fiber-reinforced structure is found in all wood species; however, the shape of the cells and the thickness of the cell walls vary widely even within the same species. The fiber-reinforced and honeycomb structure is responsible for the lightness and excellent strength of wood in the L direction (Mark, 1967).



Figure 2. (a) *Three different directions of wood;* (b) *honeycomb structure of wood cells;* (c) *multilayered structure of the wood cell wall (S*₁, S₂, and S₃); and (d) fiber-reinforced structure in the cell wall; *M, middle lamella; P, primary wall.*

The major components of dry wood are cellulose (50%), hemicelluloses (20–30%), and lignin (30–20%). Cellulose is a highmolecular-weight linear polymer, and it is highly crystallized into ordered strands called microfibrils. The microfibrils play an important role in the mechanical properties of wood as a reinforcement fiber (Mark, 1967; Forest Products Laboratory, 1987). Hemicelluloses are mixtures of polysaccharides that consist of different kinds of monosaccharides. The hemicelluloses, associated with a part of cellulose, are in the amorphous state and oriented to some extent along the microfibrillar axis (Åkerholm and Salmén, 2001). These amorphous polysaccharides are responsible for the strong cohesion between the crystalline fibers and the amorphous matrix. Lignin, a three-dimensional phenyl–propane polymer, is a major component of the cell wall matrix. It is chemically stable and less hygroscopic than the other matrix components. When wood is used under ambient conditions, water should be considered the fourth component. The moisture content of airdried wood is approximately 10% at 50–60% relative humidity (RH). The amorphous matrix polymers adsorb moisture, which affects most of the wood properties (described later).

2.2 Mechanical properties of wood along the grain

Since wood has a honeycomb structure, it shows strong anisotropy and its mechanical properties depend strongly on its density (ρ) (Gibson and Ashby, 1997). In general, Young's modulus of a honeycomb structure is described by the following equation,

$$E = kE_s \left(\frac{\rho}{\rho_s}\right)^n,\tag{1}$$

where E_s and ρ_s are Young's modulus and the density of the cell wall material, respectively, and k is a constant reflecting the shape of the cells. The constant n reflects the density dependency, and it is 1 for the L direction and 3 for the direction perpendicular to the L direction. Eq. (1) can roughly describe the characteristics of wood: 1) Young's modulus in the L direction (E_L) is almost proportional to ρ , 2) E_L is greater than the corresponding values in the radial (E_R) and tangential (E_T) directions; and 3) such a strong anisotropy is more pronounced with decreasing ρ . In the R direction, the n value ranges from 1 to 2 depending on the radial alignment of the cellular structure (Palka, 1973). Similar density dependency and anisotropy are observed in the other mechanical properties of wood, such as strength. To calculate the E_L value of wood, in particular, Eq. (1) can be modified as

$$E_L = \frac{E_w}{\rho_w} \rho \,, \tag{2}$$

where E_w and ρ_w are Young's modulus and the density of the wood cell wall, respectively. ρ_w is almost constant (1,400– 1,500 kg/m³), whereas ρ ranges from 300 to 600 kg/m³ for commercially available coniferous wood. The variations in E_w reflect the microstructure of the wood cell wall. Since the wood cell wall is reinforced by the oriented microfibrils (as shown in Fig. 2c), the mechanical properties of wood depend on the volume fraction (φ) and the orientation angle (θ) of the microfibrils. φ does not vary widely in mature wood cells; however, θ in the thickest S2 layer varies widely, from 0° to 50°. Consequently, E_w varies from 10 to 50 GPa depending on the value of θ , as shown in Fig. 3a (Norimoto *et al.*, 1986). Obviously, a smaller θ results in better mechanical performance in the L direction. On the other hand, an extremely large θ (>30°) is found in woody tissues associated with leaning boles and crooked limbs, and such "reaction wood" is usually not used to produce structural parts and soundboards.

Moisture content is also an important factor that affects the mechanical properties of wood. The moisture content is approximately 10% under air-dry conditions but it increases to *ca.* 30% at 100% RH. Moisture sorption results in the scission of hydrogen bonds between the matrix polymers, thereby reducing the rigidity and strength of the wood cell wall. Consequently, most of the mechanical performances of wood deteriorate with an increase in the moisture content. As shown in Fig. 3b, the *E* value of wood can be approximated by a linear function of moisture content at approximately 10% (Obataya *et al.*, 1998, 2003). Because of the presence of fiber–matrix structure in the wood cell wall (Figs. 2c and 2d), the moisture dependence is more pronounced in the R and T directions than in the L direction.



Figure 3. Plots of E_w vs. θ for Japanese cypress wood (a) and the effects of moisture content on E_L and E_R of Sitka spruce wood (b).

2.3 Vibrational properties of wood along the grain

The vibrational properties of wood are usually determined by the flexural vibration method (Hearmon, 1958). The sound velocity (*V*) or specific dynamic Young's modulus $(E'/\rho = V^2)$ of a wooden plate is calculated from the resonance frequency of its flexural vibration. The damping property of wood is generally evaluated by the mechanical loss tangent (tan δ) or the internal friction (Q^{-1}), which in turn can be calculated from the half width of the resonance curve or decrement curve at the resonance frequency.

For effective sound radiation, soundboards should have high acoustic conversion efficiency, defined as $V/\rho \tan \delta$. Theoretical calculations have predicted that at a low ρ , high $E'/\rho (= V^2)$, and low $\tan \delta$, the amplitude of sound radiated from wooden soundboards is increased (Yano and Matsuhisa, 1991); this prediction has been proved experimentally as well (Ono, 1996). In the L direction, V and $\tan \delta (V_L \text{ and } \tan \delta_L$, respectively) are independent of ρ but strongly dependent on θ (Norimoto *et al.*, 1986). Consequently, V_L and $\tan \delta_L$ show a negative correlation (see Fig. 4a) (Norimoto *et al.*, 1986; Obataya *et al.*, 2000a). This is a general trend found in many wood species (Ono and Norimoto, 1984). This correlation also suggests that a smaller θ is preferred for effective sound radiation, *i.e.*, louder sound.



Figure 4. Plots of $\tan \delta vs. V_L(a)$ and those of $\tan \delta s/\tan \delta L vs. E'/G'(b)$ for Japanese cypress (open circles) and Sitka spruce wood (filled circles). The dashed lines indicate the calculated values.

The quality of a soundboard is determined not only by loudness but also by tone quality. The tone quality of a soundboard depends on its frequency response. Since dry wood polymers are in the glassy state, their viscoelastic properties remain almost unchanged over the audio frequency range. However, the flexural vibration of wood shows clear frequency dependence: E' decreases and tan δ increases steeply with increasing frequency. Such an "apparent" frequency dependence

results from the shearing deformation in the flexural vibration (Nakao *et al.*, 1985). As shown in Fig. 4b, the ratio E_L'/G_L' (8–26) is much larger than that of isotropic materials (2–3), and $\tan \delta$ in shear $(\tan \delta_S)$ is 2–4 times greater than $\tan \delta_L$. Such a strong anisotropy results in a slight shift of the resonance frequency and a marked increase in $\tan \delta_L$ at higher frequencies; therefore, the increased $\tan \delta_L$ damps the high-frequency flexural vibration of the wooden soundboard. Theoretical and experimental studies have clarified that high E_L'/G_L' and E_R'/G_R' ratios of wood are responsible for the soft "woody" tone (Yano and Matsuhisa, 1991; Ono, 1996) as well as the characteristic transient response (Ono, 1999). The E'/G' ratios are independent of ρ in both the L (Ono, 1980) and R (Yano and Yamada, 1985) directions. Thus, it can be safely stated that a large anisotropy is essential for better tone quality of wooden soundboards.

3. EFFECTS OF AGING ON WOOD PROPERTIES

To study wood aging, many Japanese researchers use wood samples obtained from ancient temples. Note that in Japan the timber for religious constructions was usually harvested from special forests, carefully dried, and strictly classified; further, the complete history of such timber was clearly recorded. In addition, such religious constructions were well protected by the believers from war, fire, weathering and biological attacks. Therefore, minimal defects (irregular grain, stain, etc.) are present in such wood samples. Because of these reasons, researchers prefer to study wood samples from religious constructions.

3.1 Chemical changes due to aging

The cellulose content and crystallinity do not significantly vary between the aged and recent Japanese cypress wood (Kohara, 1954b; Fengel, 1991); however, slight rearrangement of the elementary fibrils may occur during prolonged aging, i.e., aging for up to 1,300 years (Tsuchikawa *et al.*, 2005; Inagaki *et al.*, 2010). In Japanese red pine wood, the crystallinity and crystal width of the cellulose fibers remain almost unchanged even after 300 years of aging (Noguchi and Obataya, 2013). On the other hand, the hemicellulose content decreases significantly, probably because of hydrolysis (Kohara, 1954b). Depolymerization of hemicelluloses is the main reason for the degradation of the mechanical properties of wood. Although the lignin content also decreases during long-term aging (Tsuchikawa *et al.*, 2005), the degradation of lignin is slower than that of polysaccharides (Kohara, 1954b). In addition, the aging may induce an increase in the degree of crosslinking of lignin (Yokoyama *et al.*, 2009).

3.2 Hygroscopicity of aged wood

According to Yokoyama *et al.* (2009), after aging for 800 years or longer at 20°C and 60% RH, the equilibrium moisture content (EMC) of Japanese cypress wood decreases from 9.2% to 7.7–8.6% and remains almost unchanged in the early stage of aging. Hirashima *et al.* (2004a) have reported that 290 years of aging do not affect the EMC of Japanese red pine wood. These results suggest that the hygroscopicity of wood is reduced only upon prolonged aging. The reduced hygroscopicity of the aged wood is usually explained by the decomposition of hemicelluloses, the most hygroscopic component of wood. Moisture sorption and desorption result in swelling, shrinkage, and various undesirable deformations such as curving and twisting. In addition, the stiffness and strength of the wood decrease with an increase in the moisture sorption in general. Thus, the reduced hygroscopicity of the aged wood directly improves its dimensional stability and indirectly enhances its mechanical performance.

3.3 Mechanical properties of aged wood

It is generally accepted that aging improves the compressive performance of wood in the L direction (Kohara, 1952; Hirashima *et al.*, 2004b). Hirashima *et al.* (2004b) tested Japanese red pine wood aged for 270–290 years and corrected the experimental results after considering the density variations within the wood samples. They concluded that the compressive Young's modulus and the compressive strength were improved by 51–59% and 19–49%, respectively.

On the other hand, the bending properties of the aged wood are still debatable. Kohara (1952) has reported that the bending Young's modulus and the bending strength of Japanese cypress wood improve after aging for 300 years. However, Kohara did not consider density variations within his wood samples. As the mechanical properties of wood strongly depend on its density, density variations should always be taken into account while considering the effects of aging. Yokoyama *et al.* (2009) have recently conducted more precise measurements for calculating the variations in density, moisture content, and microfibril angle in wood samples. From the corrected results (shown in Fig. 5), they concluded that aging has negligible impact on the bending performance of wood.

The scattered plots in Fig. 5 suggest that long-term aging (>1,200 years) does not improve the bending performance of wood. However, the E_L and σ_L values of wood aged for 500–900 years are significantly greater than those of recent wood, implying that the bending performance can be improved by aging for a few hundreds years. This fact is consistent with another result reported by Hirashima *et al.* (2004a): Japanese red pine wood shows significant increase in the bending Young's modulus (27–42 %) and bending strength (11–17%) after 270–290 years of aging. In this case, the differences between the aged and recent wood samples are not due to density variations. From these results, it is safe to conclude that although the bending performance of wood is slightly enhanced after a few hundred years of aging, it does not significantly decrease even after 1,000 years of aging.

At the same time, aging makes wood fragile to impact bending and tensile loading. For example, Japanese cypress wood absorbs 40% lesser energy during impact bending after 300 years of aging (Kohara, 1954a), and Japanese red pine wood

absorbs 22–27% lesser energy after 270–290 years of aging (Hirashima *et al.*, 2005). Similar degradation has also been observed in the rupture energy in static bending (Yokoyama *et al.*, 2009) as well as for tensile strength (Hirashima *et al.*, 2004a). These results suggest that the aged wood is more brittle and less tough than recent wood, especially under tensile loading.



Figure 5. Bending Young's modulus (E_L) and bending strength (σ_L) of Japanese cypress wood in the L direction, plotted against the age of wood (Yokoyama et al., 2009). Original data were re-plotted with permission from Dr. Yokoyama.

Tsuchikawa *et al.* (2005) analyzed the crystallinity and accessibility of aged and recent cypress wood and concluded that the cellulose microfibrils are loosely arranged after aging for 1,000 years. If bundled cellulose microfibrils undergo a similar loosening, the toughness of the wood will significantly decrease. Meanwhile, Yokoyama *et al.* (2009) suggested that the reduced toughness of the aged wood was due to the depolymerization of hemicelluloses as well as the crosslinking of lignin during aging. Since the hemicelluloses are responsible for strong fiber–matrix cohesion in the wood cell wall, their decomposition possibly reduces the toughness of the fiber-reinforced wood cell wall. In addition, the crosslinking of lignin may increase the brittleness of the lignified part, especially in the middle lamella (M, in Fig. 2c) joining adjacent wood cells. These interpretations sound reasonable because aging reduces the strength of the wood, particularly in the R direction.

3.4 Vibrational properties of aged wood

Figure 6 shows the V_L , tan δ_L , and E_L'/G_L' values of Japanese red pine wood plotted against the aging time (Noguchi *et al.*, 2012; and Noguchi and Obataya, 2013). The aged wood shows slightly higher V_L and smaller tan δ_L . No clear trend is recognized in E_L'/G_L' , but this ratio does not decrease during aging. These results suggest that the aged wood gives more effective sound radiation without degrading the tone quality.



Figure 6. V_L , $tan \delta_L$, and E_L'/G_L' of Japanese red pine wood plotted against the aging duration. Filled circles, results of a previous study (Noguchi et al., 2012); open circles, recent unpublished data (Noguchi and Obataya, 2013); bars, standard deviations.

The reduced tan δ of the aged wood is attributable to the increase in the crosslinking of lignin. However, it is still difficult to explain the slight increase in V_L . The V_L value reflects Young's modulus $(E'/\rho = V^2)$ of the wood cell wall, and it is determined by the volume fraction of the cellulose microfibrils (φ) and their inclination angle (θ). Noguchi *et al.* (2012) had speculated on the reason for the crystallization of cellulose, and concluded that the increase in φ was responsible for the increase in V_L . However, this speculation has been recently challenged on the basis of X-ray diffractometry (XRD) analysis, which indicated that the θ and φ values of aged and recent wood samples are almost the same (Noguchi and Obataya, 2013). Similar results have been obtained by near infrared (NIR) spectroscopy and XRD (Tsuchikawa *et al.*, 2005; Inagaki *et al.*, 2010). Therefore, the enhanced stiffness of the aged wood cannot be attributed to changes in crystalline cellulose alone. Now, we reconsider the structural changes in the amorphous components during aging. Among different amorphous components, polysaccharides are the most important, and they are responsible for the strong fiber–matrix cohesion. During

aging, these polysaccharides show alternate moisture sorption and desorption, accompanied by swelling and shrinkage. Such a hygroscopic stimulation might improve the orientation of the polysaccharides and enhance the stiffness of the wood cell wall. Otherwise, the rearrangement of the polysaccharides may involve "hornification" to make the wood cell walls rigid. Hornification results from the irreversible hydrogen bonding between polysaccharides, which makes paper less flexible during recycling (Kato and Cameron, 1999).

In any case, we do not have sufficient information about the structure and conformation of amorphous wood polymers, though the crystalline region of wood cellulose has been studied in detail. For better understanding of wood aging, further investigations focusing on the amorphous region of the wood cell wall must be carried out.

4. EFFECTS OF HEATING ON WOOD PROPERTIES

4.1 Heat treatment of wood for property enhancement

Heat treatment helps in modifying wood without using complicated equipment and harmful chemicals. Since the 1950s, various heating methods have been proposed to improve the dimensional stability (Seborg *et al.*, 1953; Hillis, 1984; Bekhta and Niemz, 2003; Dubey *et al.*, 2011) and durability (Kamdem *et al.*, 2002) of wood. Heat treatment is sometimes called "accelerated aging" (Millett and Gerhards, 1972) because the brittleness, reduced hygroscopic stability, and the dark color of the heat-treated wood are similar to those of naturally aged wood. Matsuo *et al.* (2010, 2011) studied the kinetics of the heat-treatment process and proposed that the color of the aged wood can be successfully reproduced by heating the wood in an oven (dry heating). However, perfect reproduction of aged wood has not yet been realized, because the mechanical and acoustic properties of heat-treated wood are still different from those of naturally aged wood (described later).

4.2 Chemical changes due to heat treatment

In the early stage of heating, a part of wood cellulose crystallizes, especially in the presence of moisture, and is depolymerized upon prolonged heating (Bhuiyan *et al.*, 2000). This fact suggests that heating is intrinsically different from aging, because the cellulose crystallite remains unchanged during aging (Tsuchikawa *et al.*, 2005; Inagaki *et al.*, 2010; Noguchi and Obataya, 2013). On the other hand, hemicelluloses and a part of cellulose are depolymerized by heating, particularly in the presence of moisture (Mitchell *et al.*, 1953; Kubinsky and Ifju, 1973). Such decomposition of polysaccharides is similar to that observed during long-term aging. Lignin is relatively stable to heating, but crosslinking occurs upon heating under dry conditions (Tjeerdsma *et al.*, 1998; Wikberg and Maunu, 2004).

The thermal degradation of wood is frequently evaluated by the weight loss (WL) due to heating. In Fig. 7, the time for 5% WL is plotted against the reciprocal of heating temperature (1/T) (Stamm, 1956; Millett and Gerhards, 1972; Obataya *et al.*, 2002, 2006). In "dry heating," the wood is first dried and then heated in the absence of moisture (0% RH), whereas in "steaming," the wood is heated in saturated water vapor (100% RH). Steaming always results in faster degradation than does dry heating because the hydrolysis of polysaccharides is remarkably accelerated in the presence of moisture. In other words, the moisture or relative humidity is an important factor that determines the performances of heat-treated wood; however, only fragmented data are available to corroborate the effects of heating at moderate RH (20–90%).



Figure 7. Time for 5% weight loss (WL) due to heating plotted against the reciprocal of heating temperature (1/T). Open symbols, dry heating; filled symbols, steaming.

4.3 Hygoscopicity of heat-treated wood

The most important advantage of heat treatment is the reduction in hygroscopicity, *i.e.*, improvement of the dimensional stability (Bekhta and Niemz, 2003; Dubey *et al.*, 2011). The reduced hygroscopicity of heat-treated wood is usually explained by the loss of hygroscopic hemicelluloses (Hillis, 1984) and the crosslinking of lignin (Tjeerdsma *et al.*, 1998). Though both the dry heating and steaming reduce the hygroscopicity of wood, their effects are qualitatively different: dry heating results in greater reduction in EMC at higher RH, whereas steaming gives the opposite effect (Obataya *et al.*, 2002).

Probably the swelling of wood is effectively restricted by an increase in the lignin crosslinking due to dry heating, whereas such a restriction is not induced by steaming, where the wood is heated in fully swollen state. The moisture sorption characteristics of the aged wood are similar to those of dry-heated wood rather than steamed wood (Obataya, 2007), but again, little is known about the effects of heating at moderate RHs on the hygroscopicity of wood.

4.4 Mechanical properties of heat-treated wood

Figure 8 shows the bending Young's modulus, bending strength, and maximum tensile strain of heat-treated wood as a function of WL due to heating (Millett and Gerhards, 1972; Obataya *et al.*, 2006). Young's modulus of wood often shows a slight increase upon short-term heating. Such a stiffening is attributed to the reduced hygroscopicity (Obataya *et al.*, 2000b, 2006) and/or crystallization of cellulose (Kubojima *et al.*, 1998). The strength of the wood is reduced by heating, mainly because of the decomposition of hemicelluloses (Millett and Gerhards, 1972; Hillis, 1984). The significant reduction in the maximum tensile strain indicates the brittleness of the heat-treated wood. These changes are similar to those resulting from long-term aging as a whole.

Strictly speaking, however, the effects of heating and aging are qualitatively different. Despite the significant crystallization of cellulose, the bending strength of wood always decreases on heating but remains almost unchanged or rather increases during aging, as shown in Fig. 5. This fact indirectly proves that the amorphous region plays a greater role in the mechanical performance of heat-treated wood and naturally aged wood than does the crystalline region.



Figure 8. Bending Young's modulus (E_L) and bending strength (ρb) of cypress wood along the grain plotted against loss in weight (WL) due to heating. Open symbols, dry heating; filled symbols, steaming.

4.5 Vibrational properties of heat-treated wood

Kubojima *et al.* (1998) tried to improve the acoustic quality of Sitka spruce wood by heating it in dry nitrogen gas. They found that the specific dynamic Young's modulus (E'/ρ) increased after a few hours of heating at 160–200°C, as shown in Fig. 9. However, this treatment also induced a marked increase (10–20%) in tan δ in the L direction. In addition, the increase in specific dynamic shear modulus (G_L ') was greater than that in E_L , *i.e.*, the E_L'/G_L ' ratio decreased upon heating. These results indicate that the acoustic conversion efficiency and the tone quality of wood are not improved but degraded by dry heating, even when the oxidative degradation is prevented. Kubojima *et al.* (2000) also reported that E'/ρ decreases and tan δ_L increases when green wood is heated in a closed system (\approx steaming). Therefore, heat treatment is still considered risky for wood used to fabricate musical instruments.



Figure 9. Relative values of specific dynamic Young's modulus (E/ρ) and mechanical loss tangent $(tan\delta)$ of heat-treated Sitka spruce wood in the longitudinal (L) and radial (R) directions as a function of heating time (Kubojima et al., 1998). Selected data was re-plotted with permission from Dr. *Kubojima*.

4.6 Future attempts for the reproduction of aged wood

Heat treatment is a useful method to improve the practical performance of wood, such as dimensional stability and durability, and is beneficial for reproducing the color of aged wood (Matsuo *et al.*, 2010, 2011). However, it is still difficult to reproduce the mechanical and vibrational properties of aged wood by the conventional heat treatment methods, *i.e.*, dry heating and steaming, as already described.

Since the chemical changes in wood components are very sensitive to moisture, heating at moderate RHs may be more conducive for accelerating the aging process. Hygroscopic stimulation, *i.e.*, alternate moistening and drying on mild heating, is another promising method to accelerate rearrangement and hornification in amorphous wood polymers.

5. CONCLUSION

- Long-term aging improves the compressive Young's modulus and compressive strength of wood along the grain. The bending Young's modulus and bending strength of wood remain unchanged or increase slightly during aging. On the other hand, wood becomes brittle and less ductile during aging: the impact bending strength and tensile strength are significantly reduced. These changes are mainly due to the decomposition of polysaccharides and the crosslinking of lignin in the wood cell wall. The crystalline cellulose remains almost unchanged during aging.
- Aged wood shows higher sound velocity and lower damping than does recent wood, and hence gives better sound clarity when used for making soundboards of musical instruments. The reduced damping is attributed to the lignin crosslinking; however, there is no convincing explanation for the enhanced sound velocity.
- Heat treatment is a useful method to reproduce the brittleness and the dark color of aged wood. However, the improved stiffness, reduced damping, and enhanced anisotropy achieved by natural aging cannot be reproduced by conventional heat treatments. Appropriate moisture conditioning may be necessary for true acceleration of aging.

REFERENCES

- Åkerholm M. and Salmén L., "Interactions between wood polymers studied by dynamic FT-IR spectroscopy," *Polymer*, **42**, (2001), pp.963–969.
- Bekhta P. and Niemz P., "Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood," *Holzforschung*, **57**, (2003), pp.539–546.
- Bhuiyan M.T.R., Hirai N. and Sobue N., "Changes of crystallinity in wood cellulose by heat treatment under dried and moist conditions," *J. Wood Sci.*, **46**, (2000), pp.431–436.
- Dubey M.K., Pang S. and Walker J, "Effect of oil heating age on colour and dimensional stability of heat treated Pinus radiata," *Eur. J. Wood Wood Prod.*, **69**, (2011), pp.255–262.
- Fengel D., "Aging and fossilization of wood and its components," Wood Sci. Technol., 25, (1991), pp.153–177.
- Forest Product Laboratory, "Wood handbook: Wood as an engineering material," Agriculture Handbook No. 72, (1987), U.S. Department of Agriculture, Washington DC.
- Gibson L.J. and Ashby M.F., *Cellular Solids: Structure and Properties*, Second Edition, (1997), Cambridge University Press, Cambridge, U.K.
- Hearmon R.F.S., "The influence of shear and rotatory inertia on the free flexural vibration of wooden beams," *Br. J. Appl. Phys.* 9, (1958), pp.381–388.
- Hillis W.E., "High temperature and chemical effects on wood stability. Part 1: General considerations," *Wood Sci. Technol.*, **18**, (1984), pp.281–293.
- Hirashima Y., Sugihara M., Sasaki Y., Ando K. and Yamasaki M., "Strength properties of aged wood I, tensile strength properties of aged Keyaki and Akamatsu woods (in Japanese)," *Mokuzai Gakkaishi*, 50, (2004a), pp.301–309.
- Hirashima Y., Sugihara M., Sasaki Y., Ando K. and Yamasaki M., "Strength properties of aged wood II, compressive strength properties, shearing strength, and hardness of aged Keyaki and Akamatsu woods (in Japanese)," *Mokuzai Gakkaishi*, **50**, (2004b), pp.368–375.
- Hirashima Y., Sugihara M., Sasaki Y., Ando K. and Yamasaki M., "Strength properties of aged wood III, static and impact bending strength properties of aged Keyaki and Akamatsu woods (in Japanese)," *Mokuzai Gakkaishi*, **51**, (2005), pp.146–152.

- Inagaki T., Siesler H.W., Mitsui K. and Tsuchikawa S., "Difference of the crystal structure of cellulose in wood after hydrothermal and aging degradation: An NIR spectroscopy and XRD study," *Biomacromolecules*, **11**, (2010), pp.2300–2305.
- Kamdem D.P., Pizzi A. and Jermannaud A., "Durability of heat-treated wood," *Holz als Roh-und Werkstoff*, **60**, (2002), pp.1–6.
- Kato K.L. and Cameron R.E., "A review of the relationship between thermally-accelerated ageing of paper and hornification," *Cellulose*, **6**, (1999), pp.23–40.
- Kohara J., "Studies on the durability of wood I, mechanical properties of old timbers (in Japanese)," *Bull. Kyoto Prefectural Univ.*, **2**, (1952), pp.116–131.
- Kohara J., "Studies on the permanence of wood VI, the changes of mechanical properties of old timbers (in Japanese)," *Bull. Kyoto Prefectural Univ.*, **6**, (1954a), pp.164–174.
- Kohara J., "Studies on the permanence of wood VII, the influence of age on the components of wood (*Chamaecyparis obtusa* Endlicher) (in Japanese)," *Bull. Kyoto Prefectural Univ.*, **6**, (1954b), pp.175–182.
- Kubinsky E. and Ifju G., "Influence of steaming on the properties of red oak. Part I. Structural and chemical changes," *Wood Sci.*, **6**, (1973), pp.87–94.
- Kubojima Y., Okano T. and Ohta M., "Vibrational properties of Sitka spruce heat-treated in nitrogen gas," J. Wood Sci., 44, (1998), pp.73–77.
- Kubojima Y., Okano T. and Ohta M., "Vibrational properties of heat-treated green wood," *J. Wood Sci.*, **46**, (2000), pp.63–67.
- Mark R.E., Cell Wall Mechanics of Tracheids, (1967), Yale University Press, New Haven, U.S.A.
- Matsuo M., Yokoyama M., Umemura K., Gril J., Yano K. and Kawai S., "Color changes in wood during heating: Kinetic analysis by applying a time-temperature superposition method," *Appl. Phys. A.*, **99**, (2010), pp.47–52.
- Matsuo M., Yokoyama M., Umemura K., Sugiyama J., Kawai S., Gril J., Kubodera S., Mitsutani T., Ozaki H., Sakamoto M. and Imamura M., "Aging of wood: Analysis of color changes during natural aging and heat treatment," *Holzforschung*, **65**, (2011), pp.361–368.
- Mitchell R.L., Seborg R.M. and Millett M.A., "Effect of heat on the properties and chemical composition of Douglas-fir wood and its major components," *J. Forest Prod. Res. Soc.*, **3**, (1953), pp.38–42, 72–73.
- Millett M.A. and Gerhards C.C., "Accelerated aging: Residual weight and flexural properties of wood heated in air at 115° to 175°C," *Wood Sci.*, **4**, (1972), pp.193–201.
- Nakao T., Okano T. and Asano I., "Theoretical and experimental analysis of flexural vibration of viscoelastic Timoshenko beam," J. Appl. Mech., 52, (1985), pp.728–736.
- Noguchi T., Obataya E. and Ando K., "Effects of aging on the vibrational properties of wood," *J. Cultural Heritage*, **13S**, (2012), pp.S21–S25.
- Noguchi T. and Obataya E., (2013), unpublished data.
- Norimoto M., Tanaka F., Ohgama T. and Ikimune R., "Specific dynamic Young's modulus and internal friction of wood in the longitudinal direction," *Wood Res. Tech. Notes*, **22**, (1986), pp.53–65.
- Obataya E., Gril J. and Norimoto M., "The effects of adsorbed water on dynamic mechanical properties of wood," *Polymer*, **39**, (1998), pp.3059–3064.
- Obataya E., Ono T. and Norimoto M., "Vibrational properties of wood along the grain," *J. Mater. Sci.*, **35**, (2000a), pp.2993–3001, 6317.
- Obataya E., Norimoto M. and Tomita B., "Moisture dependence of vibrational properties of heat-treated wood (in Japanese)," *Mokuzai Gakkaishi*, **46**, (2000b), pp.88–94.
- Obataya E., Higashihara T. and Tomita B., "Hygroscopicity of heat-treated wood III. Effects of steaming on the hygroscopicity of wood (in Japanese)," *Mokuzai Gakkaishi*, **48**, (2002), pp.348–355.
- Obataya E., Furuta Y. and Gril J., "Dynamic viscoelastic properties of wood acetylated with acetic anhydride solution of glucose pentaacetate," J. Wood Sci., 49, (2003), pp.152–157.
- Obataya E., Shibutani S., Hanata K and Doi S. "Effects of high temperature kiln drying on the practical performances of Japanese cedar wood II: Changes in mechanical properties due to heating," *J. Wood Sci.*, **52**, (2006), pp.111–114.

- Obataya E., "Characteristics of aged wood and Japanese traditional coating technology for wood protection," *Proceeding of CONSERVER AUJOURD'HUI, LES "VIEILLISSEMENTS" DU BOIS, La Journée d'Etude de Cité de la Musique, Paris,* (2007), pp.4–43.
- Ono T., "The dynamic rigidity modulus and internal friction of several woods in torsional vibration," *Mokuzai Gakkaishi*, **26**, (1980), pp.139–145.
- Ono T. and Norimoto M., "On physical criteria for the selection of wood for soundboards of musical instruments," *Rheologica Acta*, **23**, (1984), pp.652–656.
- Ono T., "Frequency responses of wood for musical instruments in relation to the vibrational properties," *J. Acoust. Soc. Jpn. (E)*, **17**, (1996), pp.183–193.
- Ono T., "Transient response of wood for musical instruments and its mechanism in vibrational property," J. Acoust. Soc. Jpn. (E), 20, (1999), pp.117–124.
- Palka L.C., "Predicting the effect of specific gravity, moisture content, temperature and strain rate on the elastic properties of softwood," *Wood Sci. Technol.*, **7**, (1973), pp.127–141.
- Seborg R.M., Tarkow H. and Stamm A.J., "Effect of heat upon the dimensional stabilization of wood," *J. Forest Prod. Res. Soc.*, **3**, (1953), pp.59–67.
- Stamm A.J., "Thermal degradation of wood and cellulose," Ind. Eng. Chem., 48, (1956), pp.413-417.
- Tjeerdsma B.F., Boonstra M., Pizzi A., Tekely P. and Militz H., "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Holz als Roh-und Werkstoff*, 56, (1998), pp.149–153.
- Tsuchikawa S., Yonenobu H. and Siesler H.W., "Near-infrared spectroscopic observation of the ageing process in archaeological wood using a deuterium exchange method," *Analyst*, **130**, (2005), pp.379–384.
- Yano H. and Yamada T., "The dynamic mechanical properties of wood in the radial direction (in Japanese)," *Mokuzai Gakkaishi*, **31**, (1985), pp.222–230.
- Yano H. and Matsuhisa H., "Study on the timber of wood II, analysis of the sound spectrum of wood using viscoelastic Timoshenko equation," *Sci. Rep. Kyoto Prefectural Univ.*, **43**, (1991), pp.24–31.
- Yokoyama M., Gril J., Matsuo M., Yano H., Sugiyama J., Clair B., Kubodera S., Mitsutani T., Sakamoto M., Ozaki H., Imamura M. and Kawai S., "Mechanical characteristics of aged Hinoki wood from Japanese historical buildings," *Comp. Rend. Phys.*, **10**, (2009), pp.601–611.
- Wikberg H. and Maunu S.L., "Characterisation of thermally modified hard- and softwoods by ¹³C CPMAS NMR," *Carbohydr. Polym.*, **58**, (2004), pp.461–466.