# Characteristics of aged wood and Japanese traditional coating technology for wood protection

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The experiments conducted by Kohara in the 1950s on aged wood are introduced. The results indicate that the stiffness, strength and the dimensional stability of wood improve slightly by hundreds of years of ageing, while its rigidity and flexibility degrade significantly. These changes are attributed to the chemical changes in wood constituents. The ageing-like effects of heating are discussed. Quantitative and qualitative differences between the effects of dry heating and steaming suggest that careful moisture conditioning is required for artificial ageing. Furthermore, reversible changes in the hygroscopicity of heat-treated wood are explained by annealing, i.e. the physical ageing of wood polymers. Finally, a traditional Japanese lacquer (urushi) is introduced to suggest its promising features as the coating for musical instruments.

# I Introduction

In Japan, wood has been the most important building material. Even in this age of concrete, 45% of common houses are constructed by using wood. The oldest wooden construction is Horyu-ji temple that was built in 607 (Figure1). Its commanding appearance has been retained by its wooden framework for over 1400 years. This fact suggests that the wood remains incredibly durable when it is appropriately maintained and protected from weathering and biological attacks. The Japanese consider the dark-coloured aged wood not as old wood but as a venerable object that reminds them of its long history involved.



Figure 1. The five-storeyed pagoda in Horyu-ji temple (Nara, Japan).

Aged wood is also venerated by musicians and artisans. It is believed that ageing improves the stiffness and stability of wood, and therefore, quality instruments can be made using aged wood. In

this sense, ageing is not a negative senescence but a positive treatment to increase the value of wood.

In any case, the characteristics of aged wood should be understood well. The reduced strength and flexibility of aged wood should be taken into account for the appropriate maintenance of old wooden constructions. Meanwhile, the improved stiffness and stability of aged wood suggest that artificial ageing can be used for future property enhancement of wood. In this paper, the effects of ageing and heating are described in detail for the clear understanding of their advantages and disadvantages. Furthermore, the incredible durability of a Japanese traditional coating (urushi) is introduced to suggest its potential for protecting wooden musical instruments.

# II Characteristics of aged wood

#### II.1 The results of Kohara

In the 1950s, Jiro Kohara tested the chemical and mechanical properties of several hundreds of aged wood samples [1–6]. Thus far, many attempts have been made to study wood ageing; however, the results of Kohara are regarded as most reliable because the samples in his study were obtained from ancient temples. It should be noted that the timbers for religious constructions were usually harvested from special forests, carefully dried and strictly classified. In addition, such religious constructions have been well protected by the believers from war, fire, weathering and biological attacks. Consequently, minimal defects (irregular grain, stain, etc.) are present in the samples used by Kohara. Figure 2a shows the effects of ageing on the chemical components of cypress wood (*Chamaecyparis obtusa*). The cypress wood is a popular species in Japan as a material for buildings and religious sculptures. With the passage of time, there is a decrease in the content of holocellulose and  $\alpha$ -cellulose in the wood and an increase in the content of alkali-soluble extractives, while the apparent lignin content remains almost unchanged. These results indicate that a part of the polysaccharides are degraded into alkali-soluble substances, while the degradation of lignin is relatively slow.



Figure 2. The effects of ageing on the chemical components of cypress (**a**) and zelkova (**b**) wood [4,5].

A similar trend is observed in zelkova wood (*Zelkowa serrata*), as shown in Figure 2b, but clearly the chemical degradation in zelkova wood is faster than that in cypress wood. Thus, the choice of cypress wood by the ancient Japanese for their buildings is only logical with respect to its chemical stability. The prolonged ageing also induces conformational changes in cellulose. Figure 3 shows the changes in the amount of the crystalline part during ageing. The crystalline cellulose slightly increases in the first 300 years and then gradually decreases. Probably, the crystallization and decomposition of cellulose are compensated to produce an obscure peak at around 300 years.



Figure 3. The changes in crystalline part due to ageing [6].

Figure 4 shows the bending Young's modulus (*E*), bending strength ( $\sigma_b$ ), longitudinal compressive strength ( $\sigma_c$ ) and the hardness (*H*) of cypress wood as a function of the ageing period. Although the scattered plot renders it difficult to draw smooth curves, the aged wood seems stiffer, stronger and harder than the new wood. The most significant change is recognized in the compressive strength of wood along the grain: it increases by 50% in the first 300 years and thereafter remains almost unchanged.



Figure 4. The bending Young's modulus (*E*), bending strength ( $\sigma_b$ ), compressive strength ( $\sigma_c$ ) and the hardness (*H*) of aged cypress wood [3]. Each plot indicates the average of 20 replicates.

The mechanical properties of wood generally depend on its moisture content. In the present case, the moisture content of wood varies from 13.9% (new wood) to 10.7% (1300-year old wood). Due to this, Kohara has revised the data in Figure 4 by considering the moisture dependencies of wood properties. Figure 5 shows the revised results for the compressive strength. The compressive strength increases for the first 300 years and then tends to decrease. It is incredible that the strength of the oldest wood (1300 years) is still greater than that of the new one. This proves that the wood can serve as an incredibly durable material when it is appropriately maintained.



Figure 5. The effects of ageing on the compressive strength ( $\sigma_c$ ) at the same moisture content [3].

Interestingly, the trend in Figure 5 is similar to that in Figure 3. This fact is an indirect evidence that the crystallization of cellulose is responsible for the improvement in the mechanical properties for a few hundreds years. Figure 6 shows the microstructure of wood. The wood cell wall is a fibre-reinforced composite in which the crystalline cellulose 'fibres' are embedded in an amorphous 'matrix' of hemicelluloses and lignin. A part of cellulose is in a disordered (amorphous) state, but fairly oriented along the fibre axis and readily crystallized by thermal activation. The crystalline fibre plays an important role in the mechanical properties of wood because its stiffness is much greater than that of the matrix substances: the Young's modulus of crystalline cellulose is about 130 GPa [7] while that of the matrix substance is 8 GPa at most [8,9]. Therefore, the crystallization of disordered cellulose results in greater stiffness of wood, unless the fibre-matrix cohesion is weakened.



Figure 6. The cellular structure of wood (a), and the FRP-like structure in the cell wall (b).

On the other hand, the effect of ageing is not always positive for the practical performances of wood. Figure 7 shows the absorbed energy in impact bending (*AE*), shear strength ( $\sigma_s$ ) and cleavage

resistance (*CR*) of aged wood. All these properties are degraded by ageing. This fact indicates that the wood becomes fragile during ageing. The fragile nature of aged wood is attributable to the chemical degradation of the amorphous matrix substances. Among the matrix substances, hemicelluloses are particularly important for tight cohesion between the fibre and the matrix. It is acknowledged that the fibre-matrix cohesion is necessary for the rigidity, flexibility and toughness of the composite, whereas the stiffness and strength of the composite (along the fibre axis) are determined by reinforcement fibres. Therefore, it is natural that the wood becomes fragile when the fibre-matrix cohesion is weakened by the degradation and the loss of hemicelluloses. A similar phenomenon is observed when wood is steamed at high temperatures, at which the hydrolysis of the hemicelluloses is accelerated in the presence of moisture.



Figure 7. The absorbed energy in impact bending (*AE*), shear strength ( $\sigma_s$ ) and the cleavage resistance (*CR*) of cypress wood plotted against the ageing duration [3].

In Figure 8, the *AE* values of aged wood are plotted against the moisture content. The new wood shows greater *AE* at higher moisture contents because the moisture sorption and softening of matrix substances enhance the flexibility of wood. On the contrary, the *AE* value of aged wood decreases with moisture sorption. This fact suggests that the aged wood should be carefully treated, especially in a highly humid condition. In addition, this is an indirect evidence that the fragility of aged wood results from the degradation of moisture-sensitive constituents such as hemicelluloses.

The biggest advantage of wood ageing is its stabilization effect. Figure 9 shows the changes in the maximum tangential shrinkage of cypress wood due to ageing. The smaller shrinkage of aged wood indicates its greater dimensional stability under changing humidity. Such a dimensional stabilization effect of ageing is explained by the decomposition and loss of hygroscopic hemicelluloses as well as the crystallization of cellulose during ageing. The improved stability of aged wood could be favourable for musical instruments whose performance should be stable against the changes in humidity.



Figure 8. The moisture dependencies of absorbed energy in impact bending (AE) [1].



Figure 4. The bending Young's modulus (*E*), bending strength ( $\sigma_b$ ), compressive strength ( $\sigma_c$ ) and the hardness (*H*) of aged cypress wood [3]. Each plot indicates the average of 20 replicates.

#### II.2 Recalculation of Kohara's data

Kohara has not discussed the density variation in his wood samples. Strictly speaking, however, the density of wood should be taken into consideration when we discuss the structural changes in the wood cell wall.

The Young's modulus of wood along the grain ( $E_L$ ) is related to that of the cell wall ( $E_w$ ) according to the following equation:

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

where  $\rho$  and  $\rho_w$  are the densities of wood and cell wall, respectively. Since  $\rho_w$  is almost constant (ca.1400 kg/m<sup>3</sup>), the specific Young's modulus ( $E_L/\rho$ ) can be a direct indication of the stiffness of the cell wall itself.

The  $E_L/\rho$  has another importance for the quality evaluation of wooden soundboards. Since the  $E_L$  of wood is proportional to its dynamic Young's modulus ( $E_L$ ) [10], the  $E_L/\rho$  of wood is related to the sound velocity along the grain ( $V_L$ ):

$$V_L \approx \sqrt{\frac{E_L}{\rho}}$$
.

The higher  $V_L$  value coincides with the smaller mechanical damping irrespective of the wood species [11] because both of them depend on the microfibril angle in the wood cell wall: the smaller the microfibril angle, the greater the  $V_L$  value and smaller the damping [12]. Accordingly, the higher the value of  $V_L$ , the greater is the acoustic converting efficiency of the wood. In fact, soundboards are

usually made of woods having high  $V_L$  values, such as Sitka spruce wood [10,13,14]. Thus, a high value of  $V_L$  is the minimum requirement for quality soundboards.

The mechanical anisotropy of wood is also an important property. Owing to the orientation of cellulose microfibrils, the *E* value of wood is much greater than its shear modulus (*G*). Therefore, wood shows larger E/G values (~30) than isotropic materials (2~3). In addition, the damping of wood in shear deformation is 2–4 times greater than that in axial deformation [12]. Consequently, the wood with a greater E/G value shows greater damping at high frequencies to produce a softer 'woody' tone [14–16].

Here, we recalculate Kohara's data to evaluate the acoustic quality of aged wood. The  $V_L$  value was calculated from the bending Young's modulus of wood and its oven-dry density. Unfortunately, the *G* values were not available in the articles of Kohara; consequently, the shear strength ( $\sigma_s$ ) was used instead of *G* to obtain the factor of anisotropy ( $E/\sigma_s$ ). In Figure 10, the  $V_L$  and  $E/\sigma_s$  values of wood are plotted against its age. The  $V_L$  value increases in the first 300 years and then tends to decrease. Although the scattered plots of  $E/\sigma_s$  do not exhibit a clear trend, the  $E/\sigma_s$  values of aged wood are greater than those of new wood. These facts suggest that the acoustic quality of wood can be enhanced by 300 years of ageing.



Figure 10. Sound velocity along the grain ( $V_L$ ) and the factor of anisotropy ( $E/\sigma_s$ ) of cypress wood as a function of the ageing period. Recalculated from Kohara's data [3].

Thus far, various methods of chemical modification have been proposed to improve the acoustic quality of wood. These are actually effective to modify the values of E,  $V_L$  and other factors affecting the time-dependent characteristics of soundboards. However, theoretical calculation has predicted that any chemical treatments can hardly enhance the acoustic converting efficiency and the anisotropy of wood simultaneously [12]. In this sense, it is worth waiting for 300 years rather than treating the wood with chemicals to obtain a better soundboard.

# **III Effects of heating**

#### II.3 Is it possible to reproduce aged wood by heating?

Heating is sometimes regarded as 'accelerated ageing' because chemical reactions are generally accelerated by elevating the temperature. In fact, heat-treated wood is very similar to aged wood with respect to its darker colour, fragile nature and improved stability against humidity change. However, it is still difficult to realize the 'true' acceleration of ageing, i.e. complete reproduction of aged wood by short-term heating.

It is noteworthy that wood is aged under variable conditions where both the temperature and relative humidity (*RH*) fluctuate irregularly and widely ( $10-35^{\circ}C$  and 20-90%*RH* in Japan). Unfortunately, it is practically difficult to reproduce such environmental changes at higher temperatures because the hygroscopicity of wood depends on the temperature as well as the *RH*. A possible way is to heat the wood with alternate moistening and drying, but few attempts have been made so far.

In general, the strength of wood is reduced by heat treatment or high-temperature kiln drying mainly due to the decomposition of hemicelluloses [17–20]. The stiffness of wood is also reduced by long-term heating, but it often shows a slight increase at the initial stage of heating. Such an increase in the stiffness is attributed to the reduced hygroscopicity [20,21], crystallization of cellulose [22] and/or the chemical changes in minor constituents such as heartwood extractives [20]. All these changes are qualitatively similar to those resulting from ageing. However, according to Kubojima et al. [22], the maximum increase in the specific dynamic Young's modulus ( $E/\rho$ ) is 5%, while it is about 10% in specific shear modulus ( $G/\rho$ ). As stated in the previous chapter, a higher value of E/G' is required for quality wooden soundboards. Therefore, heating is still a risky treatment for musical instruments because it possibly degrades the tone quality of soundboard with a significant reduction in the E/G' value of wood.

Of course, I do not deny the possibility of heat treatment because it is an easy and effective method to reduce the hygroscopicity of wood. The reduced hygroscopicity gives greater dimensional stability against humidity change. In addition, various moisture-dependent properties of wood are indirectly stabilized with the reduction in hygroscopicity. These are the reasons why many researchers have dealt with the ageing-like effects of heating on the hygroscopicity and dimensional stability of wood.

In this chapter, the moisture sorption characteristics of heat-treated wood are detailed to suggest the importance of moisture conditioning for the effective stabilization by heating. Furthermore, the recent application of heat-treated wood for the imitation of ancient wooden statues is introduced briefly.

# II.4 The different effects of dry heating and steaming on the hygroscopicity of wood [23]

When wood is heated, a part of the wood components are depolymerized and lost. Therefore, the weight loss (*WL*) due to heating is an indication of the thermal degradation involved. Figure11 shows the plots of heating time vs. heating temperature to attain 10% *WL* of wood [23–25].



Figure 11. Logarithm of heating time vs. temperature to attain 10%*WL* of wood. *Hatched area*, the possible range for dry heating [e.g. 24]; open square, ageing at room temperature (estimated from the changes in the amount of wood constituents [4]); *closed square and solid line*, steaming [23,24]; open *circle*; heated at 85°C with alternate moistening and drying (80–30%*RH*) [25].

In « dry heating », the wood is first dried and then heated in the absence of moisture whereas in « steaming », the wood is heated in saturated water vapour. Above 100°C, steaming always results in faster degradation than dry heating because the hydrolysis of cellulose and hemicelluloses are accelerated in the presence of moisture [18,24,26,27]. On the other hand, the lack of data at lower temperatures (<100°C), where the chemical reactions proceed at moderate relative humidity, renders it difficult to determine the precise degradation rate in ageing.

Although Figure 11 is useful for an approximate evaluation of thermal degradation, it does not reflect the qualitative differences between dry-heated wood and steamed wood. Figure 12 shows the WL of wood as a function of heating duration (**a**) and the effects of WL on the water-soluble extractives content in heat-treated wood (**b**).



Figure 12. The effect of heating duration on the percentage weight loss (*WL*) of spruce wood (a) and the content of water-soluble extractives in the heat-treated wood plotted against the *WL* (b). *Open plots*, completely dry wood was heated in the absence of moisture (dry heating); *closed plots*, moistened wood (27~30% moisture content) was heated in saturated water vapour (steaming).

Even at the same *WL*, the amount of extractives in the steamed wood is considerably greater than that in the dry-heated wood. The water-soluble decomposition residues are not major components in the cell-wall framework. Therefore, these extractives should be removed when we compare the effects of dry heating and steaming on the structure of framework polymers.

Figure 13 shows the equilibrium moisture content (M) of heat-treated wood at 33% and 97% relative humidities (RH) plotted against the WL. In this case, the water-soluble extractives have been removed prior to the hygroscopicity measurements. No difference is observed between the M of dry-heated wood and steamed wood at 33% RH whereas at 97% RH, dry-heating results in a smaller M than that due to steaming.



Figure 13. The equilibrium moisture content (*M*) of heat-treated spruce wood at 25°C as a function of weight loss (*WL*). Open plots, dry heated; closed plots, steamed.

Here, we apply the Hailwood-Horrobin adsorption equation [28] to separate the adsorbed water into hydrated water ( $M_h$ ) and dissolved water ( $M_s$ ), as shown in Figure 14a. In general, the  $M_h$  reflects the

number of active adsorption sites, while the  $M_s$  is sensitive to the large-scale conformation of wood polymers. In Figure 14b, the changes in  $M_h$  and  $M_s$  are plotted against the *WL*. The amount of  $M_h$  decreases linearly with an increase in the *WL* regardless of the heating methods. On the other hand, the  $M_s$  changes only slightly by steaming, while it decreases significantly by dry heating.



Figure 14. The moisture sorption isotherms of untreated spruce wood (a) and the changes in the amount of hydrated water ( $M_h$ ) and dissolved water ( $M_s$ ) due to heating (b). *Circles*, changes in  $M_h$ ; *squares*, changes in  $M_s$ ; *open plots*, the effects of dry heating; *closed plots*, the effects of steaming.

The reduced hygroscopicity and the improved dimensional stability of heat-treated wood are often explained by the decomposition of hygroscopic hemicelluloses and other carbohydrates and their condensation or polymerization [26]. If this is the case, the  $M_s$  should be significantly reduced by steaming rather than dry heating because the decomposition of hemicelluloses and the crystallization of cellulose are accelerated in the presence of moisture [18,24,26,27,29]. However, the experimental results do not meet this expectation. This fact implies that the  $M_s$  of heat-treated wood reflects large-scale conformational changes in the wood polymers.

During dry heating, various chemical changes such as depolymerization, condensation and crystallization proceed in a 'shrunk' state wherein the intermolecular spacing is minimized. Although the formation of ether cross links has been disproved by early investigations [30], the condensation of lignin and the formation of strong hydrogen bonds (so-called hornification) possibly restricts the swelling of wood to reduce  $M_s$ . On the contrary, such a tight structure cannot be formed during steaming because the chemical changes occur in the 'swollen' state wherein the intermolecular spacing is maximized. Consequently,  $M_s$  is not significantly reduced by steaming, whereas dry heating results in a remarkable reduction in  $M_s$ . These speculations are supported by the changes in the wet volume due to heating. Figure 15 shows the swelling of heat-treated wood in water as a function of WL. In contrast to the effective restriction of swelling by dry heating, the wet volume of steamed wood shows a slight increase at low WLs and is always greater than that of dry-heated wood at the same WL. Thus, dry heating appears to be a better option than steaming when we want to reduce the hygroscopicity of wood and improve its dimensional stability with minimal thermal degradation.



Figure 15. The volumetric swelling of heat-treated wood in water plotted against the *WL*. The swelling value was based on the volume of wood in its untreated and completely dry condition.

In Figure 16, the moisture sorption characteristics of aged wood are compared to those of heat-treated wood. Since the sorption equation is not applicable to the limited data for the aged wood, the relative moisture content ( $M_{treated}/M_{untreated}$ ) of aged and heat-treated wood is plotted against the *RH*. The effects of ageing are qualitatively similar to those of dry heating rather than steaming. Probably, the ageing involves little steaming-like effect such as the radical hydrolysis of hemicelluloses and the loosening of the cell wall structure because the wood is maintained in a dry condition (at about 10% moisture content) during ageing.



Figure 16. The relative moisture content ( $M_{\text{treated}}/M_{\text{untreated}}$ ) of aged and heat-treated wood as a function of relative humidity (*RH*). Open plots, dry heating at 180°C for 24h (*WL* = 9.3%); *closed plots*, steaming at 180°C for 0.5 h (*WL* = 20.7%); *cross plots*, ageing for 1300 years (recalculated from [6]).

Finally, the effects of typical chemical modifications are introduced. As shown in Figure 17a, hydroxyl groups in the amorphous wood polymers are replaced with acetyl groups by acetylation, whereas the formaldehyde treatment introduces oxymethylene bridges between the wood polymers. The effects of these treatments are shown in Figure 17b. The acetylation provides a greater reduction in M at lower RH because the  $M_h$ , rather than the  $M_s$ , is reduced by the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups. On the contrary, the effect of formaldehyde treatment is greater at a higher RH because the  $M_s$  is effectively reduced by the cross-link formation. With respect to the moisture sorption characteristics, the effects of ageing and dry heating are qualitatively similar to that of formaldehyde treatment.



Figure 17. The structural changes in amorphous wood polymers due to chemical modifications (a), and the effects of these chemical modifications on the hygroscopicity of wood (b) [31].

# II.5 The reversible and irreversible effects of heating [32]

The effects of heating are usually explained by irreversible chemical changes such as hydrolysis, condensation and crystallization in the wood constituents. Consequently, the hygroscopicity of heat-treated wood should remain unchanged by after-treatments involving no chemical changes. However, the effects of heating are not always irreversible as described below.

In Figure 18, the equilibrium moisture content (*M*) of dry-heated wood is plotted against the loss in weight (*WL*) due to the heating. The *M* of wood remains unchanged by repeating measurements at 97%RH (2~4), but it shows a significant recovery in the second measurement at 57%RH (1~3). This suggests that the effect of dry heating is partly reversible, and such a temporary effect disappears by moistening at high *RH*s.



Figure 18. The equilibrium moisture content (*M*) of heat-treated wood at 25°C as a function of weight loss (*WL*) due to heating. *Circles*, at 57%*RH*; squares, at 97%*RH*. The numbers indicate the order of measurements.

A possible interpretation of the reversible effects of dry heating is the annealing or the physical ageing of wood polymers. Figure 19 illustrates a simplified model of wood consisting of an amorphous viscoelastic part (a), adsorbed moisture (b) and a rigid hydrophobic part (c) to explain the annealing-like effect of heating.



Figure 19. An interpretation of the reversible changes in the hygroscopicity of heat-treated wood.

During the drying of wood from its natural green state (**A**), some stress or strain occurs in the amorphous part because its shrinkage is restricted by the rigid hydrophobic part. Such a distortion remains unrecovered in the dry condition because the mobility of amorphous molecules is very low (**B**). However, the amorphous part becomes mobile with moisture sorption (**C**) and it recovers its initial « natural » state in a highly humid condition (**D**). On dry heating, the remaining stress is relaxed with the thermal activation of amorphous polymers (**E**), and such a stabilized, i.e. annealed structure, restricts the moisture sorption at low relative humidity (**F**). At high relative humidity, however, the amorphous molecules recover their initial state as their mobility increases (**G**). Indeed, the structure of wood is not so simple, but the viscoelastic nature of the amorphous wood polymers should be considered to understand the reversible changes in hygroscopicity due to heating and moistening. Such an annealing effect might be induced during hundreds years of ageing. Since the wood is usually aged in a dry condition, the amorphous wood polymers are maintained in a glassy state and are almost « frozen » during ageing. However, they may gradually rearrange and stabilize with alternate swelling and shrinking due to humidity fluctuations.

# II.6 The repair of ancient statues using heat-treated wood [33]

In general, the colour of wood darkens by heating. The brownish colour of heat-treated wood is not always preferable for common uses, but it is useful for a particular purpose: the repairing of ancient wooden statues. Although various synthetic stains and paints and available, it is still difficult to imitate the natural colour and lustre of aged wood. In addition, the combination of new and old wood is not preferable because it possibly causes unexpected problems due to different dimensional changes under humidity fluctuation. In this case, heating is a promising method to reproduce parts for ancient wooden statues because it provides an «antique» appearance as well as improved dimensional stability. Figure 20 shows the successful repairing of a Buddhist statue by using heat-treated wooden « hair ».



Figure 20. Changes in the colour of cypress wood due to heating at 180°C and the repairing of ancient wooden statue using heat-treated parts ('Yakushinyorai' in Okubo-dera temple, 8<sup>th</sup> century).

#### III Japanese traditional coating technology for wood protection

#### III.1 Urushi, an excellent natural lacquer

In recent years, various natural lacquers and vanishes were evaluated for their safety and sustainability. Among them, 'urushi' is the most excellent choice owing to its beautiful appearance and extraordinary practical performance. Figure 21a shows an ancient wooden comb with a three-layered urushi coating. Although the teeth are broken, its frame has been protected from weathering and biological attacks by the durable urushi coating for 6800 years. Urushi is still widely used as a coating for tableware, ornaments and other daily necessities in Japan and other east-Asian countries. Since it symbolizes traditional Japanese aesthetics owing to its deep colour and beautiful lustre, the artistic lacquerware are generally known as 'japan'. The urushi coating is not only beautiful but also durable against water, acid, alkali and most of the organic solvents. The antibacterial property of the urushi coating is also favourable for tableware, as shown in Figure 21b. As urushi is applicable to metals, it presents a fascinating collaboration of traditional beauty and modern technology, as shown in Figure 21c.



Figure 21. Ancient wooden comb coated with urushi, 6800 years old (a), traditional Japanese tableware coated with urushi (b) and a recent application of urushi coating on a digital camera (c) The photograph of wooden comb was provided by the Ishikawa Archaeological Foundation.

It should be emphasized that urushi exhibits strong adhesion with wood and other cellulosic materials. Probably, bees are the earliest creatures to have discovered urushi as an adhesive: they sometimes joined their houses to the branch of a tree by using the urushi and a similar sap of the lacquer tree. The strong cohesion between urushi and hemp enabled the realization of earliest FRPs in which the layered-hemp cloths are solidified with urushi. This FRP-like material (*kanshitsu*, in Japanese) was used for making Buddhist statues in the Middle ages.

# III.2 Chemical components and structure of the urushi coating

Urushi is made from the sap of the lacquer tree, *Rhus vernicifera*, as shown in Figures 22a and 22b. The sap consists of water ( $20 \sim 25\%$ ), water-insoluble urushiol ( $55 \sim 70\%$ ), glycoproteins ( $1 \sim 3\%$ ), water-soluble polysaccharides ( $6 \sim 10\%$ ) and enzymes (laccase and so on,  $\sim 1\%$ ). Urushiol, the major component of the sap, is a mixture of some catechol derivatives, as shown in Figure 22c [34].



Figure 22. Lacquer tree (a), sap extruding from the trunk (b) and the structure of urushiol (c) [34]

In the traditional lacquer ware, the sap is sufficiently stirred with mild heating (40~50°C). This 'kurome' process results in the evaporation of water, the polymerization of urushiol and the reaction of glycoproteins with urushiol. At the same time, the lacquer constituents are well homogenized and the polysaccharides disperse into the oil phase in which the urushiol-glycoproteins complex is formed. Consequently, each spherical grain of the polymerized urushiol is surrounded by a thin wall of polysaccharides in the urushi coating, as shown in Figure 23a. Such a fine 'core-shell' structure is believed to be responsible for the excellent durability of the urushi coating owing to the high barrier of polysaccharide-wall against oxygen [35]. Although the anti-oxidation effect of the polysaccharides shell is still debatable [36], it is clear that the fine surface of the kurome-processed lacquer is responsible for its attractive lustre.



Figure 23. The structural changes in the urushi lacquer during traditional processing (a) and the fine structure image of urushi coating using atomic force microscope (b).

#### III.3 Future potential of urushi as a coating for musical instruments

Although the excellent properties of urushi coating have been fully investigated, only a few studies have been conducted on the acoustic properties of urushi-coated wood [37,38]. The viscoelastic profile of the urushi coating is characterized by three relaxation processes, as shown in Figure 24. Owing to the tight cross linkage among the urushiol polymers, the mechanical damping of the urushi coating is relatively low and stable at room temperature in the audio frequency range. Such characteristics of urushi coating are very similar to those of the polyurethane coating used for the soundboards of a harp and other similar instruments [37]. This fact suggests that the urushi is a favourable lacquer for wooden soundboards in which lower damping, a long lifetime and an artistic appearance are required.



Figure 24. The temperature variations of dynamic Young's modulus (*E*) and the mechanical loss tangent (tan $\delta$ ) of the urushi film at 11 Hz.  $\alpha$ , glass transition of urushiol polymers;  $\beta$ , motions of adsorbed water molecules;  $\gamma$ , motions of methylene groups in the side-chains of urushiol.

In any case, delicate application of the coating is needed because the acoustic properties of soundboards are considerably influenced by the thickness of the coating. Although a thicker coating provides greater stability against environmental changes [38], it reduces both the acoustic converting efficiency and anisotropy of wooden soundboards [37].

#### **IV General conclusions**

Wood is incredibly durable when it is appropriately maintained. The improved stiffness and anisotropy of aged wood appear to be favourable for wooden soundboards. However, the fragile nature of wood, particularly in a humid condition, should be considered.

The effects of ageing are qualitatively similar to those of dry heating with respect to the moisture sorption characteristics of wood. However, the reduced anisotropy of heat-treated wood possibly deteriorates the quality of wooden soundboards.

A traditional Japanese lacquer, urushi, has promising features as an excellent coating for wooden musical instruments.

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