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Mechanical properties of wood in an unstable state due to temperature changes, and analysis of the relevant mechanism III: effect of quenching on stress relaxation of chemically modified woods

Abstract In order to understand the mechanism of destabilization occurring when wood is quenched, we applied chemical modifications, and controlled the number of moisture adsorption sites in wood. The degree of destabilization was evaluated according to the fluidity $(1 - E_t/E_0)$, increase in fluidity, and relative fluidity in relation to the nonmodified wood, and was discussed by comparing these quantities with the hygroscopicity or swelling of wood. We found that destabilization of chemically modified wood was lower than that in nonmodified wood, and the amount of adsorbed water controlled the magnitude of flow of wood. Moreover, according to the analysis of water state by the Hailwood-Horrobin equation, it was shown that the function of dissolved water to the fluidity is almost identical for both chemical modifications, whereas hydrated water has more effect on acetylated wood than on formaldehyde-treated wood. We speculate that the motion of water molecules due to quenching accompanied with the redistribution of energy resulting from the exchange of their potential energy and movement to attain a new balance, and the introduced acetyl groups and cross-linking restrict the water molecule movement.

Key words Quenching · Chemically modified wood · Stress relaxation · Destabilization · Adsorbed water

Introduction

The mechanical properties of wood, equilibrated with ambient temperature or relative humidity, have been thoroughly investigated.[1,2] However, it was recently found that the mechanical properties of wood that has undergone a sudden change of temperature or relative humidity differ remarkably from those equilibrated under constant conditions.[3–6]

Kudo et al.[3] showed that the modulus of elasticity (MOE) and relative relaxation modulus (E_t/E_0) of the water-swollen wood quenched from 30°–80°C to 20°C were much smaller, and fluidity $(1 - E_t/E_0)$ was larger than that of wood kept at 20°C for a long time. Moreover, Kamei et al.[4] found that the MOE decreased and fluidity increased with increased cooling rate. Meanwhile, when the temperature of water-swollen wood rose rapidly from 20°C to 30°–80°C, the fluidity of wood peaked around 50°–60°C, and above this, it tended to decrease.[5] These phenomena have been explained by the occurrence of destabilization in wood.

Recently, Wang et al.[6] reported that the fluidity of water-swollen wood quenched from 100°–140°C to 20°C has a constant value, while that of wood quenched from 150°–180°C to 20°C increased depending on the range of temperature change, and the relative fluidity was 3.2 times larger than that of the control. These results were all explained by the destabilization occurring in wood when it undergoes a rapid change in temperature, and it was inferred that the destabilization is closely related with the number of water molecules. It is known that acetylation[7] and formalization[8,9] improved the dimensional stability of wood[10] and can reduce the hygroscopicity and adsorbed water through exchange of hydroxyl groups. Moreover, the mechanical properties of acetylated wood, such as Young's modulus and strength, hardly change,[11] while the MOE of formaldehyde-treated wood does not change appreciably in the longitudinal direction.[12] It is thought that acetylation and formaldehyde treatment are optimum for discussion of the relationship between destabilization and adsorbed water.

In this article, we examine the mechanism of destabilization in quenched wood by relating fluidity with hygroscopicity and volumetric swelling. We prepared chemically modified woods, in which the numbers of moisture adsorption sites can be arbitrarily controlled. The information from chemically modified wood should also be applicable to the mechanism of destabilization in nonmodified wood.

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Materials and methods

Materials

The wood samples were cut from the heartwood of hinoki (*Chamaecyparis obtusa* Endl.). The specimen size was 15 (T) × 4 (L) × 120 mm (R) for stress relaxation measurement and 20 (T) × 4 (L) × 40 mm (R) for the adsorption test. Before acetylation or formaldehyde treatment, extraction was carried out with ethanol–benzene (v/v = 1 : 2) for 8 h and then ethanol for 8 h.

Acetylation and formaldehyde treatment

Acetylation was carried out with acetic anhydride without a catalyst at 120°C. Formaldehyde treatment was administered according to the method described by Minato et al.[13] The reaction durations were 1, 3, 8, and 24 h.

For each reaction condition, two samples for stress relaxation and one sample for adsorption testing were treated together. After the reaction, all samples were thoroughly rinsed with running water, and air-dried at room temperature for 3 days. The samples were then oven-dried at 103°C for 4 h. The weight gain (WG) was calculated on the basis of the oven-dried weight before and after the reaction. The values of WG for acetylated wood were 0.59%–5.42% and those for formaldehyde-treated wood were 16.7%–24.5%. There was a positive correlation between WG and reaction time.

Prior to the successive quenching, water was impregnated into nonmodified wood as well as chemically modified wood under reduced pressure, and the samples were kept in a water bath at 20°C for more than 1 month to attain the stable state.

Quenching and stress relaxation measurement

The water-swollen wood for stress relaxation measurement was preheated at 80°C for 3 h and quenched to 20°C. After maintenance for 3 min, stress relaxation was measured in the radial direction for 2 h at 20°C. The measurement was conducted in the same way for the control, which was kept at 20°C for a long time. This process was performed in a water bath.

The relaxation modulus (E_t) and relative relaxation modulus (E_t/E_0) were calculated from the stress relaxation curves. The fluidity ($1 - E_t/E_0$) of quenched wood and changes in fluidity of quenched wood relative to the control were used to evaluate the destabilization of wood.

Moisture adsorption test

The swollen wood was oven-dried at 103°C for 4 h once more and conditioned to equilibrium at relative humidity of 22.8%, 42.6%, 65.0%, 75.4%, and 93.0% over saturated salt solutions at 20°C.

Results and discussion

Effect of quenching on stress relaxation of chemically modified wood

Figure 1 shows the relative relaxation modulus of acetylated and formaldehyde-treated wood. The relative relaxation modulus of control wood treated by chemical modifications slightly increased with weight gain; however, that of the quenched wood was lower than the respective control wood, whether acetylated or formaldehyde treated. The relative relaxation modulus of chemically modified wood when quenched was larger than that of nonmodified wood when quenched. These results show that chemical modifications stabilize the dimensional and mechanical properties of wood.

Hygroscopicity of chemically modified wood

The results of moisture adsorption tests are summarized in Table 1. Moisture adsorption data were analyzed by the
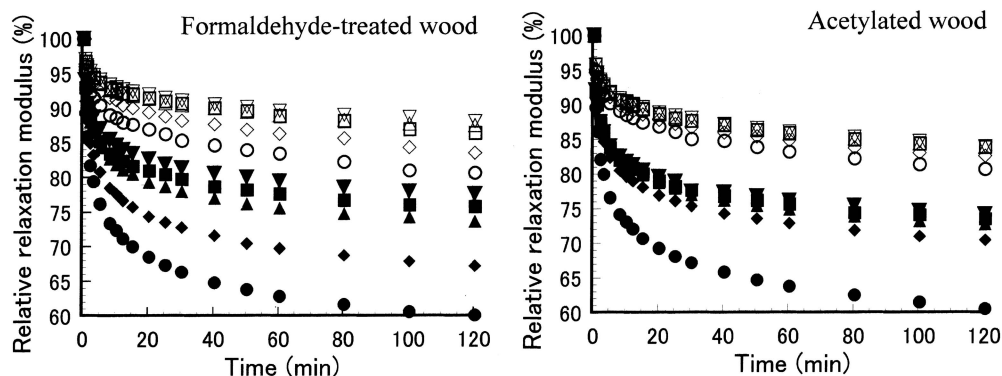

Fig. 1. Relative relaxation modulus curves for control wood (*hollow symbols*) and quenched wood (*solid symbols*) treated with formaldehyde (*left*) and by acetylation (*right*). For formaldehyde-treated wood: *circles*, nonmodified wood; diamonds, weight gain (*WG*) 0.59%; *tri-angles*, WG 2.39%; squares, WG 3.44%; *inverted triangles*, WG 5.42%. Acetylated wood: *circles*, nonmodified wood; *diamonds*, WG 16.7%; *triangles*, WG 18.8%; *squares*, WG 21.4%; *inverted triangles*, WG 24.5%

Table 1. Equilibrium moisture content (EMC) at each relative humidity level at 20°C for acetylated wood and formaldehyde-treated wood

Sample	Weight gain (%)	EMC				
		22.8% RH	42.6% RH	65% RH	75.4% RH	93% RH
Formaldehyde-treated wood	0 (Nonmodified)	4.53	7.58	11.1	14.0	22.4
	0.59	4.30	7.01	10.1	12.6	18.7
	2.39	3.50	5.67	7.93	9.87	13.9
	3.44	2.81	4.44	6.09	7.43	10.3
	5.42	2.34	3.59	4.90	5.83	7.74
Acetylated wood	0 (Nonmodified)	4.52	7.55	11.1	14.0	22.3
	16.7	1.98	3.65	5.55	7.37	12.4
	18.8	1.71	3.22	4.92	6.61	10.9
	21.4	1.49	2.82	4.31	5.82	9.69
	24.5	1.15	2.30	3.56	4.87	7.95

RH, relative humidity

Table 2. Parameters of Hailwood-Horrobin equation, hydrated water, and dissolved water at 93% RH for formaldehyde-treated and acetylated wood

Sample	Weight gain (%)	γ^2	W(g)	K_1	K_2	M_h	M_s
Formaldehyde-treated wood	0 (Nonmodified)	0.971	279.1	5.82	0.756	4.98	15.3
	0.59	0.974	289.1	5.94	0.728	4.79	13.0
	2.39	0.957	351.3	6.02	0.717	3.95	10.2
	3.44	0.967	451.8	7.21	0.680	3.18	6.86
	5.42	0.993	536.4	7.68	0.645	2.69	5.03
Acetylated wood	0 (Nonmodified)	0.973	279.9	5.85	0.753	4.97	15.0
	16.7	0.966	545.2	3.31	0.816	2.10	10.4
	18.8	0.964	582.2	2.87	0.792	1.79	8.65
	21.4	0.962	670.6	2.89	0.795	1.56	7.61
	24.5	0.957	731.2	1.97	0.836	1.01	6.49

γ^2, contribution coefficient; W, weight of dry wood per mole of sorption sites; K_1, equilibrium constant where the hydrate is formed from dissolved water and dry wood; K_2, equilibrium constant between dissolved water and water vapor; M_h, amount of hydrated water; M_s, amount of dissolved water

Hailwood-Horrobin adsorption equation,[14] which is well suited for chemically modified wood.[15] The adsorption equation is defined as follows:

$$h/M = A + Bh - Ch^2$$

$$A = \frac{W}{18K_2(K_1 + 1)}$$

$$B = \frac{(K_1 - 1)W}{1800(K_1 + 1)}$$

$$C = \frac{K_1 K_2 W}{18000(K_1 + 1)}$$

$$W = 1800\sqrt{B^2 + 4AC}$$

where h is relative humidity (%), M is equilibrium moisture content (%), K_1 is the equilibrium constant where the hydrate is formed from dissolved water and dry wood, K_2 is the equilibrium constant between dissolved water and water vapor, W is the weight of dry wood per mole of sorption sites and $1/W$ indicates the amount of sorption sites. Then the amounts of hydrated water (M_h) and dissolved water (M_s) are expressed as functions of relative humidity (H) as follows:

$$M_h = \frac{1800K_1 K_2 H}{W(100 - K_1 K_2 H)}$$

$$M_s = \frac{1800K_2 H}{W(100 - K_2 H)}$$

The parameters of the Hailwood-Horrobin adsorption equation such as the amounts of hydrated water and dissolved water and so on, at each WG are summarized in Table 2. High contribution coefficients (γ^2) indicate that the Hailwood-Horrobin adsorption equation was suitable for the observed data.

The value of W for each chemically modified wood was greater than that for nonmodified wood. This reflects the decrease of moisture adsorption sites and resulting reduction in the amount of adsorbed water. The hydrated water of acetylated wood was less than that of formaldehyde-treated wood, whereas the dissolved water of acetylated wood was more than that of formaldehyde-treated wood.

Dependence of the destabilization of chemically modified wood on adsorbed water

Effects of chemical modification on the fluidity of wood are shown in Fig. 2. The fluidity of chemically modified wood reduced with increase of weight gain. To discuss the effect of adsorbed water on the destabilization of wood caused by
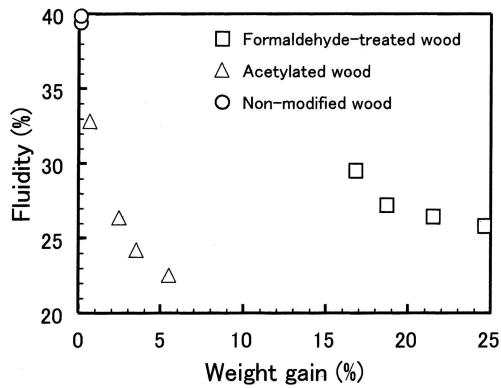
Fig. 2. Effect of chemical modifications on fluidity of quenched wood

Fig. 4. The amounts of hydrated water (M_h) and dissolved water (M_s) at 93% RH for chemically modified wood. *Squares*, formaldehyde-treated wood; *triangles*, acetylated wood, *open symbols*, M_h; *filled symbols*, M_s
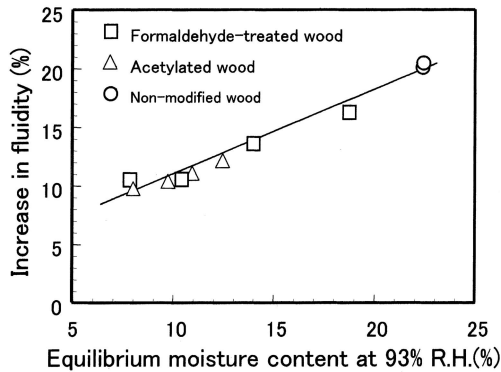

Fig. 3. Relationship between increase in fluidity and equilibrium moisture content at 93% relative humidity (RH) for chemically modified wood

quenching, increase in fluidity was defined as a measure of destabilization as follows

$$\text{Increase in fluidity (\%)} = [(1 - E_t/E_0)_q - (1 - E_t/E_0)_c] \times 100\%$$

where $(1 - E_t/E_0)_q$ and $(1 - E_t/E_0)_c$ are the fluidities of quenched and unquenched woods, respectively, treated together and hence having the same weight gain. For the relaxation modulus (Et), values at 120 min were adopted.

Figure 3 shows the relationship between increase in fluidity by quenching and equilibrium moisture content at 93% relative humidity (RH). The fluidity of nonmodified wood was around 20%, while that of chemically modified wood decreased linearly with reduced equilibrium moisture content irrespective of chemical modification. This result shows that the destabilization of wood is mainly influenced by the amount of adsorbed water. Generally, water molecules have their stable state depending on temperature. When the temperature changes instantaneously, however, water molecules in wood cannot respond immediately to their new state, hence the water molecules may become unstable in energy and/or low in entropy. To attain a new balance, it is thought that two phenomena occur among neighboring water molecules; redistribution owing to the exchange of localized energy, and movement of the water
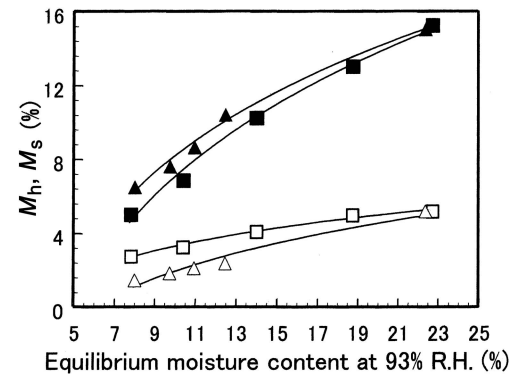
molecules themselves, promoting the flow of wood during stress relaxation. Therefore, the number of water molecules participating in the redistribution largely influences the degree of destabilization.

According to the Hailwood-Horrobin adsorption theory, adsorbed water is divided into hydrated water and dissolved water. In Fig. 4, the amounts of these aqueous forms are plotted against equilibrium moisture content at 93% RH. Figure 4 shows that the share of M_h and M_s was different between acetylated and formaldehyde-treated wood even at the same moisture content. This shows that hydrated wood and dissolved wood function differently depending on the kind of chemical modification.

In Fig. 5, hydrated and dissolved water at 93% RH are plotted against the increase in fluidity. The increase in fluidity decreased with reducing amounts of both hydrated water and dissolved water. It was found that either hydrated water or dissolved water influenced the destabilization of acetylated and formaldehyde-treated wood.

The contribution of dissolved water to the fluidity was almost identical for both chemical modifications, whereas that of hydrated water was more marked for formaldehyde-treated wood than for acetylated wood. This is attributable to the difference of the moisture adsorption field, which is related with the characteristics of chemical modifications.

Because the adsorption energy of dissolved water was lower and the amount of dissolved water was much more than that of hydrated water, the redistribution of water molecules, which promotes the flow of wood, would start from that of dissolved water. This suggests that water molecule movement is notably high for dissolved water.

Effect of structural changes on the destabilization of chemically modified wood

It is also necessary to consider the effect of the cell wall structure on destabilization, because it changes during chemical modifications. To clarify the influence of changes in microstructure on the destabilization of quenched wood,

Fig. 5. Dependences of increase in fluidity on the amount of hydrated water (*left*) and dissolved water (*right*) at 93% RH. *Circles*, nonmodified wood; *triangles*, acetylated wood; *squares*, formaldehyde-treated wood
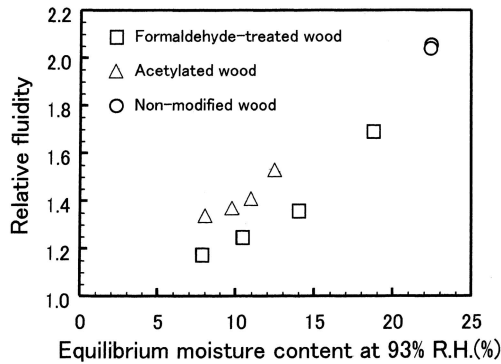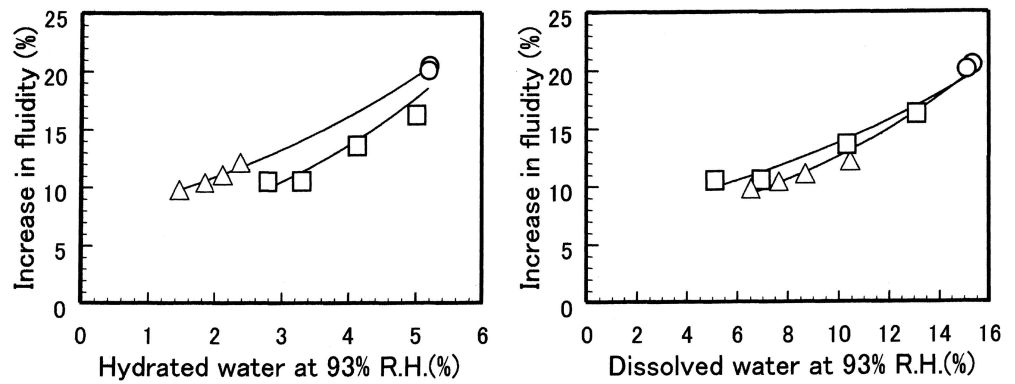

Fig. 6. Relationship between relative fluidity and equilibrium moisture content at 93% RH for chemically modified wood

Fig. 7. Relationship between decrease in volumetric swelling and antiswelling efficiency at 93% RH for chemically modified wood

the relative change in fluidity of chemically modified with respect to nonmodified wood was calculated according to

$$\text{Relative fluidity} = \frac{(1 - E_t/E_0)_q}{(1 - E_t/E_0)_{c,0}}$$

where $(1 - E_t/E_0)_q$ is the fluidity of quenched wood at each weight gain, $(1 - E_t/E_0)_{c,0}$ is that of nonmodified wood kept at 20°C for a long time, and the values of Et at 120 min were used. The results are shown in Fig. 6.

Figure 6 shows that the relative fluidity of acetylated wood is larger than that of formaldehyde-treated wood at a given moisture content. The difference of relative fluidity between acetylated and formaldehyde-treated wood is due to the difference in microstructure change between both modifications. It is likely that cross-linking between two hydroxyl groups can reduce the destabilization of wood more than exchange of hydroxyl groups with acetyl groups.

Furthermore, from the viewpoint of the redistribution of water molecules, the cross-linking and large acetyl groups in cellulose chains would obstruct the movement of water molecules. To examine such steric hindrance, we considered the cell wall structure of chemically modified wood by volumetric swelling and so-called antiswelling efficiency (ASE).
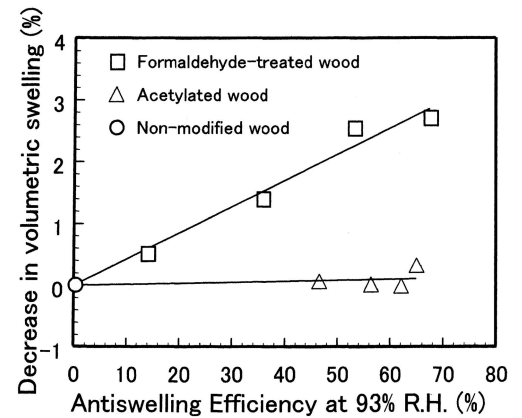
Decrease in volumetric swelling (%) $= S_{c,0} - S_m$

$$\text{ASE}(\%) = \frac{S_{c,0} - S_t}{S_{c,0}} \times 100\%$$

where S_m is the volumetric swelling of chemically modified wood based on the dimension before chemical modifications, $S_{c,0}$ is that of nonmodified wood, and S_t is that of chemically modified wood based on the dimension after chemical modifications. The value of volumetric swelling is from oven dry to 93% RH.

Figure 7 shows the relationship between the decrease in volumetric swelling and ASE at 93% RH for acetylated and formaldehyde-treated wood. The volumetric swelling of formaldehyde-treated wood was restricted because of the cross-linking between two hydroxyl groups, whereas that of acetylated wood was not restrained. The volumetric swelling of acetylated wood is almost the same as nonmodified wood. In the acetylated wood, there remains significant space available for the movement of water molecules, which is closely related with the flow of wood.

When chemically modified wood is quenched, the acetyl group and cross-linking should become an obstacle to the movement of water molecules and movement should be restricted in the finite range. Nevertheless, volumetric swelling showed that the adsorbed water in acetylated wood

had larger interspaces than formaldehyde-treated wood. The water molecules in acetylated wood may be easier to move than those in formaldehyde-treated wood. As a result, acetylated wood was much more unstable than formaldehyde-treated wood at the same equilibrium moisture content.

Conclusions

The destabilization of chemically modified wood was less remarkable than that of nonmodified wood, and there was a positive correlation between the amount of adsorbed water and changes in fluidity as a measure of destabilization. From the analysis of the moisture adsorption isotherm by the Hailwood-Horrobin equation, it was found that both hydrated wood and dissolved water affect the destabilization of wood, but the function of dissolved water to the fluidity was almost the same for both chemical modifications, whereas that of hydrated water was more for formaldehyde-treated wood than for acetylated wood. It was suggested that the acetyl group and cross-linking in chemically modified wood restrict the movement of water molecules, and reduce destabilization.

References

1. Forest Products Laboratory (1987) Wood handbook: wood as an engineering material. US Department of Agriculture, pp 4-1–4-44
2. Fushitani Y, Kikata Y, Okano T, Sadoh K, Takemura F, Norimoto M, Arima T, Tsutsumi J, Hirai N (1995) The physical properties of wood (in Japanese). Buneido, Tokyo, pp 88–191
3. Kudo K, Iida I, Ishimaru Y, Furuta Y (2003) The effects of quenching on the mechanical properties of wet wood (in Japanese). Mokuzai Gakkaishi 49:253–259
4. Kamei K, Iida I, Ishimaru Y, Furuta Y (2004) Effect of samples preparation methods on mechanical properties of wood I. Effect of period and temperature of water storage, and cooling rate after heating on water-swollen wood (in Japanese). Mokuzai Gakkaishi 50:10–17
5. Ooi K, Wang Y, Iida I, Ishimaru Y, Furuta Y (2005) Changes of mechanical properties of wood under an unstable state by heating or cooling (in Japanese). Mokuzai Gakkaishi 51:357–363
6. Wang Y, Iida I, Ishimaru Y, Furuta Y (2006) Mechanical properties of wood in an unstable state due to temperature changes, and an analysis of the relevant mechanism I. Stress relaxation behavior of swollen wood after quenching (in Japanese). Mokuzai Gakkaishi 52:83–92
7. Tarkow H, Stamm AJ, Erichson ECO (1950) Acetylated wood. USDA Forest Service, Forest Products Laboratory, Report No. 1593
8. Stamm AJ (1959) Dimensional stabilization of wood by thermal reaction and formaldehyde cross-linking. TAPPI 42:39–44
9. Stamm AJ (1959) Dimensional stabilization of paper by catalyzed heat treatment and cross-linking with formaldehyde. TAPPI 42:44–50
10. Minato K, Yusuf S, Imamura Y, Takahashi M (1992) Resistance of formaldehyde-treated wood to biological attacks (in Japanese). Mokuzai Gakkaishi 38:1050–1056
11. Zhao G, Norimoto M, Tanaka F, Yamada T, Rowll RM (1987) The structure and properties of acetylated wood I. Changes in the degree of crystallinity and dielectric properties by acetylation (in Japanese). Mokuzai Gakkaishi 33:136–142
12. Yasuda R (1995) Physical properties of wood modified with cross-linking reagents. PhD dissertation, Research Division of Agriculture, Graduate School of Kyoto Prefectural University, Kyoto, p 41
13. Minato K, Yasuda R, Yano H (1990) Improvement of dimensional stability and acoustic properties of wood for musical instruments with cyclic oxymethylenes II. Formalization with tetraoxane. Mokuzai Gakkaishi 36:990–996
14. Hailwood AJ, Horrobin S (1946) Absorption of water by polymers: analysis in terms of sample model. Trans Faraday Soc 42B:84–92
15. Yasusa R, Minato K, Norimoto M (1995) Moisture adsorption thermodynamics of chemically modified wood. Holzforschung 49:548–554