J Wood Sci (2001) 47:317–321

NOTE

Eiichi Obataya · Kazuya Minato · Bunichiro Tomita

Influence of moisture content on the vibrational properties of hematoxylin-impregnated wood

Received: June 2, 2000 / Accepted: September 6, 2000

Abstract The vibrational property of hematoxylin-impregnated wood was investigated from the aspect of moisture content dependence. The specific dynamic Young's modulus (E/γ) and loss tangent ($\tan\delta$) of hematoxylin-impregnated wood were determined in the relative humidity (RH) range of 0%–97%, and were compared with those of the untreated and some conventional chemically treated woods. The changes in the E/γ and $\tan\delta$ of wood with increasing RH were suppressed by acetylation and formaldehyde treatment because of a marked reduction in the hygroscopicity of the wood. Although the hematoxylin impregnation did not significantly affect the hygroscopicity of the wood, its influence on E/γ and $\tan\delta$ were similar to that of formaldehyde treatment at low RH and of acetylation at medium RH. It was supposed that at low to medium RH hematoxylin restrains the molecular motion of amorphous substances in the cell wall because of its bulkiness and rigidity. On the other hand, at high RH it seems to work as a plasticizer with adsorbed water molecules.

Key words Vibrational properties · Chemical treatment · Moisture content

Introduction

Many chemical treatments have been applied to improve the soundboard of wooden musical instruments.[1,2] Although it is not sure whether chemical treatment can enhance the quality of the soundboard,[3] it is one of the most effective methods for controlling the vibrational property of wood while keeping its cell wall structure.[4,5]

Among the vibrational properties, the mechanical loss tangent of wood ($\tan\delta$) increases after impregnation of water-soluble compounds such as polyethylene glycol (PEG) into the cell wall.[3–5] In contrast, Matsunaga and coworkers have recently reported that the $\tan\delta$ of wood in the air-dried state is markedly reduced by impregnation of water-soluble chroman compounds, such as hematoxylin and protosappanin B, which are extractives found in the heartwood of leguminous trees growing in tropical forests.[6–10] Because these compounds penetrate the cell wall without any reaction with wood components, the effect of their impregnation on the vibrational property was presumed to be analogous to the case for PEG impregnation. Therefore, the above results suggested us to reconsider the function of water-soluble substances in the cell wall in terms of the vibrational property of wood.

The working relation of hematoxylin to the vibrational property has not been fully clarified. Therefore, it is meaningful to compare the vibrational properties of hematoxylin-impregnated and conventional chemically treated woods. The influence of moisture content on the vibrational property should especially differ for those treatments. Although some researchers have dealt with the dependence of the vibrational property of chemically treated woods on relative humidity (RH), the changes in equilibrium moisture content by the treatments themselves were not taken into consideration.[1,2]

In this study the vibrational properties of the hematoxylin-impregnated wood were compared with those of untreated wood and some chemically treated woods at the same equilibrium moisture content level and the same RH. Based on the comparison of hematoxylin impregnation and some conventional chemical treatments, we discuss the behavior of hematoxylin in the wood cell wall.

E. Obataya (✉) · B. Tomita
Institute of Agricultural and Forest Engineering, University of Tsukuba, Ibaraki 305-8572, Japan
Tel. +81-298-53-7235; Fax +81-298-55-2203
e-mail: obataya@agbi.tsukuba.ac.jp

K. Minato
Department of Forest Science, Faculty of Agriculture, Kyoto Prefectural University, Sakyo-ku, Kyoto 606-8522, Japan

Materials and methods

A series of 100 sitka spruce (*Picea Sitchensis* Carr.) specimens 3 mm (T, tangential direction) × 15 mm (R, radial direction) × 150 mm (L, longitudinal direction) were used. Their vibrational properties were measured at 25°C and 60% RH; and of them, 25 specimens with analogous vibrational properties were selected and divided into five groups. One group remained untreated, and the other four groups were chemically treated. For sufficient, homogeneous treatment without serious degradation of wood constituents, the following methods were employed in this study.

Formalization: treatment with formaldehyde vapor at 120°C for 24 h under the catalysis of SO_2
Acetylation: treatment in acetic anhydride at 120°C for 8 h
PEG impregnation: soaking in 25% aqueous solution of PEG [$H(OCH_2CH_2)_nOH$, $M_w = 1000$] for 1 week
Hematoxylin impregnation: soaking in 1.7% aqueous solution of hematoxylin ($C_{16}H_{14}O_6$, $M_w = 302$) at room temperature for 12 days

After drying under atmospheric conditions and subsequent drying at 60°C in vacuo for a few days, the specimens were conditioned at 25°C and various RHs for more than 1 month. The specific dynamic Young's modulus (E/γ) and the loss tangent ($\tan\delta$) in the L direction were determined using the free-free flexural vibration method at frequencies ranging from 600 to 850 Hz. The measurements were carried out in a closed box in which the RH was controlled by various saturated salt solutions.

Table 1. Changes in weight and volume of wood specimens due to chemical treatments at absolutely dried condition

Treatment	Changes	
	Weight (%)	Volume (%)
Formalization	5.6	1.8
Acetylation	18.4	6.9
Polyethylene glycol impregnation	31.6	11.3
Hematoxylin impregnation	5.8	2.4

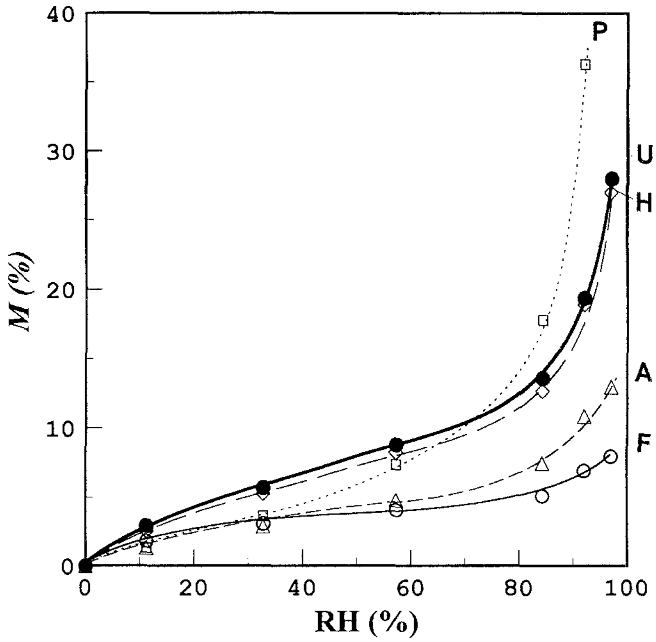

Fig. 1. Water sorption isotherms of untreated and chemically treated wood specimens at 25°C. *Filled circles*, untreated (U); *open circles*, formalization (F); *triangles*, acetylation (A); *squares*, polyethylene glycol impregnation (P); *diamonds*, hematoxylin impregnation (H); *M*, equilibrium moisture content; *RH*, relative humidity

Results and discussion

Swelling properties of chemically treated woods

Table 1 shows the changes in weight and volume of the wood specimens due to the chemical treatments. Both the weight and volume increased with the introduction of chemicals. Figure 1 shows the water sorption isotherms of the untreated and chemically treated wood specimens. The equilibrium moisture content (M) of wood was reduced by formalization and acetylation over the RH range. The PEG-impregnated wood had extremely high M values at more than 80% RH. On the other hand, hematoxylin impregnation did not affect the M values significantly.

Figure 2 shows the swelling of wood specimens with increasing M. V_t/V_u is a volume ratio based on the volume of specimens dried completely in their untreated state. The maximum volume of wood was well restricted by the formalization because of the crosslinking. Although the maximum volume was not restricted by acetylation, its swelling due to water sorption was reduced by the bulkiness of the acetyl groups introduced. The PEG-impregnated wood, which maintained the expanded volume even after treatment, swelled only slightly with increasing M. The extremely high M of the PEG-impregnated wood at high RH is attributed to the moisture sorption of PEG itself in the cell lumen, which hardly contributes to the apparent volume of wood. By impregnation of hematoxylin, the maximum volume of wood remained unchanged. This result is negative for the existence of crosslinking by the hematoxylin molecules.

Effects of relative humidity on the vibrational properties of chemically treated woods

Figure 3 shows the effects of RH on E/γ and $\tan\delta$ of the untreated and chemically treated wood specimens. It is acknowledged that the E/γ and $\tan\delta$ of wood along the grain are good indications for those of the wood cell wall itself.[11] Irrespective of the treatment, the E/γ gradually decreased up to 80% RH, above which it decreased abruptly. After formalization and acetylation, the marked drop in E/γ above 80% RH and the steep rise in $\tan\delta$ above 40% RH were fairly suppressed. These "stabilizing" effects were comparable to the results reported in the literature.[1,2] The

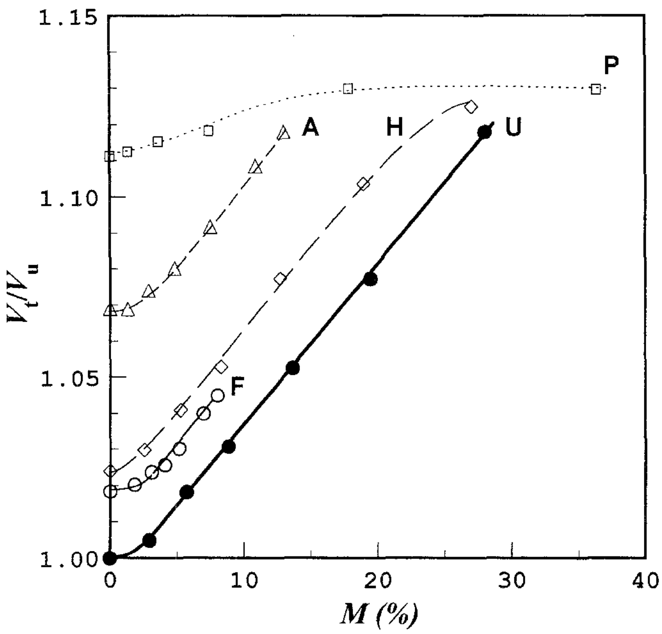

Fig. 2. Volumetric swelling (V_t/V_u) of untreated and chemically treated wood specimens plotted against the equilibrium moisture content (*M*). The volume ratio, V_t/V_u, is based on the volume of specimens dried completely in their untreated state

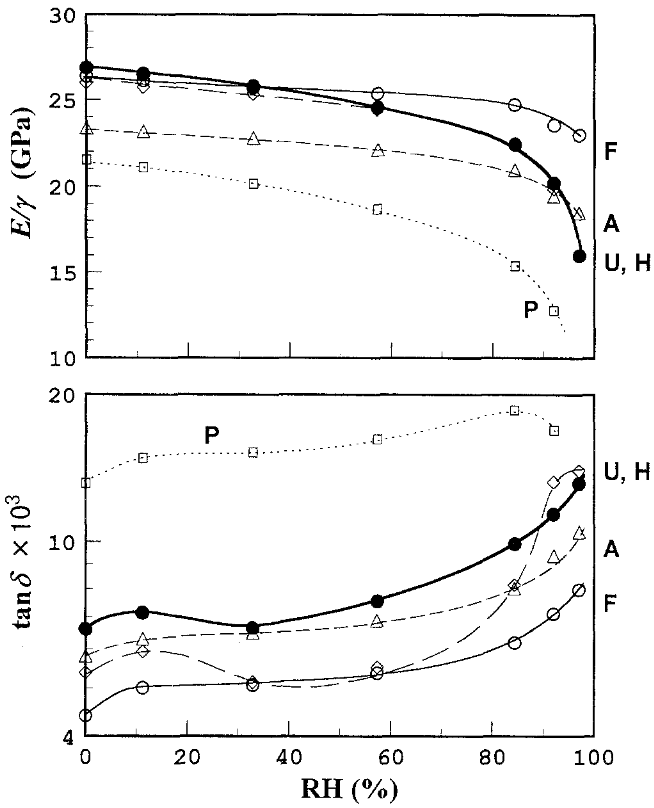

Fig. 3. Effects of relative humidity (*RH*) on the specific dynamic Young's modulus (E/γ) and loss tangent ($\tan\delta$) of the untreated and chemically treated wood specimens

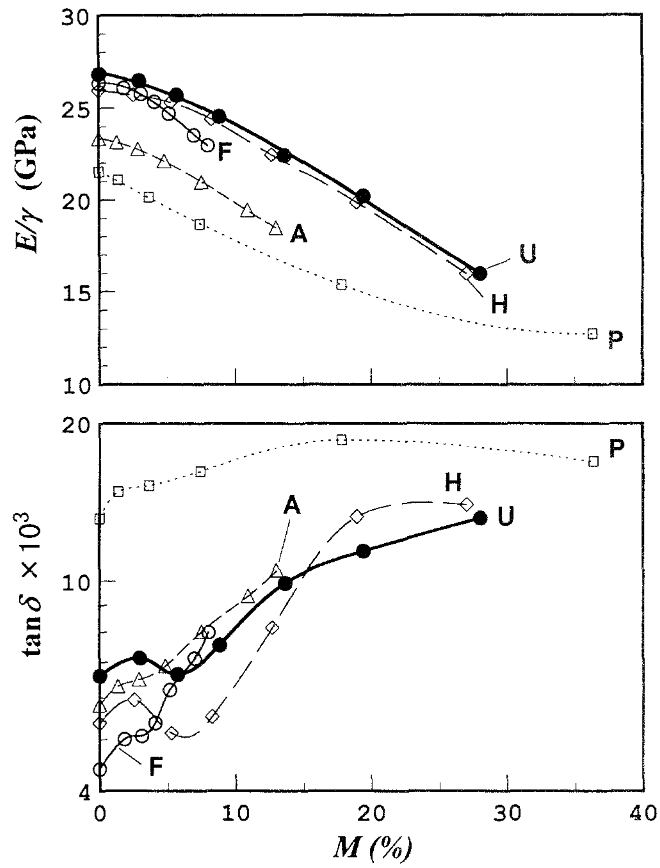

Fig. 4. Moisture dependencies of E/γ and $\tan\delta$ for the untreated and chemically treated wood specimens

$\tan\delta$ decreased after formalization and acetylation at all RH levels, whereas it was increased considerably by PEG impregnation. The $\tan\delta$ of hematoxylin-impregnated wood was lower than that of the untreated wood at low to medium RH, but the difference in $\tan\delta$ between them lessened with increasing RH.

Effects of equilibrium moisture content on the vibrational properties of chemically treated woods

The E/γ and $\tan\delta$ of the untreated and chemically treated wood specimens are plotted against *M* in Fig. 4. Although the E/γ differed among the treatments, the shapes of E/γ versus *M* curves showed an analogous trend. The peak or obscure shoulder of $\tan\delta$ at around 2% *M* can be explained by a mechanical relaxation process that appears at low temperature when a small amount of water is adsorbed.[12] The $\tan\delta$ values of the formaldehyde-treated and acetylated woods were lower than that of the untreated one below 5% *M*. However, their $\tan\delta$ increased rapidly with increasing *M* and exceeded those of the untreated wood above 5% *M*. The $\tan\delta$ of the PEG-impregnated wood was extremely high throughout the *M* range tested. The hematoxylin-impregnated wood had a lower $\tan\delta$ than did the untreated wood at lower than around 15% *M*.

Judging from the moisture dependence of E/γ and $\tan\delta$, the changes in the vibrational properties of the formaldehyde-treated and acetylated woods are somewhat larger than those of the untreated one. Thus the "stabilizing effects" by these treatments, as exhibited in Fig. 3, are mainly attributed to the marked reduction in M. On the other hand, the $\tan\delta$ of wood was markedly reduced by hematoxylin impregnation at low RH (i.e., low M range), whereas the hygroscopicity of wood remained almost unchanged over the RH range examined. This fact indicates that the reduction in $\tan\delta$ due to hematoxylin impregnation is independent of the change in the hygroscopicity of wood.

Effects of matrix swelling on the vibrational properties of chemically treated woods

Wood cell wall consists of cellulose microfibrils and amorphous matrix substances. The latter substances are viscoelastic, and their elastic moduli are lower than those of microfibrils. Therefore, the E/γ of wood decreases and the $\tan\delta$ increases owing to the swelling of matrix even if the viscoelastic properties of matrix remain unchanged. Thus, measurement of the vibrational properties at a definite swelling level offers information on the effects of introducting chemicals and water molecules on the viscoelasticity of matrix substances.

In Fig. 5 the E/γ and $\tan\delta$ of the untreated and chemically treated wood specimens are plotted against the V_t/V_u. If the chemicals and adsorbed water molecules have a similar effect on the viscoelasticity of matrix substances, all plots should lie on a common curve. However, the plots for the chemically treated wood more or less deviate from those for untreated wood.

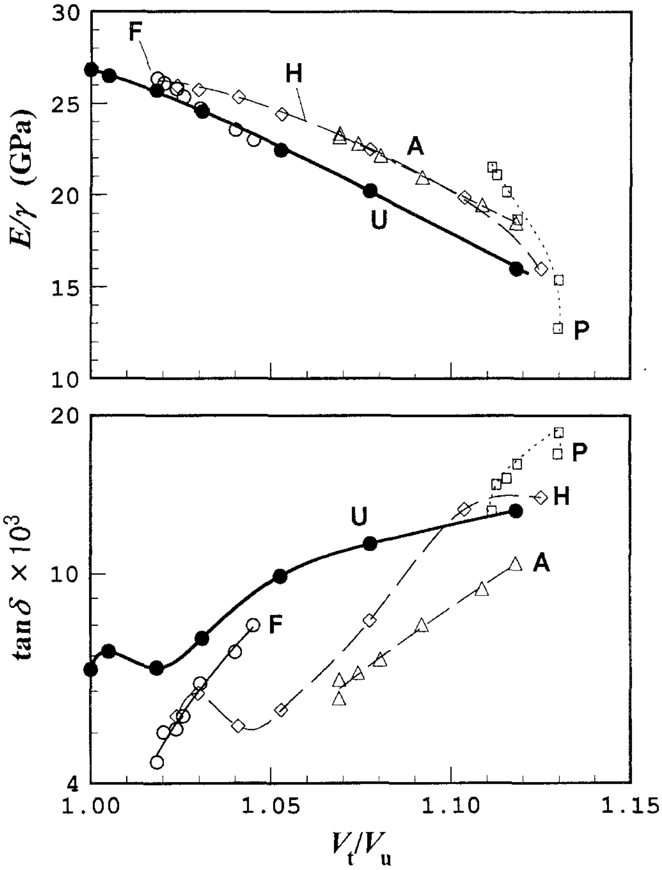

Fig. 5. E/γ and $\tan\delta$ values of the untreated and chemically treated wood specimens plotted against the volume ratio, V_t/V_u

The E/γ of formaldehyde-treated wood was almost the same as that of untreated wood, but the $\tan\delta$ was evidently lower. It is suggested that the oxymethylene crosslinking restricts the molecular motions of matrix substances and results in a reduction in $\tan\delta$, but its effect on the elastic modulus of matrix is relatively small and similar to that of the adsorbed water molecules.

The acetylated wood always showed higher E/γ and lower $\tan\delta$ values than untreated wood. Although the matrix substances are swollen by the introduction of acetyl groups, the mobility of bulky acetyl groups must be lower than that of the absorbed water molecules. In addition, the low mobility of acetyl groups can be maintained even at highly humid conditions because of its hydrophobic nature. Consequently, the molecular motions of the matrix substances might be restrained by the acetyl groups, which results in higher E/γ and lower $\tan\delta$ throughout the RH range examined.

The E/γ values of PEG-impregnated wood in the dry state ($M < 8\%$) were larger than those of untreated wood swollen with water to the same degree. It is supposed that the mobility of dry PEG molecules in the cell wall is less than that of the adsorbed water molecules; otherwise, some of the PEG in the cell lumen could enhance the Young's modulus of wood to some extent. However, the E/γ of PEG-impregnated wood decreased abruptly with slight swelling due to moisture adsorption. This marked drop in E/γ is interpreted to be due to the increase in specific gravity (γ) by the deliquescence of PEG in the cell lumen and the mobilization of PEG in the cell wall due to water sorption. Meanwhile, the $\tan\delta$ of PEG-impregnated wood was always larger than that of untreated wood. This fact might be due to the motions of PEG molecules themselves in addition to their plasticizing effect on the matrix substances.

The hematoxylin-impregnated wood exhibited interesting behavior. At low swelling levels ($V_t/V_u < 1.03$), the effects of the hematoxylin impregnation were similar to those of formalization. At middle swelling levels ($1.07 < V_t/V_u < 1.08$), the E/γ and $\tan\delta$ of the hematoxylin-impregnated wood came close to those of the acetylated wood. It was supposed that the molecular motions of matrix substances might be restricted by the bulky and rigid hematoxylin molecules tightly held in the interstices of the matrix. At high swelling levels ($1.10 < V_t/V_u$), however, both the E/γ and $\tan\delta$ of the hematoxylin-impregnated wood were comparable to those of untreated wood swollen with water. As stated above, hematoxylin does not react chemically with the matrix substances. Therefore, it is thought that the hematoxylin molecule does not restrain the molecular motions of matrix substances but acts as a plasticizer when it is surrounded by adsorbed water molecules at a highly humid condition.

The effects of impregnation of water-soluble substances have so far been simply understood as plasticization (i.e., mobilization of matrix substances due to the expanding intermolecular spacing). However, the similarity among hematoxylin impregnation, formalization, and acetylation suggests that the mobility of the impregnant itself should be taken into consideration, even though a chemical reaction does not occur between the impregnant and wood constituents.

References

1. Yano H, Norimoto M, Yamada T (1986) Changes in acoustic properties of sitka spruce due to acetylation (in Japanese). Mokuzai Gakkaishi 32:990–995
2. Yano H, Minato K (1992) Improvement of the acoustic and hygroscopic properties of wood by a chemical treatment and application to the violin parts. J Acoust Soc Am 92:1222–1227
3. Obataya E, Ono T, Norimoto M (2000) Vibrational properties of wood along the grain. J Mater Sci 35:2993–3001
4. Akitsu H, Norimoto M, Morooka T (1991) Vibrational properties of chemically modified wood (in Japanese). Mokuzai Gakkaishi 37:590–597
5. Sugiyama M, Obataya E, Norimoto M (1998) Viscoelastic properties of the matrix substance of chemically treated wood. J Mater Sci 33:3505–3510
6. Minato K, Sakai K, Matsunaga M, Nakatsubo F (1997) The vibrational properties of wood impregnated with extractives of some species of leguminosae. Mokuzai Gakkaishi 43:1035–1037
7. Sakai K, Matsunaga M, Minato K, Nakatsubo F (1999) Effects of impregnation of simple phenolic and natural polycyclic compounds on physical properties of wood. J Wood Sci 45:227–232
8. Matsunaga M, Minato K, Nakatsubo F (1999) Vibrational property changes of spruce wood by impregnation with water-soluble extractives of pernambuco (*Guilandina echinata* Spreng.). J Wood Sci 45:470–474
9. Matsunaga M, Obataya E, Minato K, Nakatsubo F (2000) Working mechanism of adsorbed water on the vibrational properties of wood impregnated with extractives of pernambuco (*Guilandina echinata* Spreng.). J Wood Sci 46:122–129
10. Matsunaga M, Sakai K, Kamitakahara H, Minato K, Nakatsubo F (2000) Vibrational property changes of spruce wood by impregnation with water-soluble extractives of pernambuco (*Guilandina echinata* Spreng) II, structural analysis of extractive components. J Wood Sci 46:253–257
11. Norimoto M, Ohgama T, Ono T, Tanaka F (1981) Young's modulus of cell wall for coniferous wood (in Japanese). Nihon Rheology Gakkaishi 9:169–175
12. Obataya E, Yokoyama M, Norimoto M (1996) Mechanical and dielectric relaxations of wood in a low temperature range I (in Japanese). Mokuzai Gakkaishi 42:243–249