J Wood Sci (1999) 45:227–232

ORIGINAL ARTICLE

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Effects of impregnation of simple phenolic and natural polycyclic compounds on physical properties of wood*

Received: July 22, 1998 / Accepted: September 25, 1998

Abstract The impregnation of various simple phenolic and natural polycyclic compounds into wood was investigated from the viewpoints of vibrational property and dimensional stabilizing effect. When simple phenolic compounds were impregnated, the loss tangent (tan δ) in the longitudinal direction increased linearly with increasing weight gain. Meanwhile, among the natural polycyclic compounds hematoxylin decreased the tan δ drastically by impregnation. It was suggested that the five hydroxyl groups and the pyran ring oxygen in the hematoxylin molecule contribute to formation of the crosslinkage-type hydrogen bonds between wood components. The rigidity of hematoxylin molecules may also be important. By impregnation of about 10% catechol, resorcinol, and saligenin, a 40% level of antiswelling efficiency (ASE) was attained, although a significant dimensional stabilizing effect was not observed after impregnation of natural polycyclic compounds.

Key words Hematoxylin · Impregnation · Vibrational property · Dimensional stability · Extractive

Introduction

Various chemical processes have been applied to enhance wood properties. However, chemical treatment tends to cause a loss of strength, and undesirable weight increase, and sometimes the chemicals themselves are toxic to the human body. Among the various wood species, some are well known for their dimensional stability, antibiological properties, and vibrational properties. Though these properties are partly due to physical characteristics, such as wood structure and specific gravity, the extractives also play an important role.

Pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.) is a Leguminosae tree grown in Brazil that was originally used for dyes in Europe. Nowadays, it is an excellent and the most popular material for violin bows. We found that the loss tangent (tan δ) of pernambuco is exceptionally low among a number of wood species examined.[1–4] Impregnation of extractives obtained from pernambuco into other wood decreases the tan δ.[3] The main components of the extractives were found to be brazilin and protosappanin B.[5]

Hematoxylin, whose chemical structure is similar to that of brazilin, is also an extractive component of Leguminosae trees, such as logwood (*Haematoxylon campechianum* Linn.), and is commercially available as a stain for microscopic observation. In this study, we investigated the effects of hematoxylin impregnation on the vibrational properties and dimensional stability of wood. Some simple phenolic and natural polycyclic compounds were studied in parallel, and the correlations between molecular features and physical properties were determined.

Materials and methods

Specimens and compounds

Specimens were cut from sitka spruce (*Picea sitchensis* Carr.) selected for the sound-boards of pianos. The dimensions of the specimen for the vibrational property measurements were 2 × 12 × 150 mm, and those for the evaluation of dimensional stability were 28 × 28 × 5 mm in tangential, radial, and longitudinal directions, respectively. The specimens were subjected to experimentation without extraction. Before the treatment, the specific dynamic Young's modulus in the longitudinal direction (E/γ) is [Young's modulus (E) divided by specific gravity (γ)] and tan δ in the

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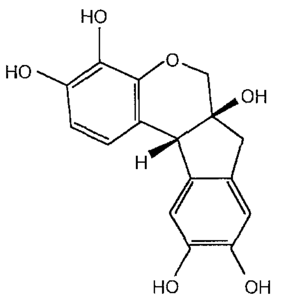
*Part of this work has been published as a Rapid Communication in *Mokuzai Gakkaishi* 43(12). It was also presented at the 48th annual meeting of the Japan Wood Research Society, Shizuoka, April 1998

Table 1. Impregnated compounds

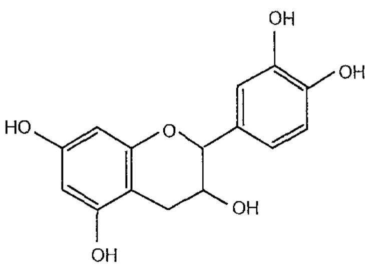
Compounds	Solvent
Simple phenolic compounds	
Catechol	W
Resorcinol	W
Hydroquinone	W
Saligenin	W
3-Hydroxybenzyl alcohol	W
4-Hydroxybenzyl alcohol	M
Pyrogallol	W
Phloroglucinol	W
1,2,4-Benzenetriol	W
Natural polycyclic compounds	
Hematoxylin[a]	W
Catechin[b]	M
Condensed tannin	M
Amur cork extractives	M

W, water; M, methanol

[a] Structure:



[b] Structure:



longitudinal direction were measured using a free–free flexural vibration method based on that of Hearmon[6] after conditioning for 2 weeks at 20°C and 65% relative humidity (RH).

As the impregnating compounds, a series of simple mono- or disubstituted phenolic compounds and some polycyclic compounds found in nature were examined (Table 1). All of the simple phenolic compounds and hematoxylin were reagent grade, and catechin was industrial grade, obtained from Gifu Shellac Manufacture. Condensed tannin was prepared by extraction with 70% acetone from the bark of Japanese larch (*Larix leptolepis* Gord.). Amur cork (*Phellodendron amurense* Rupr.) extractives were obtained by extracting with methanol in a Soxhlet extractor, and the solution was used as is.

Experimental procedure

The specimens were immersed in aqueous or methanol solution for 8 days under occasional evacuation; distilled water was used for water-soluble compounds and methanol for water-insoluble compounds. The concentrations of the impregnation solutions ranged from 1% to 5%. When the specimens were impregnated from the methanol solution, evacuation was carried out while cooling the whole solution with methanol–Dry Ice to prevent evaporation of the solvent.

After impregnation, the specimens were air-dried and then dried at 60°C for 24h under vacuum. After conditioning at 20°C/65% RH for more than 2 weeks, the vibrational properties were again determined. Percent changes of vibrational properties were defined as follows:

$$\text{Change of loss tangent (\%)} = \{(\tan\delta)_1/(\tan\delta)_0 - 1\} \times 100$$

$$\text{Change of specific dynamic Young's modulus (\%)} = \{(E/\gamma)_1/(E/\gamma)_0 - 1\} \times 100$$

where the subscripts 0 and 1 imply the values measured before and after impregnation, respectively.

The specimens for the evaluation of dimensional stability were conditioned at 20°C/66% RH over a saturated aqueous solution of $NaNO_2$ for more than 2 weeks before measurement of their dimensions. The degree of swelling at 20°C/66% RH was determined on the basis of the oven-dried dimension. From the swelling of untreated specimens (S_u) and that of impregnated specimens (S_i), the antiswelling efficiency (ASE) was calculated as follows:

$$\text{ASE (\%)} = \{1 - (S_i/S_u)\} \times 100$$

The bulking coefficient was calculated from the oven-dried volume before (V_0) and after (V_1) impregnation as follows:

$$\text{Bulking coefficient (\%)} = \{(V_1/V_0) - 1\} \times 100$$

Results

Effects of impregnation on vibrational properties

Figure 1 shows the relation between weight gain and tan δ for the specimens impregnated with simple mono- or disubstituted phenolic compounds. The negative value of weight gain is probably due to the removal of extractives originally contained in spruce during the impregnation. The tan δ increased simply with increasing weight gain, and it became twice the original value with about 10% weight gain. Though the correlation between the change of tan δ and the molecular features of the impregnated compound was not apparent, the tan δ increased more after impregnation with 3-hydroxybenzyl alcohol than with catechol and hydroquinone at the same weight gain level. This finding suggests that the change of tan δ depends somewhat on the kind of functional groups.

Figure 2 shows the same plot for the polycyclic compounds. The change of tan δ was entirely different from the cases when the simple phenolic compounds shown in Fig. 1 were impregnated. Especially by impregnation of hematoxylin, the tan δ decreased remarkably with increasing

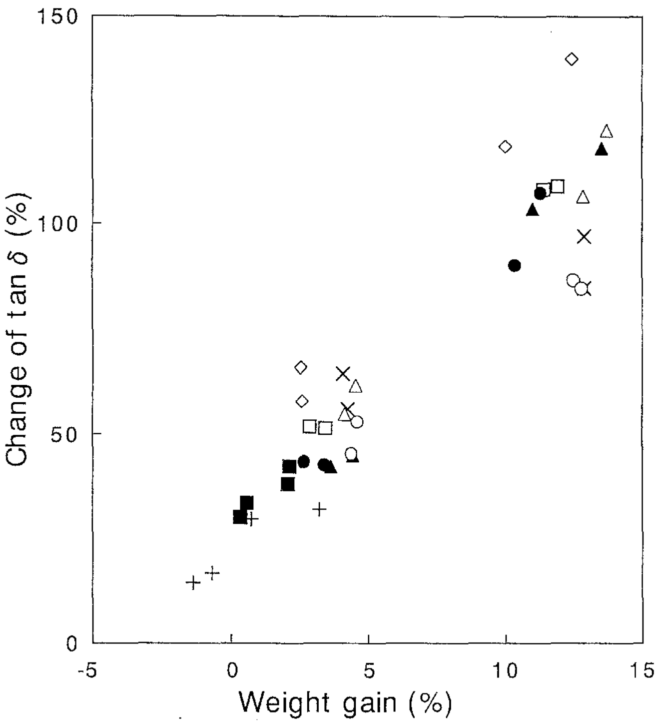


Fig. 1. Changes of tan δ in the longitudinal direction by the impregnation of simple phenolic compounds. *Open circles*, catechol; *open triangles*, resorcinol; ×, hydroquinone; *open squares*, saligenin; *open diamonds*, 3-hydroxybenzyl alcohol; +, 4-hydroxybenzyl alcohol; *filled circles*, pyrogallol; *filled squares*, phloroglucinol; *filled triangles*, 1,2,4-benzenetriol

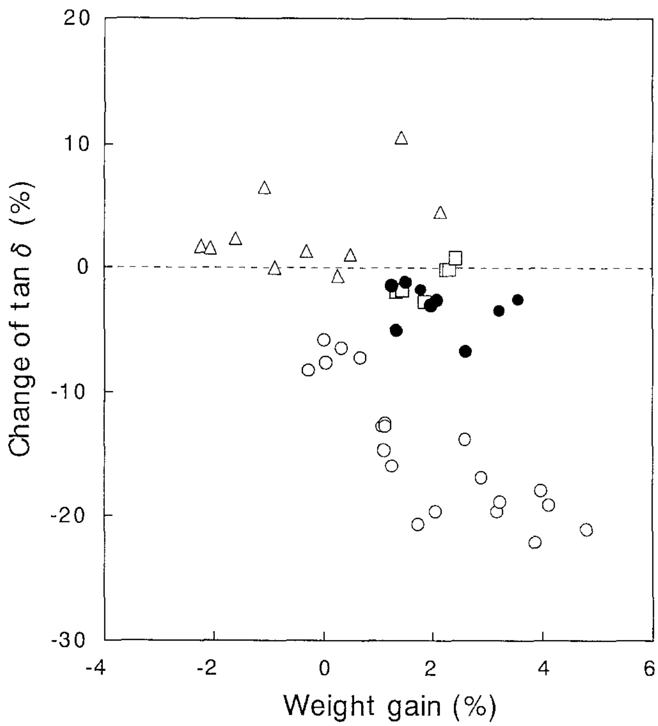


Fig. 2. Changes of tan δ in the longitudinal direction by impregnation of natural polycyclic compounds. *Open circles*, hematoxylin; *open squares*, amur cork extractives; *open triangles*, condensed tannin; *filled circles*, catechin

weight gain; the decrease of tan δ reached about 20% with a 2% weight gain. Catechin and extractives of amur cork also decreased the tan δ to some extent. On the other hand, condensed tannin did not have any effect on tan δ, although the polymer-condensed tannin contains catechin as a repeating structural unit.

Figure 3 shows the relation between weight gain and E/γ for the simple phenolic compounds. Regardless of the different molecular features of the impregnated compounds, E/γ decreased approximately linearly with increasing weight gain. The decrease in E/γ is due to both the increase in specific gravity (γ) and the lowering of E itself as a result of the expansion of the specimen by the impregnation.

The effect of weight gain on E/γ is shown in Fig. 4 for the natural polycyclic compounds. Impregnations of the polycyclic compounds changed the E/γ differently from those of the simple phenolic compounds. Hematoxylin decreased the E/γ less than the simple phenolic compounds at the same weight gain level. On the other hand, the impregnation of condensed tannin decreased E/γ more than the simple phenolic compounds.

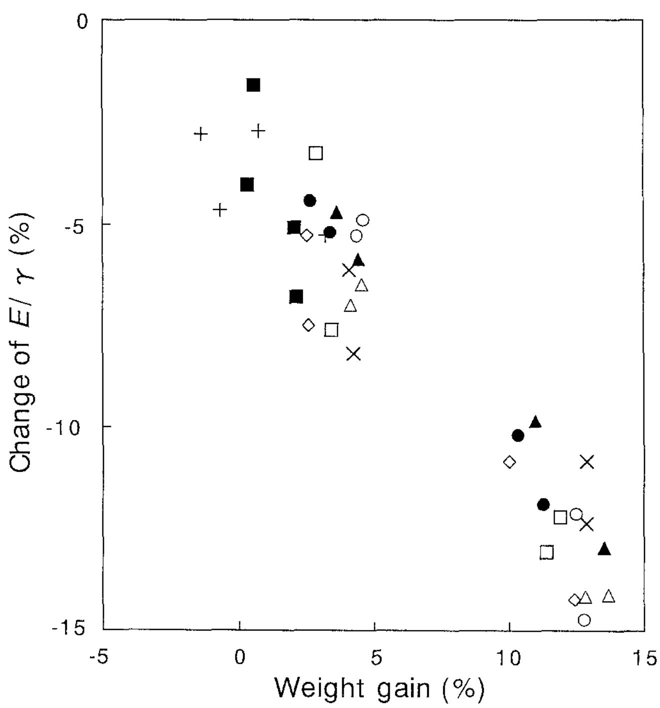


Fig. 3. Changes of E/γ in the longitudinal direction by impregnation of simple phenolic compounds. Symbols are the same as in Fig. 1

Dimensional stabilizing effect

Figure 5 shows the relation between antiswelling efficiency (ASE) and weight gain for the simple phenolic compounds.

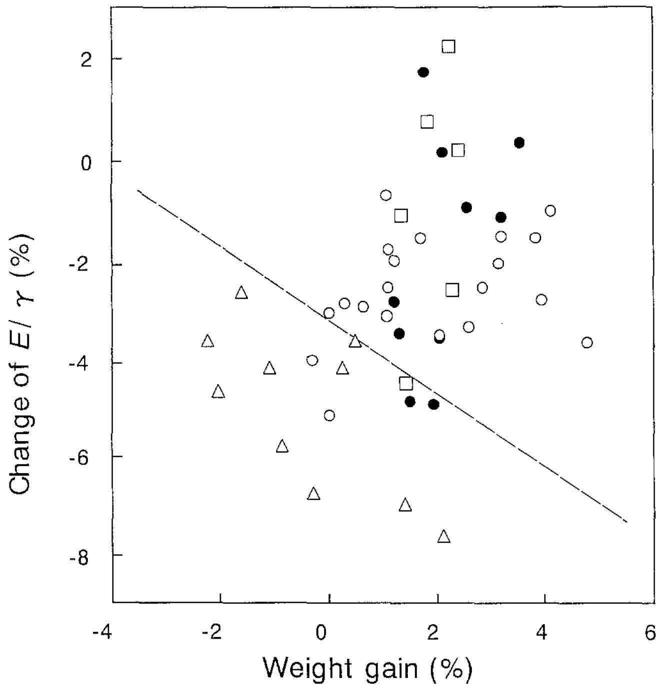


Fig. 4. Changes of E/γ in the longitudinal direction by impregnation of natural polycyclic compounds. Symbols are the same as in Fig. 2

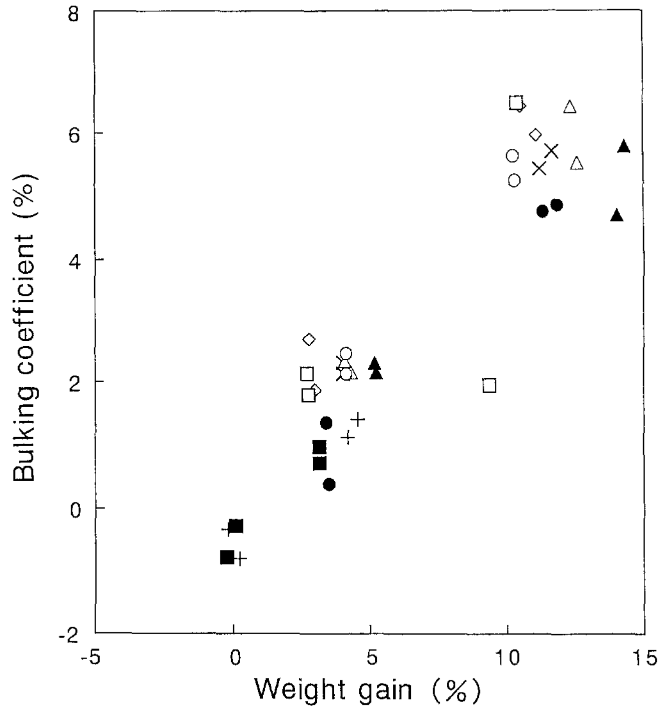


Fig. 6. Bulking coefficient by impregnation of simple phenolic compounds. Symbols are the same as in Fig. 1

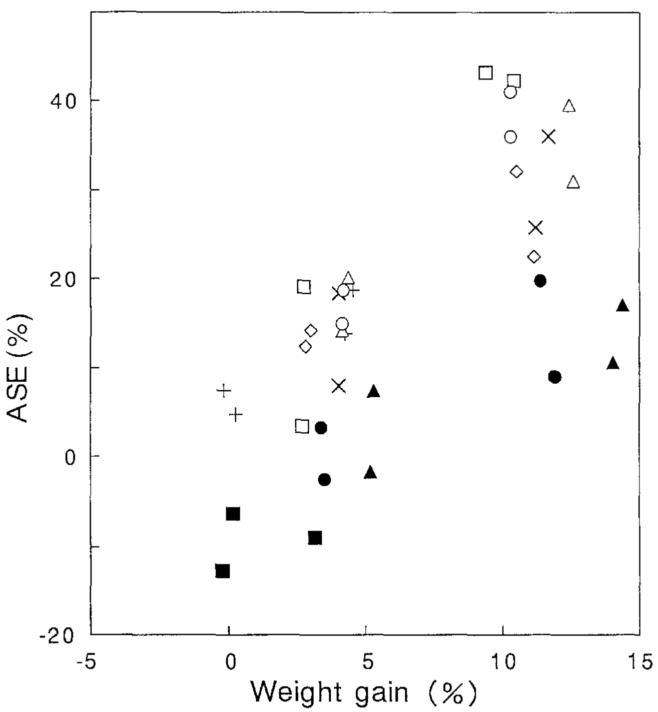


Fig. 5. Dimensional stabilizing effect by impregnation of simple phenolic compounds. Symbols are the same as in Fig. 1

The ASE increased with increasing weight gain for all compounds. Especially with catechol, resorcinol, and saligenin, the ASE reached about 40% with 10% weight gain. However, pyrogallol, 1,2,4-benzenetriol, and phloroglucinol, which have three hydroxyl groups, showed somewhat lower ASE than the others.

Figure 6 shows the bulking coefficient attained by impregnation of simple phenolic compounds. The bulking coefficient increased with increasing weight gain irrespective of the compounds. Therefore, the slightly lower ASE value found in Fig. 5 for pyrogallol, 1,2,4-benzenetriol, and phloroglucinol seems to result from the difference in hygroscopicity of the impregnated compounds.

Figure 7 shows the effect of the impregnation of natural polycyclic compounds on ASE. Hematoxylin had a slight dimensional stabilizing effect, but the other compounds did not show a clear tendency between the ASE and weight gain. As defined above, the ASE was calculated based on the degree of swelling in a conditioned state (20°C, 66% RH) but not the water-swollen state. Therefore, ASE is presumably affected by the moisture adsorptive property of the impregnated compounds.

When the natural polycyclic compounds were impregnated, the bulking coefficient generally increased accompanied by the weight gain but did not show a simple relation as in the case of simple phenolic compounds (Fig. 8). Because the molecular weights of the polycyclic compounds are in the several hundreds, some of the compound may stay in the cell lumen.

Discussion

The percent changes of tan δ and E/γ after the impregnation are summarized in Fig. 9 along with some data reported

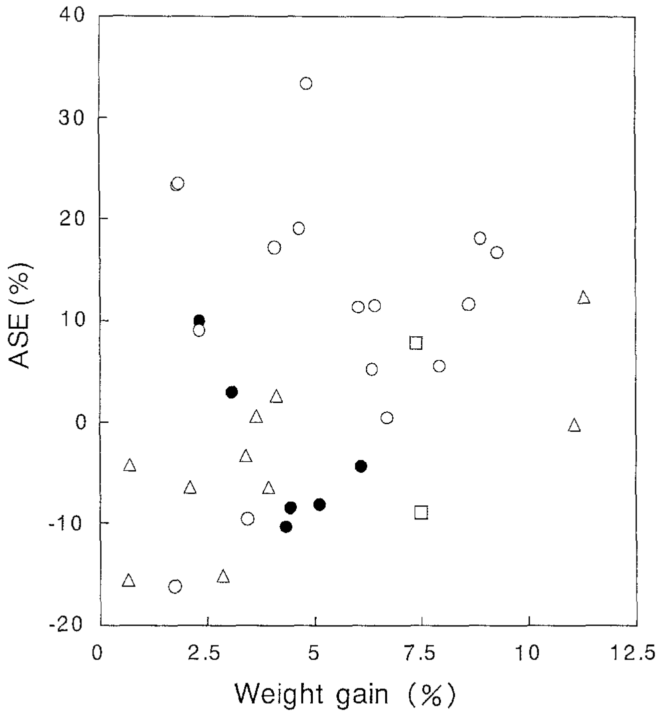


Fig. 7. Dimensional stabilizing effect by impregnation of natural polycyclic compounds. Symbols are the same as in Fig. 2

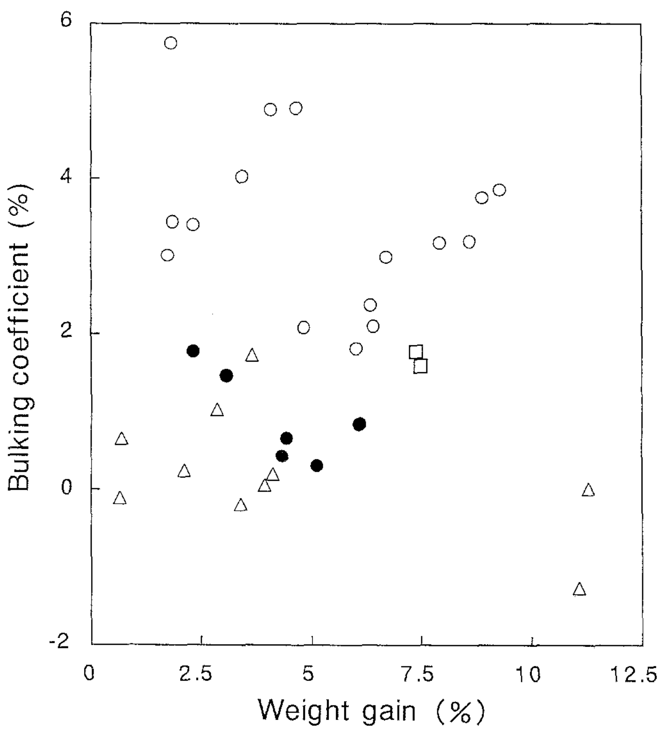


Fig. 8. Bulking coefficient by impregnation of natural polycyclic compounds. Symbols are the same as in Fig. 2

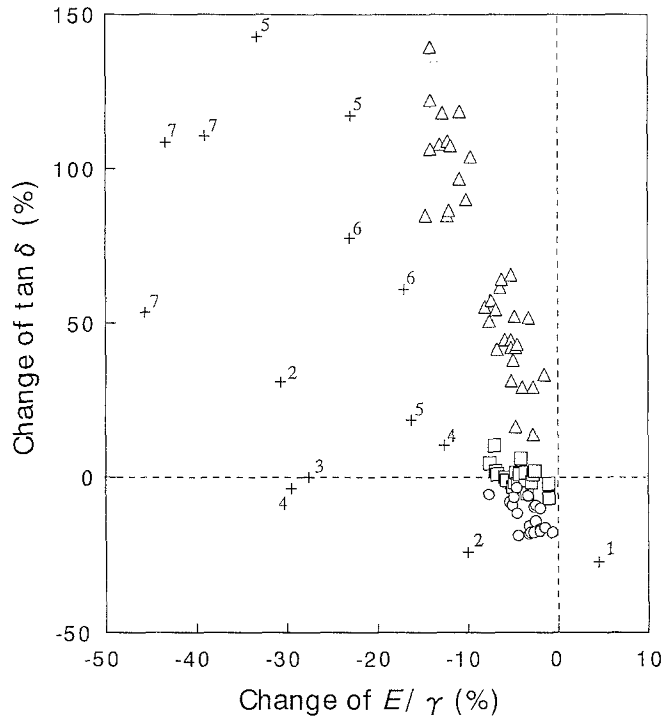


Fig. 9. Relation between change of tan δ and that of E/γ in the longitudinal direction. *Circles*, hematoxylin; *triangles*, simple phenolic compounds; *squares*, natural polycyclic compounds except hematoxylin; +, data from Akitsu et al.[7]: *1*, formalization; *2*, phenol-formaldehyde resin; *3*, acetylation; *4*, maleic acid-glycerol; *5*, polyethylene glycol; *6*, epoxide; *7*, wood plastic composite

in the literature.[7] The various treatments cited can be classified into three groups: (1) treatments in which the reagent does not react with wood components (wood plastics composite, impregnation of polyethylene glycol or epoxides); (2) treatments in which the reagent reacts with wood components (acetylation); and (3) treatments in which the reagent probably forms crosslinkages between them and wood components (treatment with maleic acid-glycerol, phenol-formaldehyde resin, vaporous formaldehyde). In the first group tan δ increased and E/γ decreased; in the second group tan δ hardly changed and E/γ decreased; and in the last group tan δ decreased with or without a decrease in E/γ. Therefore, the only case where the tan δ decreased even slightly was attributed to the crosslinking between wood components. In other words, so far the tan δ did not decrease without formation of crosslinkages by covalent bonds.

In this study the reagents were impregnated at room temperature followed by drying at 60°C under vacuum. It is improbable under this treatment condition that covalent bonds are formed between reagents and the wood components. Therefore, it is unusual that the tan δ decreased remarkably by simple impregnation of hematoxylin. We cannot interpret this finding in any way other than that hematoxylin forms unusually strong crosslinking-type hydrogen bonds with wood components.

As a common molecular feature of sweet taste, Shallenberger and Acree[8] have proposed that sweet-tasting compounds have a proton donor moiety (AH) and a proton acceptor moiety (B) at a definite distance. Meanwhile, taste bud receptor sites have also AH-B systems, and the complementary hydrogen bonds between AH-B systems cause the sweet taste. Applying the AH-B model, Arnoldi et al.[9] explained the sweetness of hematoxylin. The strong hydrogen bond speculated above may also exist between the AH-B system in wood components (e.g., hydroxyl group and the oxygen atom in the pyranose ring) and that in hematoxylin. Moreover, because hematoxylin has at least two pairs of the AH-B system, the formation of crosslinkage is probable.

The same speculation seems to be applicable also for catechin. In fact, the impregnation of catechin decreased the tan δ slightly. The difference of tan δ-decreasing effect may be due to the rigidity or hydroxylation patterns of the molecule. The reason simple mono- and diphenolic compounds did not decrease the tan δ is also explainable from the fact that these compounds have only a single pair of the AH-B system in a molecule.

The E/γ was increased only by formaldehyde treatment, resulting from a decrease in equilibrium moisture content, which causes a marked increase of Young's modulus[10] and only a slight increase in specific gravity (γ). In this respect, the impregnation of hematoxylin and the other treatments were disadvantageous for attaining a high E/γ.

It is generally recognized that low tan δ and high E/γ are necessary conditions for soundboards of wooden musical instruments,[11] although those will not be sufficient condition. By impregnation with hematoxylin, the tan δ decreased with a slight weight gain and without a large decrease in E/γ. Moreover, it can be speculated that the mechanical strength is maintained because of the mild treatment conditions. Therefore, impregnation with hematoxylin is of interest for application to the soundboards of wooden musical instruments.

Conclusion

Among some natural polycyclic compounds, we found that impregnation with hematoxylin or catechin is able to decrease the tan δ of spruce wood. Such a phenomenon was not observed after impregnation with any of the simple mono- or disubstituted phenolic compounds examined here.

Concerning the dimensional stabilizing effect, the impregnation of some simple phenolic compounds increased the ASE up to about 40% with 10% weight gain. On the other hand, natural polycyclic compounds hardly enhanced the dimensional stability.

Acknowledgments The authors thank Associate Prof. Dr. Y. Ishimaru, Faculty of Agriculture Kyoto Prefectural University, for his invaluable suggestions and Prof. Dr. Hou-Min Chang, North Carolina State University, for his critical reading of the manuscript.

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