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Vibrational property changes of spruce wood by impregnation with water-soluble extractives of pernambuco (*Guilandina echinata* Spreng.)

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Abstract Sitka spruce (*Picea sitchensis* Carr.) was treated with water-soluble extractive components of pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.) by two methods: impregnation under evacuation using an aspirator and repetitive surface application using a brush. The influence of these treatments on the vibrational properties were examined. The loss tangent (tan δ) of the impregnated specimen decreased, up to nearly a half of its original value, with increasing weight gain. It is suggested that the decrease in tan δ results from impregnation of the extractive components into the amorphous region of cell walls, forming secondary bonds between matrix substances. The surface application of the extractive components, on the other hand, hardly brought about the desirable change in vibrational properties.

Key words Pernambuco · Vibrational property · Extractives · Impregnation · Musical instrument

Introduction

Pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.) is the most suitable material for the violin bow. In previous studies[1,2] we found that the loss tangent (tan δ) of pernambuco was exceptionally low among many wood species examined and proposed that low tan δ is a necessary factor for bow material. We also reported that low tan δ is attributed to the large amount of extractive components in pernambuco. Although the tan δ of wood may also vary with the mean microfibril angle,[3,4] the influence of extractive components was the main factor as far as pernambuco is concerned.[5]

There have been a few reports about the effect of extractive components on the physical properties of wooden substances, especially on vibrational properties. Among them, Yano[6] reported that the vibrational properties of Western red cedar (*Thuja plicata*) changed owing to extraction with methanol. Obataya and Norimoto[7,8] also reported that the tan δ of cane (*Arundo donax* L.), used for reeds of woodwind instruments, decreased after removal of water-soluble extractives. The extractive components may exert some effects on the vibrational properties of wood material, but the extractives are so different from one wood species to another that the effect also appears to vary greatly depending on the species.

We have already reported that the tan δ of pernambuco increased after extraction with water.[1] However, the possibility cannot be ruled out that the change of fine structure of wood after removing extractive components may also influence the tan δ. In this study we treated other wood species with water-soluble extractive components of pernambuco and examined the accompanying changes in vibrational properties. If the extractive components of pernambuco have the lowering effect on tan δ, one should be able to decrease the tan δ of any other wood species simply by impregnation with the extractives of pernambuco. Moreover, low tan δ is generally recognized as one of the necessary conditions for the soundboards of the piano, guitar, and other musical instruments.[9–11] Thus the quality of the soundboard could be enhanced by impregnation with water-soluble extractives from pernambuco.

Materials and methods

Materials

Sitka spruce (*Picea sitchensis* Carr.) specimens were made 150 mm (longitudinal direction) × 12 mm (radial direction)

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× 2 mm (tangential direction). There were 58 specimens. Before treatment with the extractive components, vibrational properties were measured by a free-free flexural vibration method. The specific dynamic Young's modulus (E'/γ, where E' is the dynamic Young's modulus, and γ is the specific gravity) in the longitudinal direction was calculated from the resonant frequency using the Euler-Bernoulli equation and the $\tan\delta$ from the decremental curve of the vibration at the resonant frequency. The resonant frequency of the first vibrational mode ranged from about 380 to 450 Hz. The measurements were carried out in a chamber maintained at 20°C and 65% RH.

Preparation of water-soluble extractives from pernambuco

Heartwood of pernambuco was ground by a Wiley mill, and only the fraction that passed through a sieve with 355-μm apertures but was retained by a sieve with 150-μm apertures was used. The wood meal was extracted by soaking in water with occasional stirring at ambient temperature for 24 h. The supernatant water was collected by decanting. Then fresh water was added for further extraction. The extraction was repeated 10 times. The combined supernatant was concentrated using a rotary vacuum evaporator at about 40°C to prevent chemical changes of the extractives. After removing the precipitates by centrifugation, extractives were obtained as a red-brown powder by freeze-drying the highly concentrated solution. From about 480 g (oven-dried) of wood meal, approximately 65 g of extractive was obtained (yield 13.5%).

Treatments of spruce wood with water-soluble extractives of pernambuco

Specimens of sitka spruce were treated with an aqueous solution of extractives obtained from pernambuco by the following two ways.

Impregnation under evacuation

Three or four specimens were soaked in aqueous solutions of the extractives with concentrations of 20.9, 25.7, 33.8, 51.4, and 102.8 g/l for 8 days with occasional evacuation using an aspirator. After drying under ambient conditions and subsequent drying at 60°C under vacuum for 2 days, the weight percent gain (WPG) and percent increase of oven-dried volume (bulking) of the specimens were measured. The specimens were then conditioned at 20°C and 65% RH for 2 weeks and the vibrational properties determined again. There were 36 specimens subjected to this treatment.

Surface application of the aqueous solution of extractives

Aqueous solution of extractives (131.5 g/l) was uniformly applied by a brush to all surfaces of specimens and then air-dried. This procedure was repeated 2, 5, 7, and 10 times to obtain specimens with a different WPG. The WPG, bulking, and vibrational properties were measured by the same methods stated for the impregnation treatment. There were 16 specimens subjected to this treatment.

Microscopic observation of filled specimens

A 50-μm thick cross section was cut from the treated specimen by means of a microtome (Olympus TU-213N). Epoxy resin, which scarcely dissolved the water-soluble extractives of pernambuco, was dropped on the sliced section on a slide glass, and the whole section was covered with glass. The epoxy resin was hardened overnight at 60°C. The observation was carried out under a microscope (Olympus BH2) at 40×. For observations at 200× magnification, thinner sections (3 μm thickness) were prepared.

Results and discussion

Topological aspects of the extractives-treated specimens

The relation between the WPG and bulking of specimens is shown in Fig. 1. For the specimens impregnated under evacuation, the bulking increased linearly up to around 15% WPG and then leveled off. This suggests that extractive components are impregnated in the amorphous regions of the cell wall until about 15% WPG, and in cell lumens thereafter. Figure 2 shows the cross-sectional views of the specimens impregnated to 7.6% and 25.2% WPG. For the specimen whose WPG is 7.6%, extractives did not distribute uniformly in the whole specimen but were limited to within about 0.2 mm of the surface (Fig. 2a). The late wood was

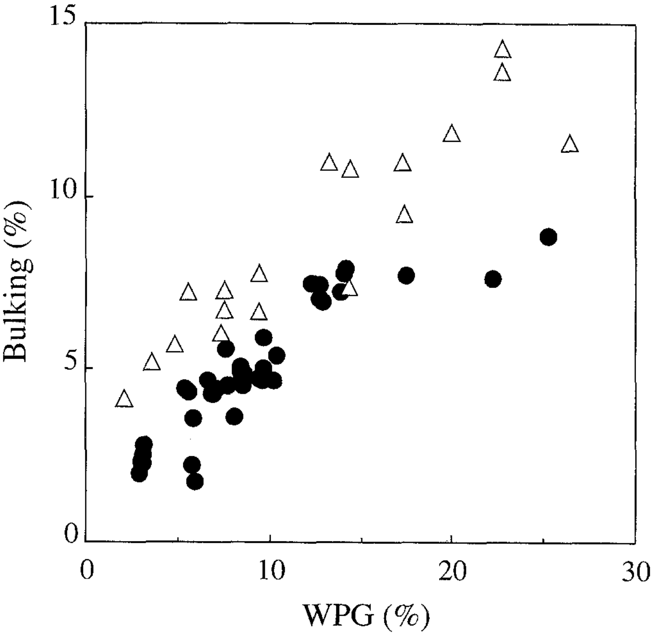

Fig. 1. Relation between the weight percent gain (*WPG*) and the percent increase of the over-dried volume (*Bulking*). *Circles*, impregnation; *triangles*, surface application

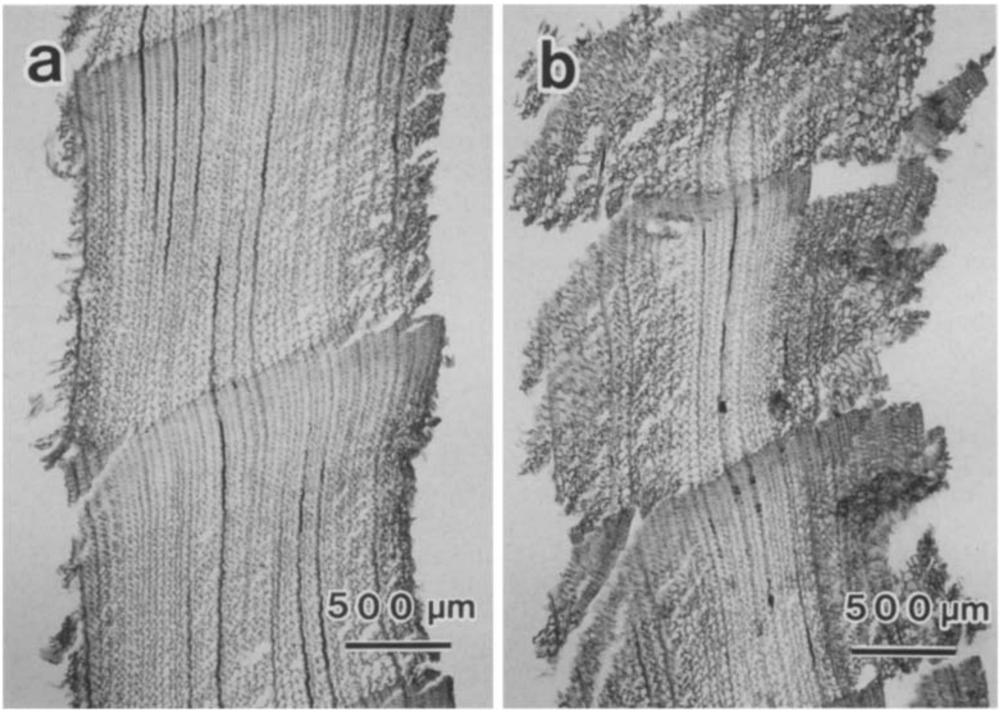

Fig. 2. Cross section of the impregnated specimen under evacuation. **a** WPG is 7.6%. **b** WPG is 25.2%

easier to impregnate than the early wood. From the observation of the thinner section at high magnification, it was found that the extractives scarcely deposited in the lumens. On the other hand, for the specimen whose WPG is 25.2%, extractives were impregnated more deeply (Fig. 2b). Moreover, extractives were observed to deposit even in some lumens in the thinner sections at high magnification. These results may explain the change in leveling off of bulking at a higher WPG, as observed in Fig. 1.

Figure 3 shows cross-sectional views of surface-applied specimens with a WPG of 17.3%. The extractives hardly penetrated the specimen. From the observation at high magnification, the extractives surely existed in both cell walls and some lumens at the vicinity of the surface. In Fig. 1, the bulking of the surface-applied specimens was somewhat higher than that of impregnated specimens at the same WPG. This seems to arise from the accumulation of applied extractives on the surface but not real bulking of specimens.

Changes of vibrational properties

Figure 4 shows the relation between WPG and percent change in E'/γ as a result of treatments. The percent change in E'/γ was defined as follows:

$$\%\text{ Change in } E'/\gamma = \frac{E'_1/\gamma_1 - E'_0/\gamma_0}{E'_0/\gamma_0} \times 100$$

where E'_0/γ_0 and E'_1/γ_1 are the E'/γ values of the specimen before and after treatment at 20°C and 65% RH, respectively. The E'/γ decreased linearly with increasing WPG in both treated specimens, but the impregnated specimen had

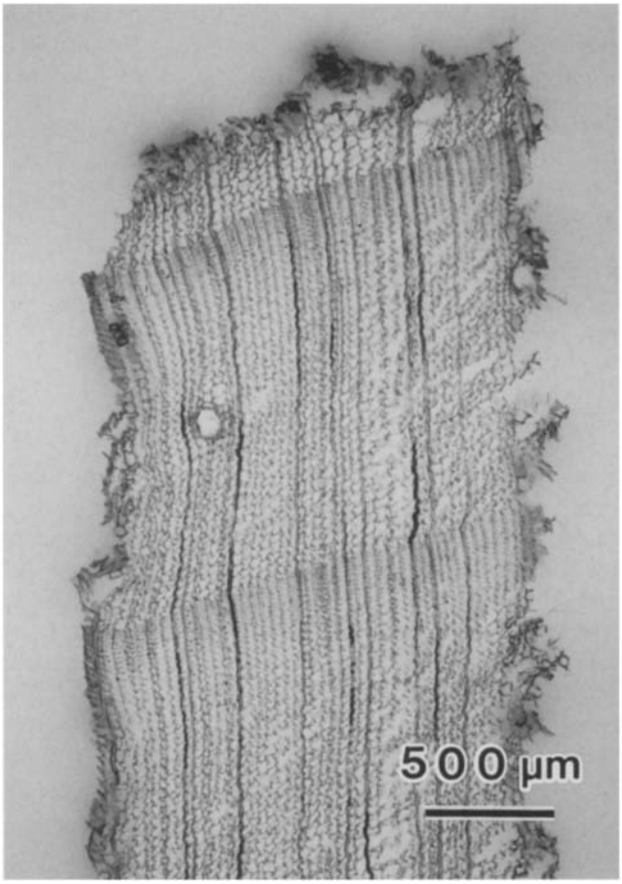

Fig. 3. Cross section of the surface-applied specimen (WPG is 17.3%)

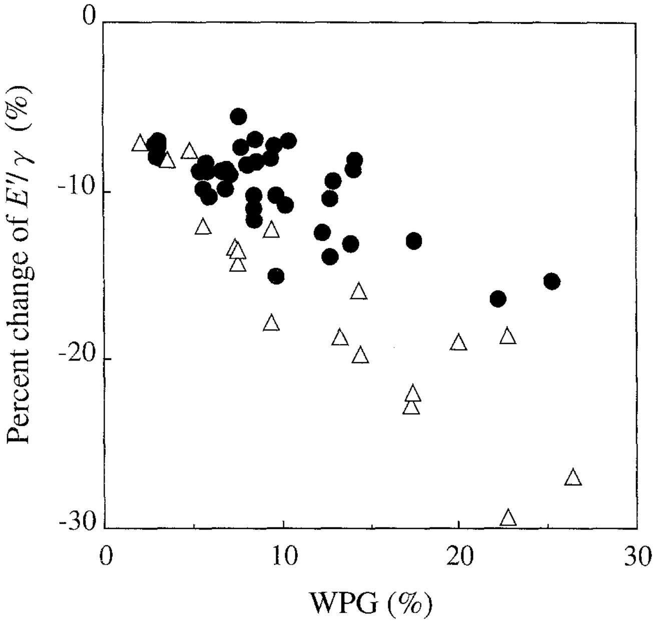

Fig. 4. Relation between WPG and percent change of E'/γ. Symbols are the same as in Fig. 1

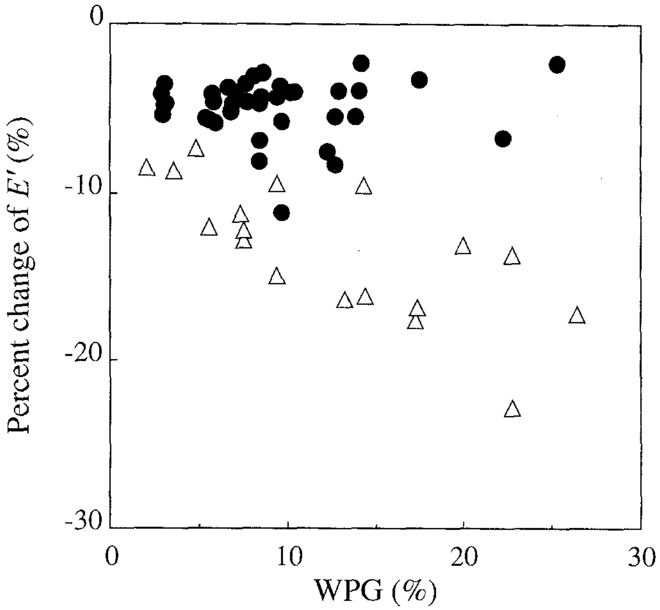

Fig. 5. Relation between WPG and percent change of E'. Symbols are the same as in Fig. 1

a gentle slope. The difference between the two treated specimens is more significant if the percent change in E' is plotted as a function of WPG (Fig. 5). For the treatment with surface application, E' decreased with the increase in WPG. For impregnation treatment, E' decreased about 5% regardless of the WPG, indicating that the continuous decrease of E'/γ with increasing WPG in Fig. 4 is due to the increase in γ. The percent change in γ for impregnated specimen was from 2.0% to 14.9%.

Figure 6 shows the relation between WPG and the percent change of tan δ. In the case of surface application, tan δ of all specimens decreased only 1–10%, and there was no correlation between WPG and the percent change in tan δ. On the other hand, the tan δ of impregnated specimens decreased significantly (20–47%), and the tan δ decreased with the increase in WPG.

There were some reports that the decrease in tan δ was due to chemical treatment. For example, formaldehyde treatment decreased the tan δ because of the formation of crosslinkages between neighboring hydroxyl groups of wood components.[12] Treatment with low-molecular-weight phenol formaldehyde resin or maleic acid–glycerol also reduced the tan δ,[13,14] again likely due to crosslinking formation. In this study, because the impregnation was done at room temperature and the successive drying at 60°C under vacuum, the formation of covalent bonds between impregnated extractives and wood components is improbable under such mild conditions. Therefore, it is plausible that the extractive components impregnated the amorphous region, forming noncovalent but secondary bonds (e.g., hydrogen bonds), resulting in the decreased tan δ. The structural characteristics or molecular weight (or both) of extractive components may also be necessary conditions.

Such secondary bonds must increase Young's modulus at least in amorphous regions of wood; nevertheless, the Young's modulus decreased as a whole. This probably arises from the relative decrease of volume fraction of the crystal region, whose Young's modulus is much greater than that of the amorphous region as a result of the expansion of the latter region due to the bulking of impregnated components.

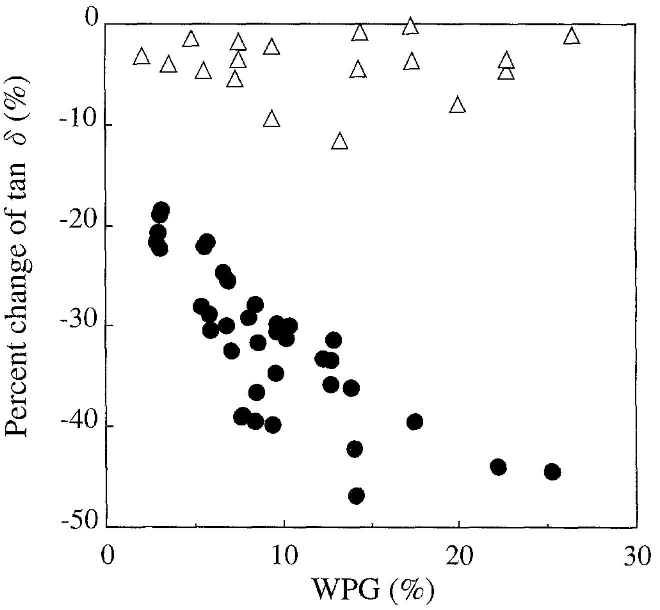

Fig. 6. Relation between WPG and percent change of tan δ. Symbols are the same as in Fig. 1

Because the bending property of the specimen influenced its flexural vibration, it is supposed that the surface characteristics dominate the properties of the whole specimen. The large change in tan δ for impregnated specimens may also be attributed to the drastic change in the vicinity of the surface. Thus if surface application of extractives could change the vibrational properties, it would be an easier process than impregnation. Moreover it would be easier for high-density wood, such as pernambuco, which is difficult to impregnate. Unfortunately, Young's modulus of the surface-applied specimen decreased, but the $\tan\delta$ hardly did so.

Thus, impregnation of wood with extractive components of pernambuco is promising for enhancing the acoustic properties of wooden musical instruments, such as the soundboards of the piano, violin, and guitar, because it drastically decreases $\tan\delta$ without a severe decrease in E'/γ or a weight increase.

Conclusions

Sitka spruce wood was treated with water-soluble extractive components of pernambuco by impregnation during evacuation and surface applications. The changes of vibrational properties were examined. In the case of the surface application, the $\tan\delta$ decreased only a small extent, whereas E'/γ decreased with the increase of WPG. On the other hand, the $\tan\delta$ of the impregnated specimens decreased drastically in proportion to the WPG, and the E'/γ decreased only moderately, due mainly to the increase in specific gravity. Almost all of the extractive components were impregnated in an amorphous region of the cell walls rather than in the lumens. It is proposed that the extractive components formed secondary bonds between matrix substances, resulting in the observed decrease in $\tan\delta$.

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