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Working mechanism of adsorbed water on the vibrational properties of wood impregnated with extractives of pernambuco (*Guilandina echinata* Spreng.)

Abstract To clarify the lowering mechanism of loss tangent (tan δ) of sitka spruce (*Picea sitchensis* Carr.) wood impregnated with extractives of pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.), we examined the vibrational properties of the impregnated wood in relation to the adsorbed water. The results obtained were as follows: (1) The equilibrium moisture content (EMC) of impregnated sitka spruce decreased to some extent compared with untreated wood. (2) Frequency dependencies of tan δ at about 400–8000 Hz showed that impregnated wood has much lower tan δ than untreated wood at around 9% moisture content (MC), except for the high-frequency region. At high relative humidity, impregnated wood has a minimum tan δ (at around 4000 Hz); and at other frequency ranges the tan δ of impregnated wood did not differ considerably from that of untreated wood. (3) The apparent activation energy of the mechanical relaxation process (ΔE) concerned with adsorbed water molecules was higher for impregnated specimens than for untreated ones at moderately high relative humidity, whereas at high relative humidity the difference was not observed. Based on these results, it is thought that the tan δ of impregnated wood decreased at low relative humidity because of the formation of direct hydrogen bonds between impregnated extractives and wood components. However, when the specimen is at higher relative humidity, the formation of direct hydrogen bonds are disturbed by the existence of a large number of water molecules, and some extractives act as a plasticizer.

Key words Pernambuco · Extractives · Adsorbed water · Vibrational property · Loss tangent

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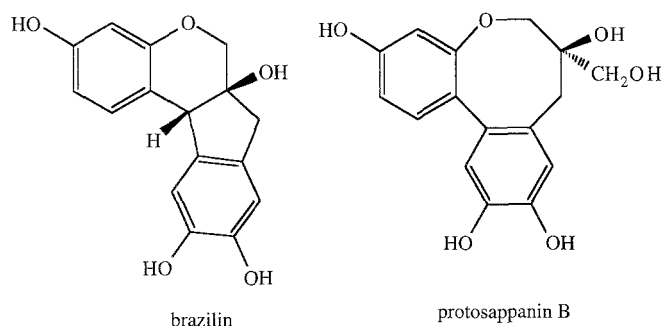Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan

Introduction

In previous studies we found that the loss tangent (tan δ) of pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.) was exceptionally low among many of the wood species examined, and that the low tan δ is attributed to the extractive components contained in pernambuco.[1–3] Impregnation with extractive components into sitka spruce (*Picea sitchensis* Carr.) significantly decreased the tan δ of the specimen.[4] The main components of the extractives of pernambuco were identified to be protosappanin B and brazilin (Fig. 1) (Matsunaga et al., unpublished data). The impregnation of hematoxylin, whose chemical structure is similar to that of brazilin, brought about an extreme decrease of tan δ.[5,6]

Sakai et al.[6] impregnated catechol, which has a chemical structure unit common with that of protosappanin B and brazilin, and several kinds of similar substituted phenolic compounds to sitka spruce wood. They reported that the impregnation with these compounds increases the tan δ simply with increasing weight percent gain (WPG) independent of their chemical structures. Akitsu et al.[7,8] also reported that the tan δ of Glehn's spruce (*Picea glehnii*) increased drastically after impregnation with polyethylene glycol and ethylene oxide, which have a dimensional stabilizing effect. Thus, the remarkable decrease of tan δ due to impregnation with extractives of pernambuco is a peculiar phenomenon; nevertheless, the reason the extractives of pernambuco lower the tan δ is not clear so far.

The tan δ of wood varies depending on the moisture content (MC); the tan δ of sitka spruce decreased roughly up to about 6% MC and then increased with increasing

brazilin   protosappanin B

Fig. 1. Main extractives of pernambuco

MC.[9] In our previous studies, we discussed the change of tan δ at a definite condition (20°C and 65% RH). However, the lowering mechanism of tan δ due to impregnation with extractives of pernambuco must be discussed relating it to the MC, because protosappanin B and brazilin have many hydroxyl groups that can absorb the water molecules. Also regarding the vibrational properties, the estimation was limited to the under 1000 Hz range so far, but it is important to determine the vibrational properties changes at a wider frequency range.

In this study, we examined the influence of impregnating extractive components found in pernambuco on the moisture adsorption property of the wood specimen. We then measured the frequency dependence of vibrational properties and temperature dependence of tan δ at various MCs. Based on the results the mechanism of lowering tan δ due to impregnation with extractives is discussed comprehensively.

Materials and methods

Preparation of water-soluble extractives from pernambuco

Approximately 65 g of water-soluble extractive was obtained from about 480 g of pernambuco wood meal.[4] A part of the wood meal before and after extraction and the freeze-dried extractives themselves were used to prepare the moisture adsorption isotherms.

Preparation of moisture adsorption isotherms

Water-soluble extractives of pernambuco (hereafter referred to as extractives), wood meal of pernambuco before and after extraction (weight loss 13.5%), wood meal of sitka spruce, and three kinds of sitka spruce meal impregnated with extractives were used for the moisture adsorption experiments. About 300 mg of each sample was subjected to the test. The impregnated meals were prepared by dipping the sitka spruce meal into the aqueous solution of extractives with occasional evacuation. The uptakes of the extractives were 5.9%, 11.5%, and 19.2% depending on the concentration of the dipping solutions. Before the moisture

adsorption test, the samples were dried at 60°C for 24 h under vacuum and weighed. Moisture adsorption isotherms were obtained over various saturated salt solutions in desiccators at 20°C. The RH values over the saturated salt solutions were adopted from the table summarized by Yano.[10] The adsorption equilibrium was attained by conditioning for more than 2 weeks. The equilibrium moisture content (EMC) was calculated on the basis of the oven-dried values after impregnation.

Treatment of spruce wood with extractives

Several spruce wood specimens were soaked in each aqueous solution of extractives, whose concentrations are 20.9, 25.7, 33.8, 51.4, and 102.8 g/l, for 8 days with occasional evacuation. After drying under ambient conditions and subsequent drying at 60°C under vacuum for 2 days, the WPG was measured. The specimens were 150 mm (longitudinal direction, L) × 12 mm (radial direction, R) × 2 mm (tangential direction, T) for the measurement of frequency dependence of vibrational properties and 75 mm (L) × 4 mm (R) × 1 mm (T) for dynamic viscoelastic properties.

Measurement of frequency dependence of vibrational properties

Vibrational properties of impregnated and untreated specimens were measured by a free-free flexural vibration method. The specific dynamic Young's modulus (E'/γ, where E' is dynamic Young's modulus, and γ is specific gravity) in the longitudinal direction was calculated from the resonant frequency using the Euler-Bernoulli equation, and the tan δ was calculated from the decremental curves of the vibration at the resonant frequency. The frequency dependencies of vibrational properties were measured at six resonant frequencies by increasing the vibrational mode from the first to sixth. Measurements were carried out in an airtight acrylic box that was kept at 24° ± 2°C. Relative humidities were adjusted by their respective saturated salt solutions: The relative humidities over the saturated salt solutions of $MgCl_2 \cdot 6H_2O$, NaBr, and KNO_3 were estimated as about 33%, 58%, and 94%, respectively.[10] The specimens were kept for more than 2 weeks at each RH before measurement. Table 1 shows the MCs of specimens at each RH. The 0% RH was achieved by replacing the box with nitrogen gas and desiccating with P_2O_5. The specimens were previously dried at 60°C for 2 days under vacuum, cooled in the box, and subjected quickly to the test.

Measurement of temperature dependence of tan δ

Impregnated and untreated specimens were conditioned at 11%, 33%, 58%, and 94% RH and at 24° ± 2°C for more than 2 weeks. The saturated salt solutions of LiCl, $MgCl_2 \cdot 6H_2O$, NaBr, and KNO_3 were used to attain respective RHs. The MCs of specimens are shown in Table 1. After conditioning at each RH, dynamic viscoelastic properties were

Table 1. Weight gain and moisture content of specimens used for measurement of frequency dependence of vibrational properties (upper) and dynamic viscoelastic properties (lower)

Weight gain (%)	Moisture content (%)		
	33% RH	58% RH	94% RH
Untreated	5.7	9.4	16.5
	5.5	9.1	16.1
	5.9	9.5	17.1
	5.5	8.7	15.9
Impregnated			
7.6	5.9	9.4	17.4
8.5	5.8	9.3	17.1
9.4	5.2	8.7	16.7
9.7	5.6	9.0	16.9
12.3	5.6	9.0	16.9
12.9	5.4	9.0	16.6
14.1	5.5	9.0	16.4
14.1	5.4	8.8	16.4
22.2	5.1	8.6	16.2

Weight gain (%)	Moisture content (%)			
	11% RH	33% RH	58% RH	94% RH
Untreated	3.2	5.8	9.6	18.1
Impregnated				
4.8	3.3	6.1	9.8	18.1
9.6	2.9	5.4	8.5	17.1
12.8	3.3	5.9	8.7	17.0
16.4	3.3	5.7	9.4	16.6

RH, relative humidity

Fig. 2. Isotherms for extractives of pernambuco and for pernambuco before and after extraction, and calculated curves for hydrated water (M_h) and dissolved water (M_s) of pernambuco before and after extraction. *Circles*, extractives of pernambuco; *triangles*, pernambuco before extraction; *squares*, pernambuco after extraction; *dotted lines*, calculated curves of pernambuco before extraction; *dashed lines*, calculated curves of pernambuco after extraction

measured by a forced vibrational method where a dynamic viscoelastic measuring apparatus (Orientec Co., Reovibron DDV-25PF) was used. Vibrations of 1, 3.5, 11, 33, and 110 Hz were subjected to the specimens under 7.84 N of tension in the span of 58 mm. The temperature range and increasing rate of the temperature were from −150° to 20°C and 1.0°C/min, respectively. The change of MC during the measurement was regarded to be negligible. The measurement was repeated after drying over P_2O_5 at 24° ± 2°C for 2 days under vacuum (about 0.3% MC) and drying at 105°C for 12 h under vacuum (regarded as 0% MC).

Results and discussion

Analysis of adsorption isotherm

Isotherms for pernambuco before and after water-extraction are illustrated in Fig. 2. The EMC increased in whole RH range by extraction. The Hailwood-Horrobin adsorption equation[11] was fitted to the isotherms (Fig. 2). With this theory, the whole adsorbed water can be classified as hydrated water (M_h) and dissolved water (M_s), which correspond to the water molecules that constitute the monolayer and multilayer in the BET adsorption equation, respectively. Both M_h and M_s increased after extraction. It is thought that the increase of M_h reflects the increase of moisture-adsorbable sites, which were occupied with ex-
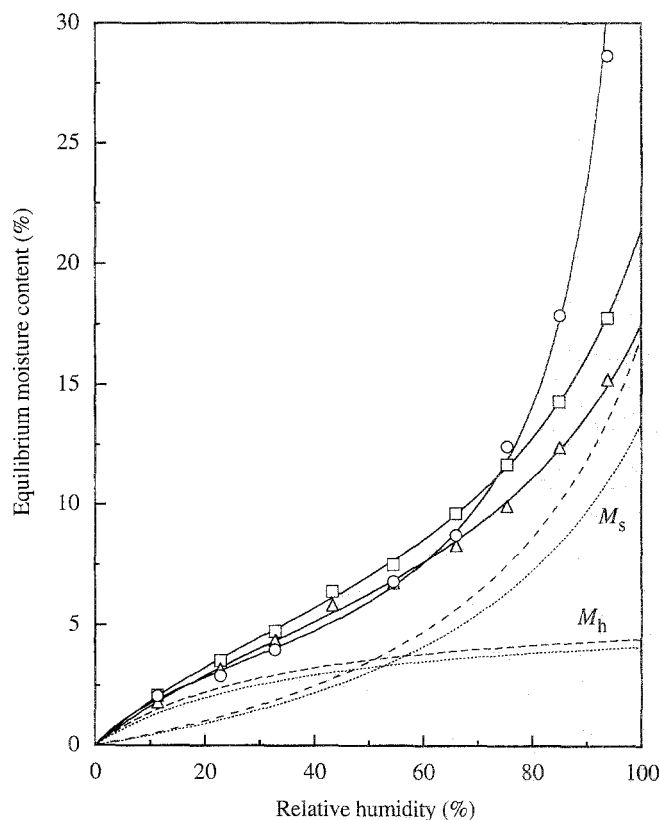
tractives before extraction. On the other hand, the increase of M_s may result from the spatial increase of the moisture-adsorbable area due to the removal of extractives.

The isotherm for extractives themselves showed a steep increase at above 80% RH (Fig. 2). Obataya et al.[12,13] reported that the isotherm for water-soluble extractives of cane (*Arundo donax* L.), whose main constituents are sugars such as glucose and fructose, showed an abrupt increase at the high RH range. Also for the extractives of pernambuco the steep increase at high RH can probably be attributed to hygroscopic sugars in the extractives. Nevertheless, the lower EMC before extraction results from the fact that the amount of sugars in extractives is not so high that it does not elevate the MC of whole wood.

Figure 3 shows the isotherms for extractives in impregnated and untreated sitka spruce wood. The EMC of impregnated sitka spruce decreased with increasing WPG. The calculated curves for M_h and M_s showed that both M_h and M_s decreased after impregnation (Fig. 4). The decrease of M_h implies a decrease in the water molecules adsorbed directly onto the wood components or extractives; therefore it is thought that one molecule of impregnated component (e.g., protosappanin B or brazilin) occupies many of the sites available for water adsorption. The decrease of M_s is
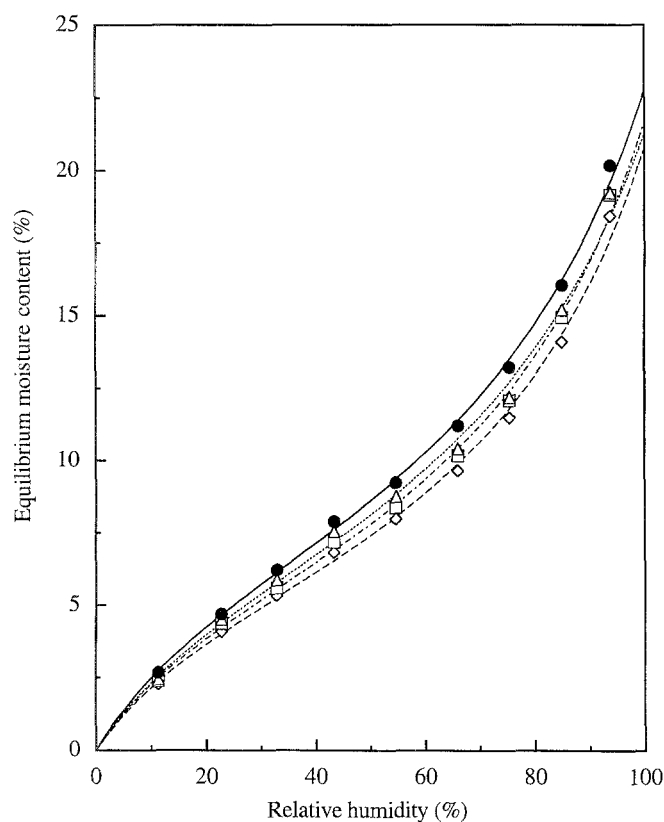
Fig. 3. Isotherms for impregnated and untreated spruce wood. *Filled circles*, untreated wood; *open circles*, weight percent gain (WPG) is 5.9%; *open squares*, WPG is 11.5%; *open diamonds*, WPG is 19.2%
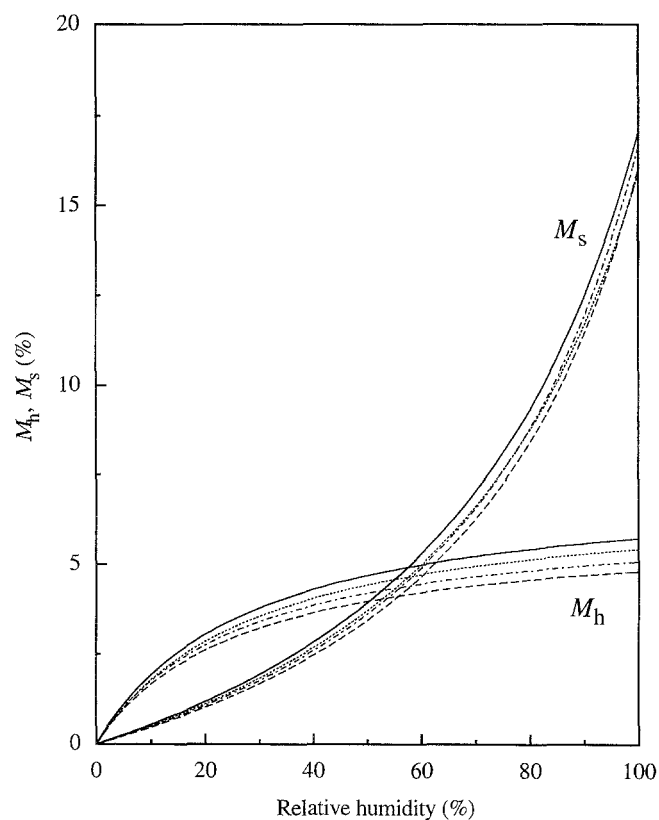

Fig. 4. Calculated curves for hydrated water (M_h) and dissolved water (M_s). *Solid lines*, untreated wood; *dotted lines*, WPG is 5.9%; *dash-dot lines*, WPG is 11.5%; *dashed lines*, WPG is 19.2%

probably due to the decreased space where multilayer adsorption can be performed.

Frequency dependence of vibrational properties

Figure 5 shows the dependence of E' and E'/γ on frequency for the impregnated and untreated specimens conditioned at 58% RH (MC 8.6%–9.5%). The E' of the impregnated specimens was almost the same as that of untreated ones over the whole frequency range. On the other hand, the E'/γ of the impregnated specimens was somewhat lower than that of the untreated ones because of the increase of γ. Impregnated specimens conditioned in other RHs had virtually the same E' and somewhat lower E'/γ than those of untreated ones.

Figure 6 shows the dependence of tan δ on frequency for impregnated and untreated specimens. When the specimens were conditioned at an absolutely dry state, 33% RH (MC 5.1%–5.9%) and 58% RH (MC 8.6%–9.5%), the tan δ decreased drastically over the whole frequency range (Fig. 6a–c). The decrease of tan δ in the high-frequency region was not as extreme. In contrast, when the impregnated specimens were conditioned at 94% RH (MC 15.9%–17.4%), the tan δ of the impregnated specimens did not differ from that of untreated ones at around 400Hz, though the plots were distributed widely (Fig. 6d). The tan δ of the

impregnated specimen decreased with increasing frequency and reached a minimum at around 4000Hz. After that, the tan δ increased with increasing frequency and approached that of untreated specimens in the high frequency region. The relation between WPG and tan δ was drawn using tan δ at 500, 4000, and 7000Hz, which were obtained by smoothing the relation between resonant frequency and tan δ of each specimen. The tan δ of impregnated specimens conditioned at 58% RH decreased with increasing WPG (Fig. 7c). In contrast, the tan δ of impregnated specimens at 94% RH increased with increasing WPG (Fig. 7d). For the specimens conditioned at the absolutely dry condition and 33% RH, no definite tendencies were observed in the range of 7.6%–22.2% WPG (Figs. 7a,b).

The influence of extractive impregnation on the tan δ varied depending on the ambient humidity. Figure 8 shows the relation between MC and tan δ at the first vibrational mode. The values for impregnated specimens (WPG 7.6%, 12.3%, 22.2%) and a mean value of untreated specimens are included in Fig. 8. This figure shows that the tan δ values of impregnated specimens were lower than those of untreated specimens below about 10% MC, whereas the difference between them was not significant at around 16%–17% MC. The tan δ of the specimen that has a high WPG seems to be more dependent on the change of MC.
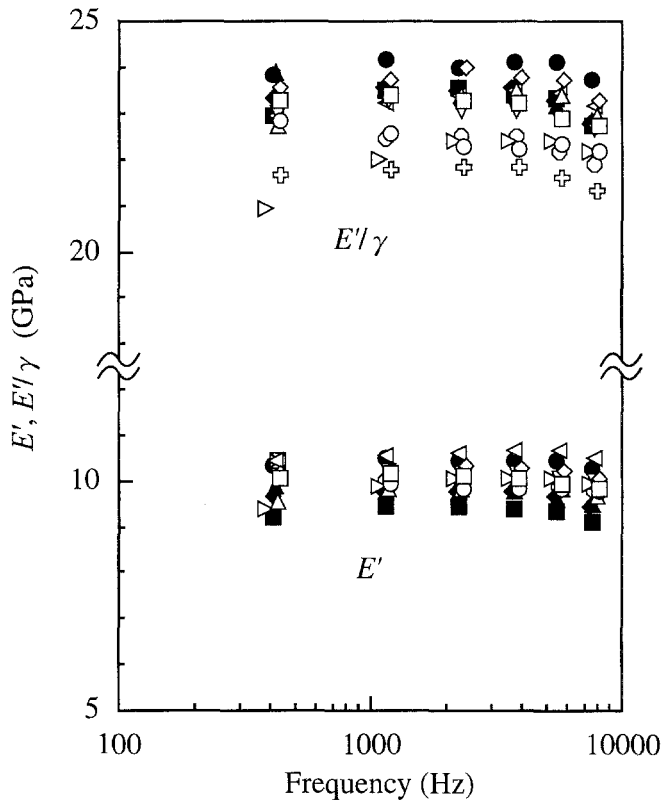
Fig. 5. Dependence of E' and E'/γ on frequency for the impregnated and untreated specimens conditioned at 58% relative humidity (RH). *Open symbols*, impregnated wood; *filled symbols*, untreated wood

Temperature dependence of tan δ

The measurement for temperature dependence of viscoelasticity will become one of the useful means to clarify why extractives influence the vibrational properties of wood. Especially, information about the motions of matrix substances or adsorbed water molecules are obtainable by measuring viscoelasticity at low temperature.

Figure 9 shows the temperature dependence of tan δ at 11 Hz for impregnated and untreated specimens. For the specimens conditioned at 58% RH (MC 8.5%–9.8%), the tan δ of impregnated specimens differed clearly from that of untreated ones at above $-50°C$ (Fig. 9a). The impregnated specimens conditioned at 0.3%, 11%, and 33% RH also showed lower tan δ than untreated ones around $0°–20°C$. In contrast, the impregnated specimens conditioned at 94% RH (MC 16.6%–18.1%) had a lower tan δ than untreated ones at above $-75°C$ (Fig. 9b), but the tan δ of impregnated specimens increased with increasing temperature at above $-25°C$, though the tan δ of untreated specimens was virtually constant at the temperature range of $-75°$ to $20°C$.

When the MC of the impregnated specimen is low, the tan δ decreased over a wide temperature range. This phenomenon corresponds to the decrease of tan δ determined over a wide frequency range at room temperature (Figs. 6a–c). Meanwhile, when MC is high, the tan δ of the impregnated specimens increased with increasing temperature at above $-25°C$. This corresponds to the increase of tan δ

Fig. 6. Dependence of tan δ on frequency for impregnated and untreated specimens conditioned at absolutely dried state (**a**), 33% RH (**b**), 58% RH (**c**), and 94% RH (**d**). Symbols are the same as in Fig. 5
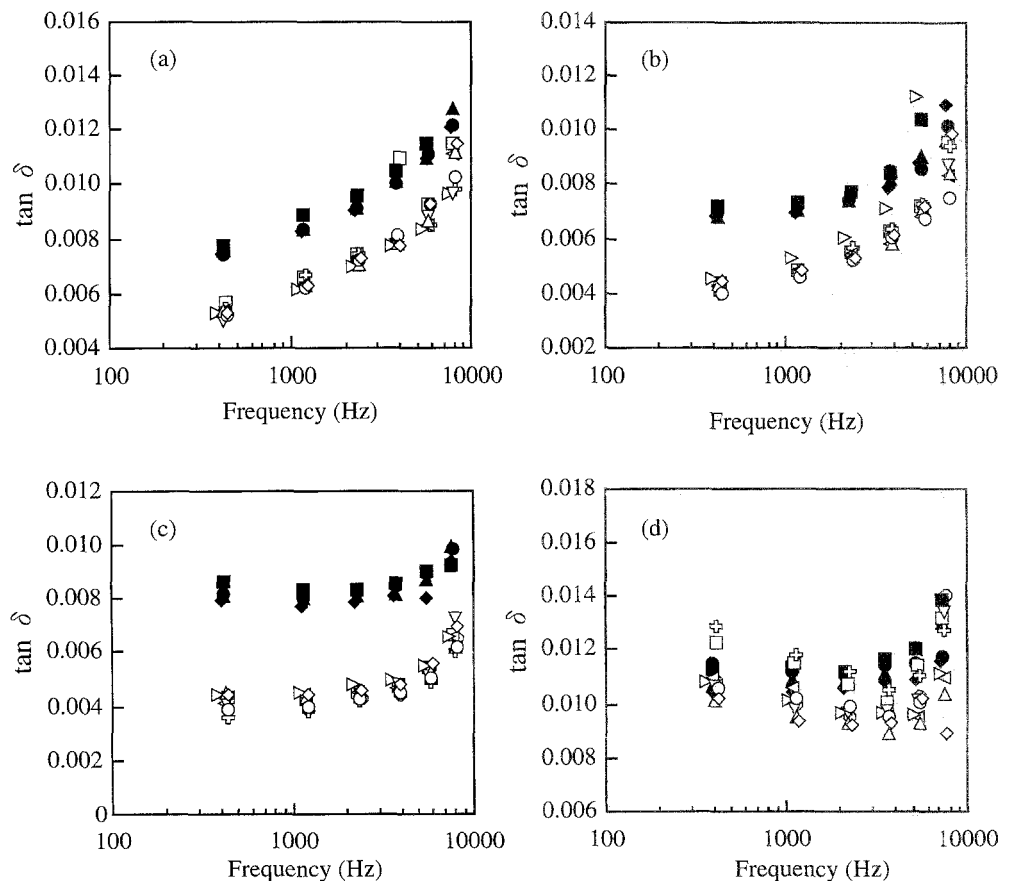
Fig. 7. Relation between weight percent gain (WPG) and calculated tan δ conditioned at absolutely dried state (**a**), 33% RH (**b**), 58% RH (**c**), and 94% RH (**d**). *Circles*, 500 Hz; *triangles*, 4000 Hz; *squares*, 7000 Hz; *open symbols*, impregnated wood; *filled symbols*; average value of untreated wood
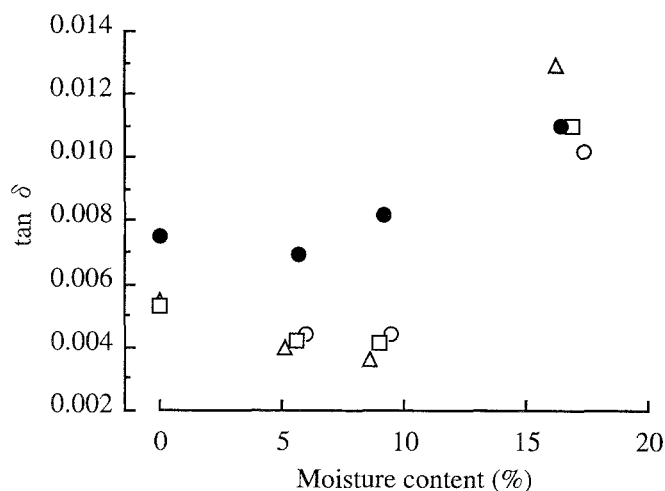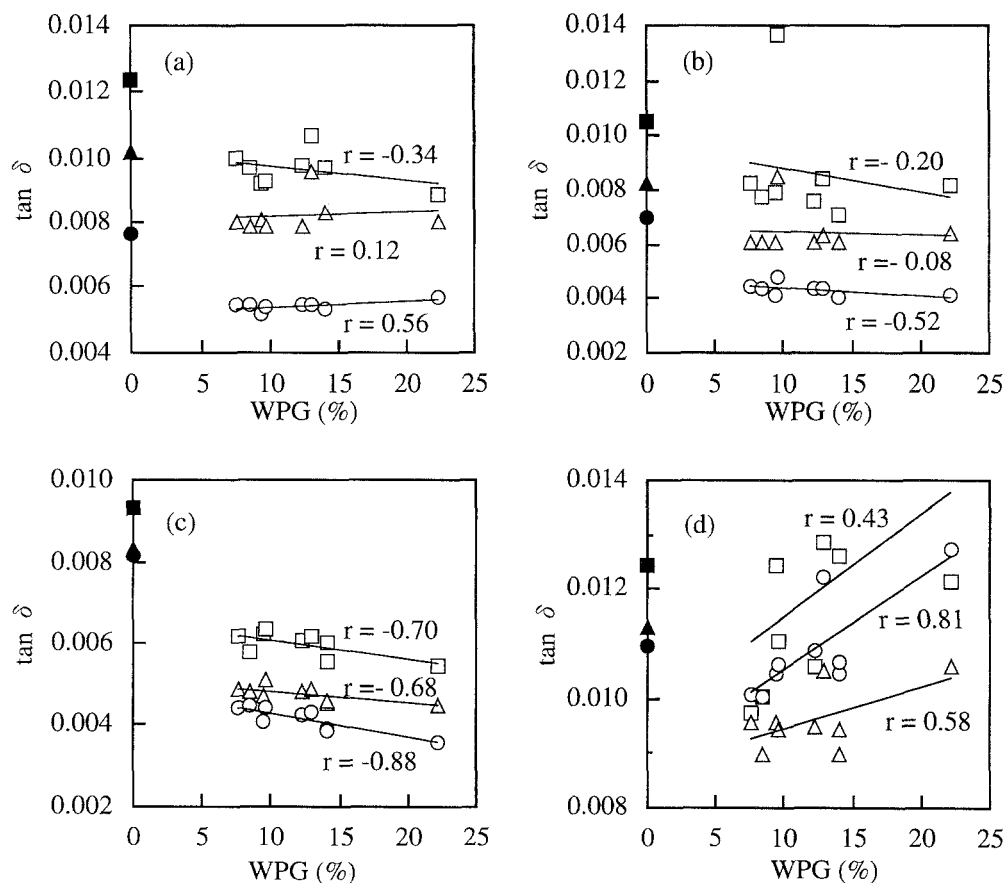

Fig. 8. Relation between moisture content and tan δ. *Open circles*, weight percent gain (WPG) is 7.6%; *open squares*, WPG is 12.3%; open triangles, WPG is 22.2%; *filled circles*, untreated wood

determined in the low-frequency range at room temperature (Fig. 6d). Figures 6d and 9b suggest that the relaxation process exists at a lower frequency or higher temperature range than the measured one. The glass transition temperature of matrix substances, such as lignin, exists at around 100°C in a humid state.[14] However, the glass transition tem-

perature is lowered by addition of formamide.[15] Therefore, it is speculated that at high MC the impregnated extractives behave as a plasticizer together with adsorbed water molecules; as the result, the glass transition temperature falls and the tan δ increases above −25°C.

The peak of tan δ found in the temperature range of this study is considered a mechanical relaxation process of adsorbed water molecules.[16] This peak is called the α relaxation process. It is thought that the change of α relaxation caused by impregnation with extractives reflects the change of mobility of adsorbed water molecules or matrix substances concerned with adsorbed water. The peak temperature (T_α) and the apparent activation energy (ΔE) of α relaxation process were plotted against the MC in Fig. 10. The ΔE was calculated as follows:

$$\Delta E = -2.303R\frac{\mathrm{d}\log f}{\mathrm{d}(1/T_\alpha)} \quad (\mathrm{kJ/mol})$$

where R is the gas constant, and f is the frequency (Hz). Except for specimens with low WPG, ΔE of impregnated specimen was generally higher than those of untreated ones at around 5%–6% MC (Fig. 10b). Therefore, it is thought that the mobility of adsorbed water molecules or matrix substances related to adsorbed water is restrained until a moderately high MC. The differences of T_α and ΔE between impregnated specimens and untreated ones were not observed in the high MC range.
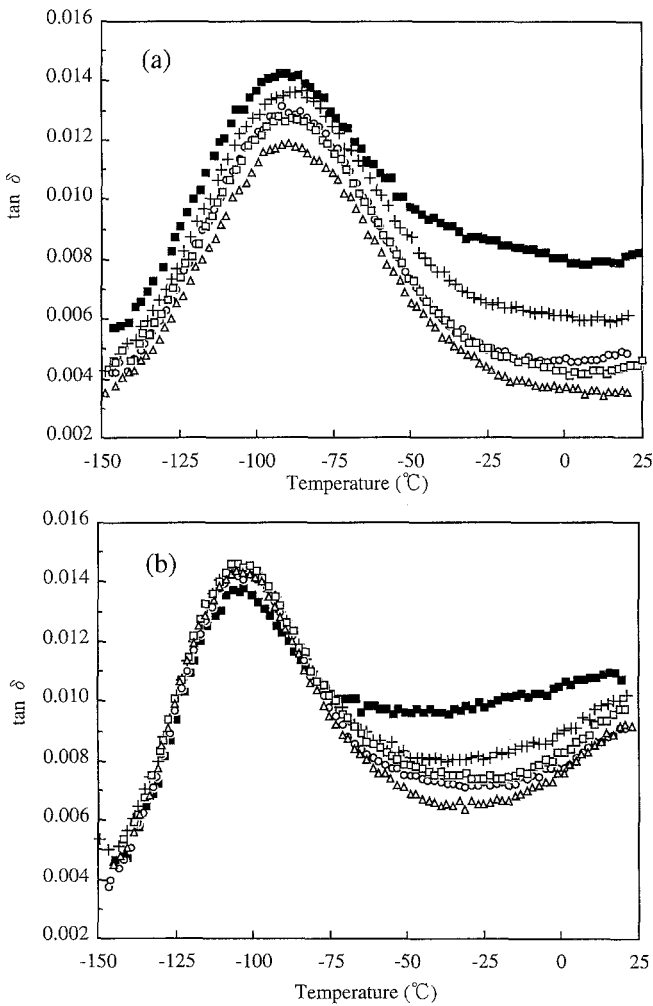
Fig. 9. Temperature dependence of tan δ at 11 Hz for impregnated and untreated specimens conditioned at 58% RH (**a**) and 94% RH (**b**). *Filled squares*, untreated wood; *crosses*, weight percent gain (WPG) is 4.8%; *open circles*, WPG is 9.7%; *open squares*, WPG is 12.8%; *open triangles*, WPG is 16.4%

Fig. 10. Peak temperature T_α (**a**) and the apparent activation energy ΔE (**b**) of a relaxation process plotted against the moisture content. Symbols are the same as in Fig. 9

From the above-mentioned results, we propose the following mechanism for the change of tan δ by extractive impregnation. At extremely low MC, the main components of extractives, such as protosappanin B and brazilin, form direct hydrogen bonds with wood components. One molecule of extractive component may form several cross-linkages with wood components, which restrains slippage between molecules or microfibrils. It is also plausible that the rigid structures of protosappanin B and brazilin cause the decreased tan δ. At moderately high MC, the functional groups of extractives that are apart from the attractive sites of the wood components can also take part in hydrogen bonding through the water molecule, which decreases the tan δ even more. At high MC, however, direct hydrogen bonding between the extractive molecule and the wood component becomes impossible because of the existence of an excessive amount of water molecules. As the result, some extractives act as plasticizers and cannot restrain the slippage between molecules or microfibrils. This leads to the increased tan δ at high MC.
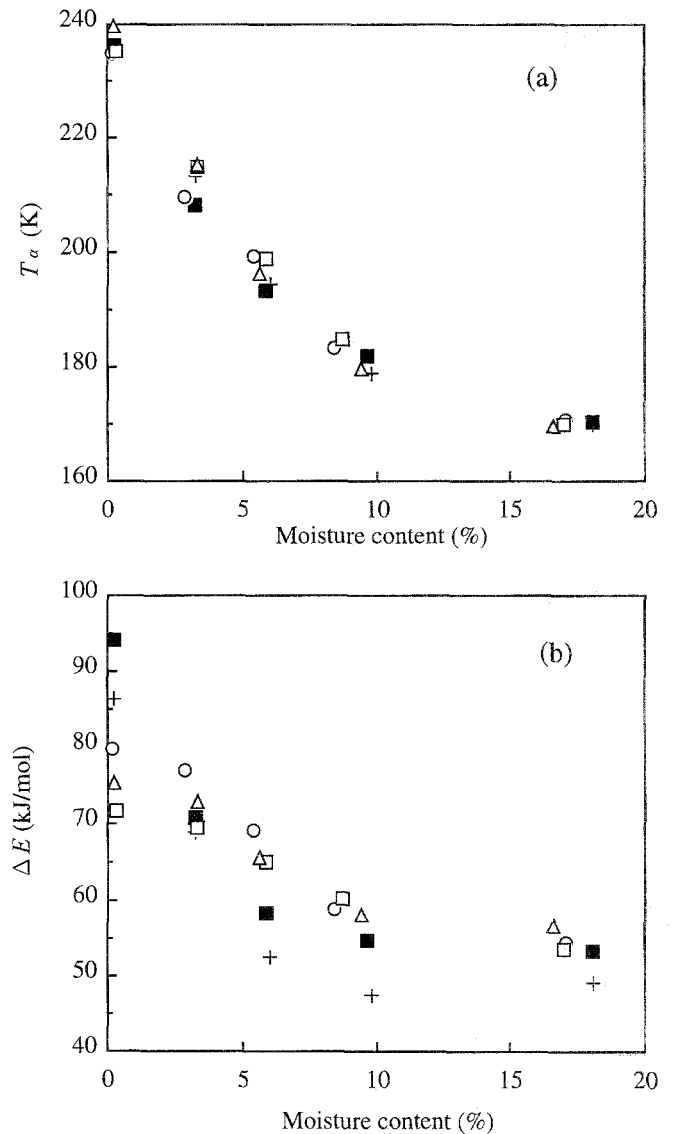
Conclusions

The impregnation of extractives obtained from pernambuco into sitka spruce wood changed the tan δ differently depending on the MC range. With low to moderate MC, the tan δ of impregnated wood decreased probably because of the formation of crosslinkage by direct hydrogen bonds between extractive molecules and wood components. With high MC, the decreasing effect of tan δ was almost lost. In particular, the fully impregnated specimens showed rather higher tan δ than the untreated ones. It is thought that the existence of a large amount of water molecules cleaves the direct hydrogen bonds between the extractive and the wood component, and some extractives behaved as plasticizers.

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