Artificial aging of wood monitored by dynamic viscoelasticity measurement

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動的粘弾性測定による木材の人為的老化過程の追跡

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Résumé

In order to accelerate the aging of wood, we successively monitored the dynamic viscoelastic properties of yellow birch heartwood during heating at elevated temperature. The dynamic Young's modulus of wood heated at 160 ℃ and over decreased from the start of heating without any signs of increase as generally reported. On the other hand, the loss tangent decreased to the appreciable extent in the initial stage of heating. The latter change is probably due to the crystallization of cellulose molecules and／or the rearrangement of hydrogen bonds. However, the change of loss tangent by short-term heating was too slight to enhance the sound quality of musical instruments. The mechanical changes caused by short-term heating at elevated temperature was not equivalent to those by leaving in the atmospheric condition for long-term. Therefore, the acceleration of desirable mechanical changes without serious thermal degradation would not be prospective unless the contribution of moisture was considered.

要　旨

加熱による木材の老化促進を目的として，熱処理に伴って起こるイエローバーチ心材の動的粘弾性の変化を連続的に測定した。160℃以上で熱処理を行った場合，動的ヤング率は加熱の初期から低下し，一般的に言われているような加熱初期の動的ヤング率の増加は認められなかった。一方，損失正接は加熱の初期に低下した。この損失正接の変化は，おそらくセルロース分子の結晶化，あるいは水素結合の再配列によるものであろう。しかしながら，損失正接の低下は楽器用材として用いた場合の音質の向上を期待できる程ではなかった。単純な高温での短時間の加熱によって起こる老化は，大気中に長期間放置した場合に起こる変化と等価とは言えず，水分の影響を考慮に入れずに，熱劣化を極力抑えつつ，望ましい力学的性質の向上をはかることは困難であろう。

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1. Introduction

From the ancient times, wood has been used as construction materials, and some wooden buildings have been preserved for over a thousand years such as Horyu-ji Temple which is one of the oldest wooden buildings in the world. On the other hand, wood has also been used for various musical instruments, and aged ones are highly praised because of their good sound qualities. For example, guitars aged for 30 to 40 years resound sweeter than the same model produced recently. Furthermore, violins produced more than 200 years ago are excellently evaluated and are active even now. These enhancements in sound quality seem to be resulted from the substantial changes related with the repeating moisture adsorption and drying, thermal changes in atmospheric temperature, the relaxation of stress by continual playing (vibration), and so on.

We can find many papers about aging of wood. Among them, Kohara[1] considered that the aging was a long-term accumulation of heating at the atmospheric temperature, and showed that the hygroscopicity and the composition of components of artificially heated wood were analogous to those of naturally aged wood. Kadita et.al[2] indicated that the dynamic Young's modulus of wood heated at 70-170℃ once increased in the initial stage of heating times and then decreased. Considering the effect of heat and water on the aging process of wood, Ikimune[3] determined the hygroscopicity and the dynamic viscoelasticity of wood heated with or without high pressure water vapor. She found that the loss tangent decreased and the specific dynamic Young's modulus increased when wood heated without moisture, and those were affected inversely when heated with high pressure water vapor. Hatakeyama et.al[4] suggested that cellulose molecules were rearranged when an amorphous cellulose film was heated under the existence of water vapor. Taking their suggestion into consideration, we can partly explain the lowering of hygroscopicity and the changes of mechanical properties in aged wood.

In order to investigate the thermal effect on artificial aging of wood from the viewpoint of mechanical property, we consecutively monitored the dynamic viscoelasticity of wood in the short-term but high temperature heating process.

2. Materials and Methods

2. 1 *Measurement of dynamic viscoelasticity by resonance vibration method*

Specimens of 0.6 mm(T)×10 mm(R)×100 mm(L) were cut from the heartwood of yellow birch (*Betula alleghaniensis* Britton). After they were absolutely oven-dried and conditioned at 20℃ and 65% R.H., the dynamic viscoelasticity was measured.

Heating was carried out in a forced-circulation oven for 1-24 h at 130-170℃ under the existence of air. Five specimens were used for each condition.

After the heated specimens were equilibrated at 20℃ and 65% R.H. by ascending the moisture content, the dynamic viscoelasticity was measured again. The dynamic Young's modulus of heated wood was calculated from the dimensions of the specimen before treatment, because the dimension hardly changed even after heating.

The dynamic viscoelasticity was determined by a free-free flexural vibration method[5,6]. From the resonance frequency (f_r:sec^{-1}) determined at the first mode and the dimension of the specimen, the dynamic Young's modulus (E:Pa) was calculated as follows:

$$E=\frac{48\pi^2 l^4 f_r^2 \rho}{m_1^4 h^2} \qquad (1)$$

where, m_1 is a constant depending on the vibration mode (= 4.730 in this case), h(cm), l(cm), and ρ are the thickness, length, and air-dried specific gravity of specimen, respectively. Logarithmic decrement (λ), which was related with the loss tangent (tan δ) as tan δ = λ / π, was also determined from the wave number (n) included in the range, where the amplitude damps to a half of the initial as follows:

$$\lambda=\frac{\ln 2}{n} \qquad (2)$$

2.2 *Measurement of the dynamic viscoelasticity by nonresonance vibration method*

The specimens of yellow birch heartwood, 0.6 mm(T)×3 mm(R)×40 mm(L), were used. The experiments were conducted by means of a measuring apparatus for dynamic viscoelasticity (RHEOVIBRON DDV-25FP, Orientec Co., Ltd.) under the tension. The outline of the apparatus is shown in Fig. 1. The specimen is located in a chamber thermally controlled. From the phase difference between the signal given through a driver to the specimen and that detected in a load cell as the response, the dynamic Young's modulus and loss tangent can be calculated. The principle of the dynamic viscoelasticity measurement under tension is as follows.

When a sine strain $\varepsilon(t)$, that is

$$\varepsilon(t)=\varepsilon_0 \sin(i\omega t) \qquad (3)$$

is given by an electromagnetic driver, the stress σ(t) caused can be expressed as,

$$\sigma(t)=\sigma_0 \cos[i(\omega t+\delta)] \qquad (4)$$

where, δ is phase difference between strain and stress, and therefrom the loss tangent (tan δ) can be derived.

Dynamic elastic modulus (E) and dynamic loss modulus (E") are defined as,

$$E = |E^*| \cos\delta \qquad (5)$$

$$E" = |E^*| \sin\delta \qquad (6)$$

where, E^* is complex elastic modulus, i.e. the ratio of dynamic strain to dynamic stress. The dynamic elastic modulus, E, can be obtained if the observed value of loss tangent was inserted into the Eq.(5).

The dynamic Young's modulus and loss tangent were measured at constant temperatures. Prior to the measurements the influence of the preload tension was examined in the range of 0.1 to 2000 gf at 150℃. The measurements at constant temperatures

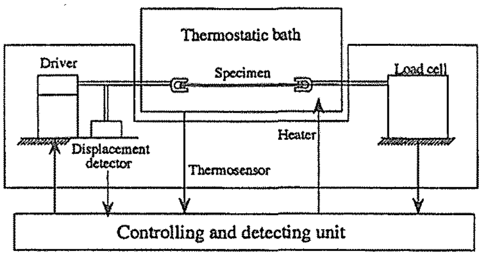

Fig. 1 Schematic diagram of the measuring apparatus of dynamic viscoelasticity by nonresonance vibration method

were carried out at 80 to 190℃. The specimens were absolutely dried before setting into the apparatus to cancel the influence of adsorbed moisture. The inherent error originated from the apparatus (e.g. a thermal characteristic of the load cell and a thermocouple) was examined by attaching an iron plate in stead of wood specimen, and was confirmed to be negligible.

3. Results and Discussion

3. 1 *Dynamic viscoelasticity change of heated wood monitored by the resonance vibration method*

Fig. 2 shows the percent change of dynamic Young's modulus during heating. At 130℃ the dynamic Young's modulus hardly changed within the examination, but it decreased slightly at 150℃ and steeply at 170℃. The increase of the dynamic Young's modulus, which is found by some investigators[1,2,7,8] in the initial stage of heating, was not appreciable in the temperature range of this study. The reason why such increase cannot be found in this study is probably due to the fact that the real change in the dynamic Young's modulus was overlapped by the individual variations among specimens.

Fig. 3 shows the percent change of loss tangent after heating. The plots is widely scattered and appreciable change with time elapse was not found. Generally, the equilibrium moisture content decreases after heating[2] and this affects to the loss tangent complicatedly[9]. Therefore, even if the loss tangent apparently changed, it is impossible to attribute it to the real heat effect. Thus, it is necessary to measure the change at the same equilibrium moisture content instead of the same relative humidity. For that reason, the ex-

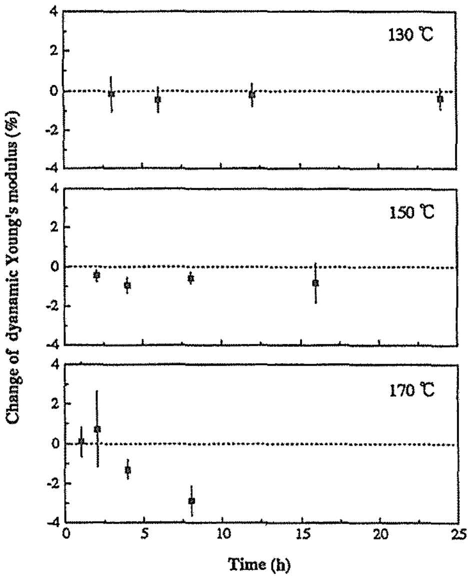

Fig. 2 Effect of heating on dynamic Young's modulus

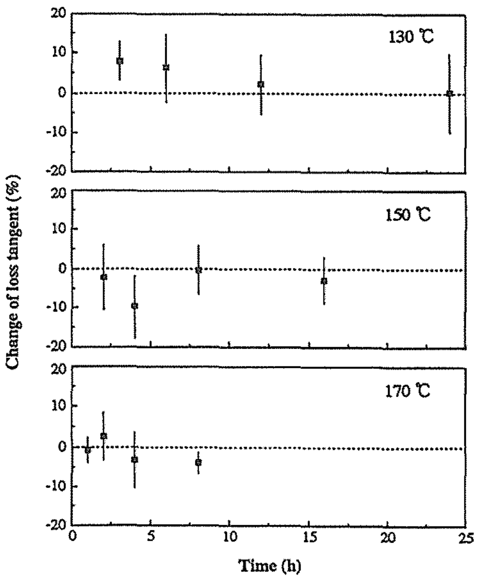

Fig. 3 Effect of heating on loss tangent

amination in 3.2 was carried out in the absolutely dried condition.

3. 2 *Dynamic viscoelasticity change of heated wood monitored by the nonresonance vibration method*

Since when the measurements were conducted under 0.1-2000.0 gf of preload at 150℃, significant difference was not found among the load, the constant preload (0.1 gf) was adopted in the following measurements.

The change of the dynamic Young's modulus during heating was shown in Fig. 4. The dynamic Young's modulus hardly changed at 80-150℃ within the duration examined. On the other hand, at 160-190℃ it decreased without any increasing signs in the initial stage of heating.

Many investigators have found that the Young's modulus of wood increases in the initial stage of heating[1,2,7,8], and some of them suggest that it reflects the enlargement of crystallinity of cellulose. As stated above, however, the hygroscopicity of wood tends to lower after heating. Therefore when the Young's modulus is measured under the constant relative humidity, it may apparently increase due to the decreased moisture content. In this point, this experiment conducted under the absolutely dried state can be neglected the influence of moisture content.

Straight lines applied to the linearly decreasing range of the Young's modulus were shown in Fig. 4-b. Taking the absolute values of the slopes to be proportional to the reaction rate constant, so-called Arrhenius' plot was drawn (Fig. 5). The Arrhenius' equation is

$$k = A \exp(-E_a / RT),$$

or

$$\ln k = \ln A - E_a / RT$$

where, k is rate constant (absolute value of slope in Fig. 4-b), A is frequency factor,

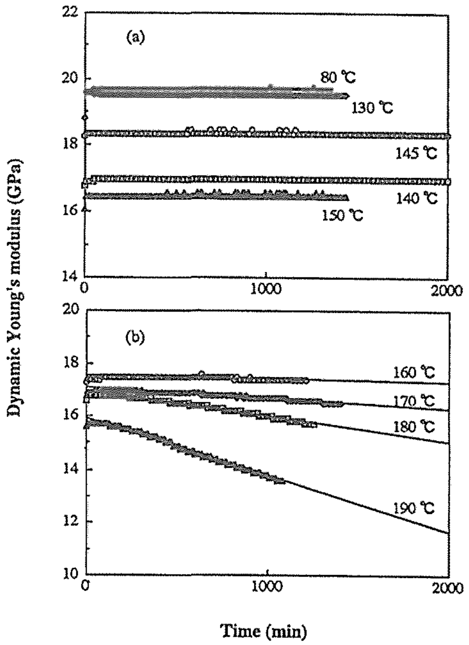

Fig. 4 Dependence of dynamic Young's modulus on heating time
Note: (a) 80-150℃, (b) 160-190℃

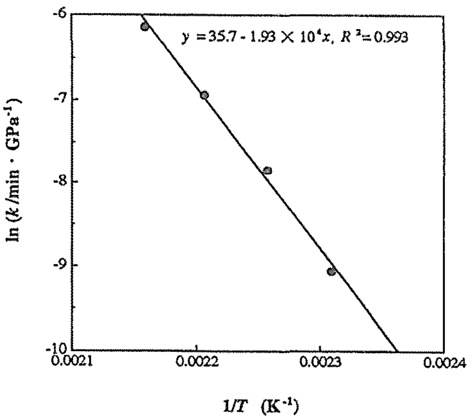

Fig. 5 Arrhenius' plot

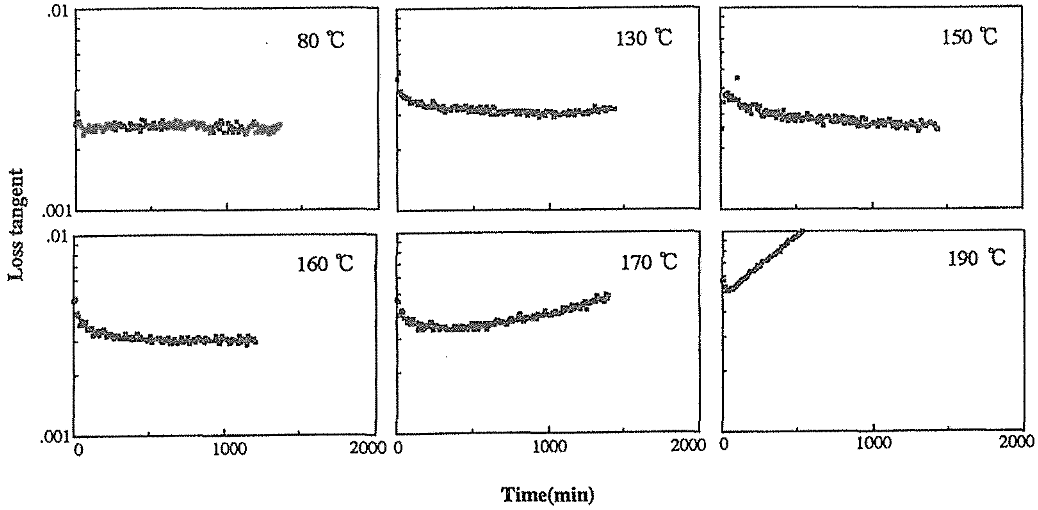

Fig. 6 Dependence of loss tangent on heating time

E_a is apparent activation energy, R is gas constant ($8.315\ J \cdot mol^{-1} \cdot K^{-1}$), and T is absolute temperature.

From the slope in Arrhenius' plot, the activation energy (E_a) of 160 kJ/mol was obtained. Okamoto[11] estimated the activation energy of thermal decomposition of wood in the atmosphere to increase from 23 kcal/mol (93 kJ/mol) to 35 kcal/mol (147 kJ/mol) with increasing temperature. The activation energy obtained here virtually agrees with that of thermal decomposition of wood at higher temperature. Therefore, the linear decrease of the dynamic Young's modulus at 160℃ and over naturally differs from the long-term thermal decomposition at ambient temperature. This suggests that it is impossible to substitute the long-term aging at ambient temperature for a simple short-term heating at elevated temperature.

The change of loss tangent during heating is shown in Fig. 6. At the temperature range examined, the loss tangent tends to decrease in the initial stage of heating. At 170℃ and over, however, the loss tangent steeply increased after the initial slight decrease. This indicates the violent thermal decomposition at elevated temperature. On the other hand, the initial decrease of loss tangent observed at 160℃ and below is probably due to the crystallization of cellulose molecules and/or the rearrangement of hydrogen bonds. In this point, the loss tangent seems to reflect the thermal effect more sensitively than the dynamic Young's modulus. Nevertheless, the decrease of loss tangent resulting from heating was much smaller than that from the formaldehyde treatment, by which the loss tangent reached to about a half of the control[12]. From the fact that the Young's modulus did not increase and that the degree of the decrease of loss tangent was only slight, we can conclude that simple heating in the air at elevated temperature has little effect on enhancement of sound quality of musical instruments, rather accelerates the thermal degradation of wood. The existence of water may play an important role on a long-term aging at ambient condition, and thus it is necessary to study the heating under the moist condition. However, heating under high pressure water vapor caused the elution of wood components and was far from the real aged wood[3]. The subject to accelerate the aging is how to control the temperature and water.

4. Conclusions

Successive measurement of the dynamic viscoelasticity showed that the dynamic Young's modulus of wood heated at elevated temperature (160-190℃) decreased from the start of heating. On the other hand, the loss tangent significantly decreased in the initial stage of heating. This suggests the crystallization of cellulose molecules and/or the rearrangement of hydrogen bonds. However the decrease of loss tangent by short-term heating was not so great as to enhance the sound quality of musical instruments. It can be concluded that simple heating is not promising to accelerate the aging effect. In other words, the changes caused by short-term heating at elevated temperature is not equivalent to those by leaving in the atmosphere for long-term. The difference may partly come from the existence of the moisture.

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