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Influence of histories on dynamic viscoelastic properties and dimensions of water-swollen wood

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Abstract The influences of heating history, cooling method, and cooling set on microstructures and the mechanical properties of water-swollen wood were studied by measuring viscoelastic properties and dimensional changes while elevating temperatures between 20°C and 90°C. Both the viscoelastic properties and dimensional changes of water-swollen wood in the first heating process were quite different from those in the other heating processes. The results revealed that the molecular state of green wood around room temperature was stabilized and could not return to this state if drying or heating was carried out. Cooling methods greatly affected the viscoelastic properties, while they hardly affected dimensional changes when the temperature was elevated. Localized stress in the microstructures of water-swollen wood produced by quenching affected the mechanical properties in the heating process, while external stress less than the proportional limit caused by a cooling set had no effect. This revealed that much greater localized stress linked to the instability of water-swollen wood than the external stress in relation to the cooling set occurred.

Key words Water-swollen wood · Unstable state · Dynamic viscoelastic property · Dimensional change · Microstructure

Introduction

Recently, it has been found that wood subjected to changes in temperature and/or swelling state shows a lower elastic

modulus and greater fluidity, judged from creep or stress relaxation measurements, than wood kept for a long time under constant temperature and humidity. This is interpreted as a result of the instability caused by localized stress in the microstructures of wood cell walls caused by changes in environmental conditions such as temperature and humidity. Moreover, such instability in wood is modified by the time the wood is kept at constant humidity and temperature. Therefore, the instability in wood, that is, an unstable wood state, is interpreted as the transition process to the true thermodynamic equilibrium.¹

Reports regarding the mechanical properties of wood in relation to the unstable state are reviewed as follows. Marked differences were first found in dynamic viscoelastic properties while elevating the temperature between green and rewet specimens with a drying history; there was a lower dynamic elastic modulus and a higher dynamic loss modulus in rewet specimens than in green specimens. Moreover, an increase in the dynamic modulus and a reduction in the dynamic loss modulus were noted for rewet specimens with time left in water around room temperature.^{2,3}

Concerning the effects of change in temperature, various characteristics for mechanical properties of unstable water-swollen wood have been reported. Water-swollen wood quenched from higher temperatures had a lower modulus of elasticity and a higher fluidity than control wood kept at 20°C for a long time, and the unstable state of water-swollen wood was produced not only by cooling, but also by heating.^{4–6} Wood immediately after changing the moisture content had higher fluidity than control wood kept in water for a long time.^{1,7–11}

Ishimaru¹ reported that such instability is attributable to an inadequate orientation among the molecular chains of wood constituents, and/or adsorption of swelling agents such as water onto lower adsorption energy sites in an unstable state compared with an equilibrium state. Nakano¹² reported that the change in the relaxation property caused by heating and the following quenching is due to the temporary free volume created by freezing of molecular chain motion of wood components, most probably lignin, during quenching. A similar phenomenon has already been found

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for various amorphous polymers.^{13,14} Amorphous polymers are not in thermodynamic equilibrium at temperatures below their glass transition and are to be regarded as solidified supercooled liquids whose volume, enthalpy, and entropy are greater than they would be in the equilibrium state. This gradual approach to equilibrium affects many properties of the material with time, and is called physical aging.

These reports pointed out that the difference in mechanical properties between the stable and unstable states resulted from differences in microstructures. Thus, to understand the mechanical properties of unstable wood, the relationship between the microstructures and mechanical properties of wood in the unstable state should be studied. However, until now, only the viscoelastic properties of wood have been measured and little attention has been paid to the relationship between viscoelastic properties and other physical properties in unstable states. It is uncertain that such a phenomenon of wet wood is caused only by free volume created by freezing of molecular chain motion of the wood component.

Therefore, in the present study, not only viscoelastic properties, but also dimensional changes were measured, and the results of both measurements are discussed comprehensively. To obtain new information about the relationship between microstructures of wood cell walls and the mechanical properties of unstable wood, three factors (heating history, cooling method, cooling set) and their effects on the microstructures and mechanical properties of water-swollen wood were investigated.

Materials and methods

Materials

Japanese hinoki (*Chamaecyparis obtusa* Endl.) was used. The specimen sizes were 30 mm in the radial direction (R), 4 mm in the tangential direction (T), and 0.7 mm in the longitudinal direction (L) for the measurements of dimensional change, and 40 mm (R), 4 mm (T), and 0.7 mm (L) for the measurements of dynamic viscoelastic properties. Both measurements were carried out in water after different pretreatments.

Methods

Temperature dependence of dynamic elastic modulus (E') and loss modulus (E'') were measured by the tensile forced oscillation method using an automatic dynamic viscoelastometer (Seiko Instruments, DMS6100). The measurements were conducted over a temperature range of about 20–90°C for water-swollen wood at programmed heating rates. Frequencies for the measurement were 0.05, 0.1, 0.2, 0.5, and 1 Hz, the span was 20 mm, and the displacement amplitude was 5 μ m. The tensile direction was radial. The dimension temperature dependence was measured by a thermomechanical analyzer (Seiko Instruments, TMA/SS6100). The

span was 20 mm and the load was 5 g, which was the minimum load for the tensile test. Both measurements of dynamic viscoelastic property and dimension were carried out under the same temperature programs.

To clarify the effects of three factors on the viscoelastic properties and dimensional changes, the specimens for both measurements were pretreated. The measuring conditions are discussed later.

Results and discussion

Influence of heating history on viscoelastic properties and dimensions changes of water-swollen wood

First, to examine the influence of heating history, the same specimen was heated repeatedly and the viscoelastic properties and dimensions of green wood were compared in the first heating process and in the second heating process at 3°C/min after cooling of the specimens at 1°C/min from 90°C to around 20°C. Figure 1 shows the measuring conditions for Fig. 2 and the heating processes in Fig. 1 correspond to those in Fig. 2.

Figure 2 shows the influence of heating history on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of green wood in the first heating process and the second heating process with a heating rate of 3°C/min. Relative E' , which is the value relative to that of green wood at 20°C, in the first heating process was larger than that in the second heating process. Below 60°C, the relative E'' , which is the value relative to that of green wood at 20°C, in the first heating process was smaller than that in the second heating process. On the other hand, above 60°C that in the first heating process was larger than that in the second heating process. Furthermore, the viscoelastic properties in the later heating processes, which are the third and the fourth heating processes, were almost the same as those in the second heating process only if the specimen was previously cooled in the same manner from a higher temperature, around 90°C. This result for viscoelastic properties

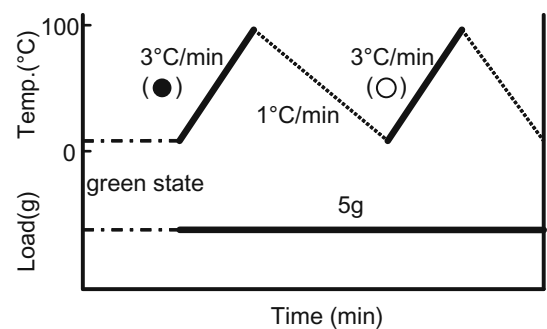


Fig. 1. Measuring conditions for results shown in Fig. 2. Temperature program for both measurements of dynamic viscoelastic properties and dimensional changes from 20°C to 90°C and load for the measurement of dimensional changes are shown. Under the temperature program, the same specimen was heated repeatedly and the behaviors of the specimen in the first (filled circle) and the second (open circle) heating processes are compared

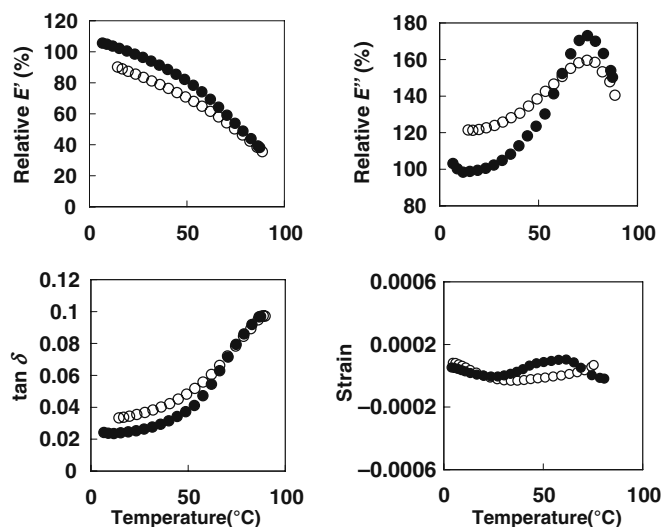


Fig. 2. Influences of heating history on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of water-swollen wood. Relative E' and E'' are relative to the values for green wood at 20°C. Filled circles, first heating process from the green condition; open circles, second heating process

agreed with the result of Furuta et al.³ Dimensional changes in the first heating process were clearly different from those in the second and later heating processes. From around 60°C, the dimensions in the first heating process decreased with increasing temperature; however, there was no drastic decrease in dimensions in the second and later heating processes. These results indicated that both the viscoelastic properties and dimensional changes in the first heating process were quite different from those in the second and the later heating processes.

The cause of the differences in the dynamic viscoelastic properties and dimensional changes between the first heating process and the second and later heating processes was considered as follows. Before any artificial processing, the wood had been a tree below 40°C in the water-swollen condition, having maintained a green condition for a long time. Also, the fiber saturation point of green wood is thought to be higher than that of rewet water-swollen wood, as interpreted by a report that the desorption isotherm from the green state was larger than other desorption isotherms.¹⁵ In addition, wood constituents with localized stress in unstable states take an inappropriate orientation, which leads to weakened resistance to deformation and to increased fluidity. It can be considered that the time keeping constituents of green wood in swollen state made the state of the molecules in the noncrystalline region of green wood more stabilized at ordinary temperatures, judging from the larger E' and smaller E'' in the first heating process. This means that the first cooling from 90°C to 5°C made the microstructures of the water-swollen wood below 60°C, which is known as the glass transition temperature for water-saturated lignin,^{3,16,17} in the second heating process more destabilized than those in the first heating process. As the molecules in the noncrystalline region in the first heating process above

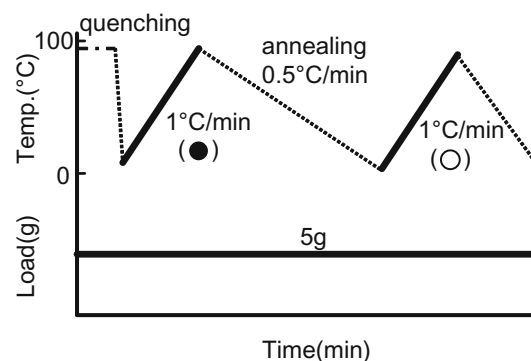


Fig. 3. Measuring conditions for results shown in Fig. 4. Temperature program for both measurements of dynamic viscoelastic properties and dimensional changes from 20°C to 90°C and load for the measurement of dimensional changes are shown. Under the temperature program, the same specimen was heated repeatedly and the behaviors of the specimen in the first (filled circle) and the second (open circle) heating processes were compared

60°C became more unstable than those in the second heating process, it is considered that the molecular arrangement in wood in the first heating process changed more drastically than in the second heating process. Heating decreased the fiber saturation point of green wood in the first heating and made the microstructures in the noncrystalline region more destabilized than for the second heating process, judging from the relative E' in the first heating that was larger than in the second. The characteristic viscoelastic properties and dimensional changes in green wood in the first heating process revealed that the molecular state of green wood around room temperature would be the most stable and irreversible. Therefore, it can be said that heating and cooling destabilize the molecular state of green wood.

Influence of cooling method on the viscoelastic properties and dimensions of water-swollen wood

With respect to cooling methods, quenching and annealing specimens were prepared in the following manner: water-swollen wood heated around 90°C was quenched by placing in water at 20°C as soon as possible and was annealed at 0.5°C/min to about 20°C. The same specimen was heated repeatedly and the viscoelastic properties and dimensions of the specimen after quenching and annealing were compared in the heating processes. Figure 3 shows the measuring conditions and the heating processes for the results given in Fig. 4.

Figure 4 shows the influence of cooling method on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of water-swollen wood in the heating processes immediately after quenching and annealing with a heating rate of 1°C/min. For the specimens immediately after quenching and annealing, viscoelastic properties were different: the relative E' (relative to wood after quenching at 25°C) was slightly larger and the relative E'' (relative to wood after quenching at 25°C) was smaller after annealing than the corresponding values after quenching. This result

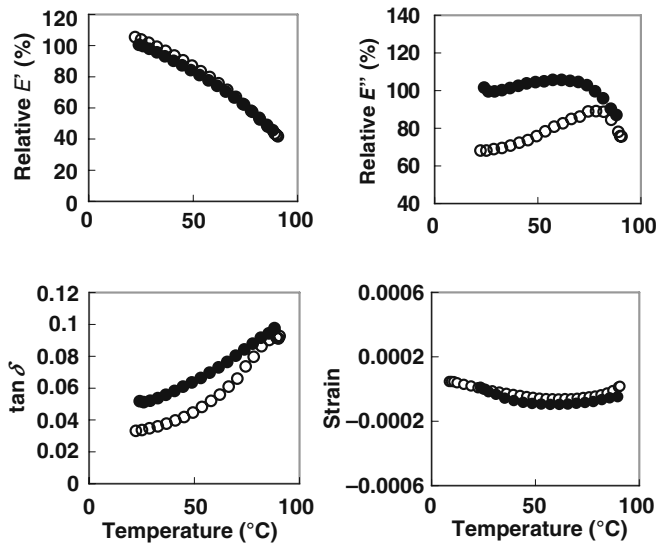


Fig. 4. Influences of cooling method on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of water-swollen wood. Relative E' and E'' are relative to the values for wood after quenching at 25°C. Filled circles, after quenching; open circles, after annealing

for viscoelastic properties agreed with the results of Furuta et al.³ and Kudo et al.⁴ Dimensional changes after quenching and annealing were almost the same.

The results mentioned above suggest that the difference in the microstructure of water-swollen wood after quenching and annealing more clearly affected the viscoelastic properties than dimensional changes in the heating processes immediately after cooling. Instability of water-swollen wood caused by localized stress in the noncrystalline region decreases with rising temperature because of active molecular motion.⁷ Takahashi et al.^{10,11} found that wood immediately after adsorption of moisture showed greater creep than wood after long moisture conditioning under constant relative humidity equal to that after the adsorption of moisture. They concluded that this phenomenon was attributable to stabilization based on the reorientation of molecular chains of wood constituents during the transition to the true equilibrium state. From the standpoint of this report, in the transition process to the more stabilized state, there is redistribution of water in the wood microstructure in the water-swollen condition, which could be considered to reflect the viscoelastic properties while the temperature rises after quenching, but hardly reflecting dimensional changes. The reason the redistribution of water little reflected the dimensional change is thought to be because one portion in the microstructure in the cell wall of water-swollen wood swelled, while one shrank, in the stabilizing process.

Influence of cooling set on the viscoelastic properties and dimensions of water-swollen wood

To clarify the relationship between the cooling set and instability of microstructures in water-swollen wood,

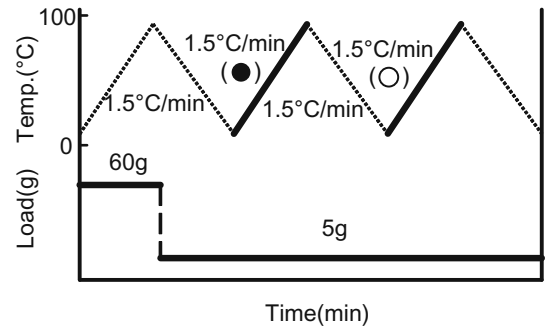


Fig. 5. Measuring conditions for results shown in Fig. 6. Temperature program for both measurements of dynamic viscoelastic properties and dimensional changes from 20°C to 90°C and load for the measurement of dimensional changes are shown. Under the temperature program, the same specimen was heated repeatedly and the behaviors of the specimen in the second (filled circle) and the third (open circle) heating processes were compared

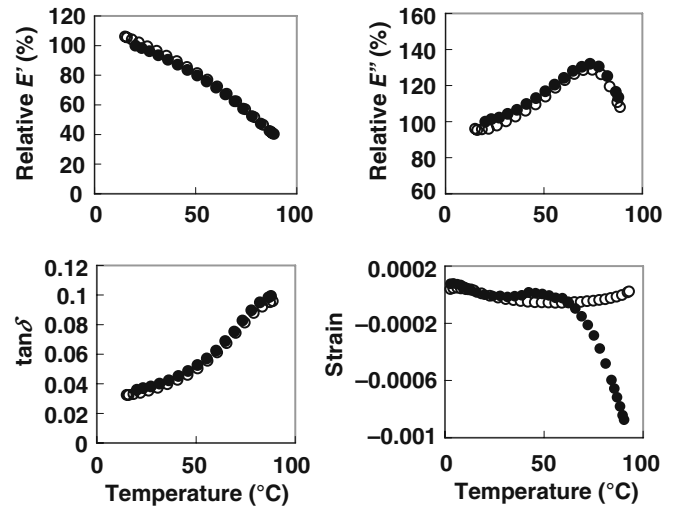


Fig. 6. Influences of cooling set on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of water-swollen wood. Relative E' and E'' are relative to the values for wood with a cooling set at 20°C. Filled circles, with cooling set; open circles, without cooling set

changes in viscoelastic properties and dimensions of water-swollen wood with a cooling set and without a cooling set were measured while raising the temperature with the same specimen. The cooling set was produced by loading 60 g less than the proportional limit in the tensile direction in the heating process and in the cooling process from 90°C to 60°C, and reducing the load from 60 g to 5 g around 60°C in the cooling process just before the heating process. Specimens with and without a cooling set were compared in the heating processes with a tensile load of 5 g and the same cooling history at a cooling rate of 1.5°C/min. Figure 5 shows the measuring conditions and the heating processes for the results shown in Fig. 6.

Figure 6 shows the effects of cooling set on viscoelastic properties at 0.05 Hz and dimensional changes in the radial direction of water-swollen wood in the heating processes

with a heating rate of 1.5°C/min after pretreatment. Relative E' and relative E'' , (both relative to wood with a cooling set at 20°C) were almost the same in the heating processes between the specimens with and without a cooling set. On the other hand, the dimensions of the specimen with a cooling set decreased greatly from around 60°C in the heating process because of the reduction due to cooling set pretreatment. Thus, dimensional changes were different for the specimens with and without a cooling set.

Cooling methods used for the measurements of the specimens with and without a cooling set were exactly the same, so the difference in the viscoelastic properties and dimensional changes in the heating processes should be attributable to the difference between the specimens with and without a cooling set. From the results in Fig. 4 and Fig. 6, it is clear that the macroscopic stress due to the cooling set and localized stress in the microstructure of water-swollen wood caused by quenching are quite different. Although both stresses decrease with rising temperature, macroscopic stress due to the cooling set did not affect the viscoelastic properties of water-swollen wood so much in comparison with localized stress caused by quenching. In contrast, macroscopic stress due to the cooling set strongly affected the dimensional changes in the heating process, while localized stress in the microstructures of water-swollen wood barely affected dimensional changes in the heating process. The results shown in Fig. 4 indicate that localized stress in the microstructures of water-swollen wood due to quenching affected mechanical properties in the heating process, while external stress less than the proportional limit caused by the cooling set has no effect. Consequently, it can be concluded that a much higher localized stress resulting from instability of water-swollen wood than external stress caused by the cooling set occurred.

Conclusions

To obtain new information about microstructures of water-swollen wood in unstable states, the influence of heating history, cooling method, and cooling set on viscoelastic properties and dimensional changes between 20°C and 90°C in heating processes were studied. The main conclusions were:

- Both the viscoelastic properties and dimensional changes of water-swollen wood in the first heating process were quite different from those in the subsequent heating processes. This revealed that the molecular state of green wood around room temperature is stable and cannot return to this state if drying or heating are carried out. Heating makes the molecular state of water-swollen wood different from the stable state for green wood.
- Cooling methods greatly affected viscoelastic properties of water-swollen wood, while they hardly affected dimensional changes with rising temperature.
- Localized stress in the microstructures of water-swollen wood produced by quenching affected mechanical properties in the heating process, while external stress lower than the proportional limit caused by the cooling set had no effect. This revealed that much greater localized stress resulting from instability of water-swollen wood occurred than external stress caused by the cooling set.

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