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ORIGINAL ARTICLE

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Thermal-softening properties and cooling set of water-saturated bamboo within proportional limit

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Abstract Thermal-softening properties and cooling set of water-saturated bamboo were investigated using stress-relaxation measurements in heating and cooling processes, followed by residual deflection measurement. In the heating process, an obvious decrease in relative relaxation modulus due to thermal-softening of lignin was found at around 60°C. On the other hand, no clear change in the relative relaxation modulus was recognized in the cooling process. After the cooling process, about 65% and 75% of residual set was measured when the specimen was loaded on the epidermis and endodermis side, respectively. Also, residual set depended on the maximum temperature reached in the heating process and the unloaded temperature in the cooling process. From these results, it was deduced that the glass transition of lignin from the rubbery to glassy state is important to fix the deformation. Comparing thermal-softening behavior between bamboo and wood, the relative relaxation modulus of wood decreased steeply at higher temperatures than for bamboo. On the other hand, while about 75% of residual set was also found for wood, almost the same as for bamboo, the recovery of deformation with time was larger for wood than for bamboo.

Key words Bamboo · Plastic working · Cooling set · Thermal-softening property

Introduction

Recently, the utilization of not only wood but also bamboo has been increasingly required; however, the practical plastic working of bamboo requires skilled craftsman. Although the morphological,[1–4] viscoelastic,[5–7] physical,[8] and mechanical[9] properties of bamboo have been reported, few investigations from the viewpoint of plastic working of bamboo have been found, except a report by Mori.[10]

In the practical plastic working of bamboo, there are traditional techniques used by skilled craftsman to straighten bamboo by loading with heating and cooling.[11] Generally, for fixing wood deformation, controlling temperature and moisture content is essential. Drying set has been studied by Norimoto and Gril[12] and Iida et al.[13] in relation to the plastic working of wood. Summarizing their interpretation on the mechanism of drying set, it is explained in terms of the elastic deformation of microfibrils composed of cellulose, and the irreversible changes between the glassy and rubbery states of the matrix composed of lignin and hemicelluloses. Namely, the removal of water molecules due to drying induces the reformation of hydrogen bonds between the molecules of the matrix constituents. Together with the temperature decrease, this process leads to a return to the glassy state, in which elastic deformation of the microfibrils and the matrix are frozen. On the other hand, in the straightening of bamboo by craftsman, it has been generally considered that the cooling process is essential to fix the deformation.[8] Although both bamboo and wood are classified as wooden resources, it is scientifically interesting why the actual working methods between wood and bamboo are so different.

In this study, to obtain fundamental knowledge about the plastic working of bamboo, we first investigated thermal-softening properties within the proportional limit and residual deflection appearing after heating and cooling processes that are used in straightening work by craftsman. Furthermore, the effects of age and culm height on thermal-softening properties and cooling set were investigated because it has been reported that some characteristics, like chemical constituents and mechanical properties, changes with age and culm height.[3] In addition, the thermal-softening properties and cooling set of wood were compared with those of bamboo.

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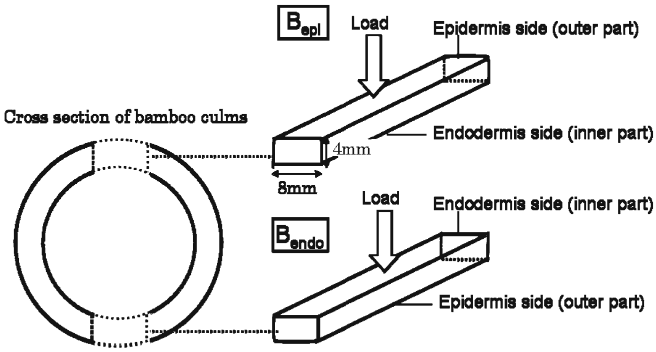

Fig. 1. Bamboo specimens used in this experiment and loading method. B_{end} and B_{epi} designate bamboo specimens loaded on the endodermis and epidermis side, respectively

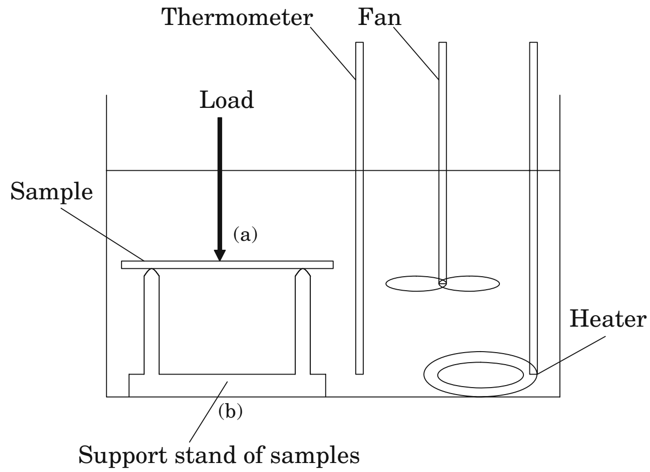

Fig. 2. Apparatus for stress-relaxation measurement under bending with elevating and lowering temperature. Top of the crosshead was 2.4 mm in curvature radius (*a*). The support stand was made of stainless steel (*b*)

Materials and methods

Materials

For bamboo samples, madake (*Phyllostachys bambusoides*) from Oita, felled in November, was used in this study. To investigate the effect of age, 1-, 3-, 4-, 5-, and 7-year-old bamboos taken from culm height of 3400–4400 mm were used. To investigate the effect of culm height from the ground, four internodes of 400–1400, 1400–2400, 2400–3400, and 3400–4400 mm culm height were used from 4-year-old bamboo. Oily components adhering to the outer surface of culms were removed by boiling (including 0.05% NaOH).[14] Wood samples were obtained from the outer part of heartwood with straight grain in a log of Japanese cypress (hinoki: *Chamaecyparis obtusa*). For both bamboo and wood, the dimensions of the specimen were 130 mm (longitudinal direction, L) × 8 mm (tangential direction, T) × 4 mm (radial direction, R), as shown in Fig. 1 (sample B_{end} and B_{epi} denote loading on the endodermis and epidermis side, respectively). The inner side of the bamboo culm was flattened, but the outer side was not flattened because it was considered that removing the outer layer would seriously influence the mechanical properties of bamboo. Moreover, the epidermis side of bamboo is important for plastic working or practical utilization of bamboo. Samples were oven-dried and then saturated with water by boiling.

Measurements

Thermal-softening properties and cooling set

Stress relaxation when elevating and lowering the temperature in water was measured. Figure 2 shows the apparatus used in this experiment. The specimen was supported on a stand with a span of 80 mm, and the initial deflection (= 1 mm within proportional limits) was applied to the center of the span at 20°C (= $T_{initial}$). Then the load necessary to keep the initial deflection was followed using a material testing instrument (Toyo Measuring Instruments, Tensilon UTM-4 L). In considering the effect of time-dependent stress relaxation, 30 min after loading when the decreasing ratio of the relaxation modulus at 20°C was almost constant, the water temperature was elevated to 90°C at a rate of 1°C/min (heating process). In the cooling process, the temperature was lowered stepwise by exchanging the water, and, finally, the temperature was lowered to 20°C. After the cooling process, the specimen was unloaded and the residual deflection was read from the chart. The residual set ratio was defined as the percentage of residual deflection to the initial deflection. In this study, it was necessary to allow for the influence of the thermal expansion of the support stand (stainless steel) on the deflection of samples. The thermal expansion coefficient of the support stand was measured using a laser displacement sensor prior to the above-mentioned experiments. The result was about 1.82×10^{-5}°C^{-1}. This value almost corresponded with the general thermal expansion coefficient of stainless steel (1.0–2.0×10^{-5}°C^{-1}), and all deflections to calculate the relaxation modulus and residual set ratio were revised using this value.

After the removal of loading, recovery of the deformation with time was followed without moving the set specimen. Also, in this case, residual deflection was read from the chart at predetermined periods after the removal of loading.

Effects of maximum and unloaded temperature on cooling set

The effects of T_{max} (maximum temperature reached in the heating process) and T_{fin} (temperature at which the specimen was unloaded during the cooling process) were examined by the following methods (A) and (B), respectively: (A) starting temperature in the heating process and T_{fin} were 20°C, and T_{max} was controlled at 30°, 40°, 50°, 60°, 70°, 80°, and 90°C; (B) starting temperature and T_{max} in the

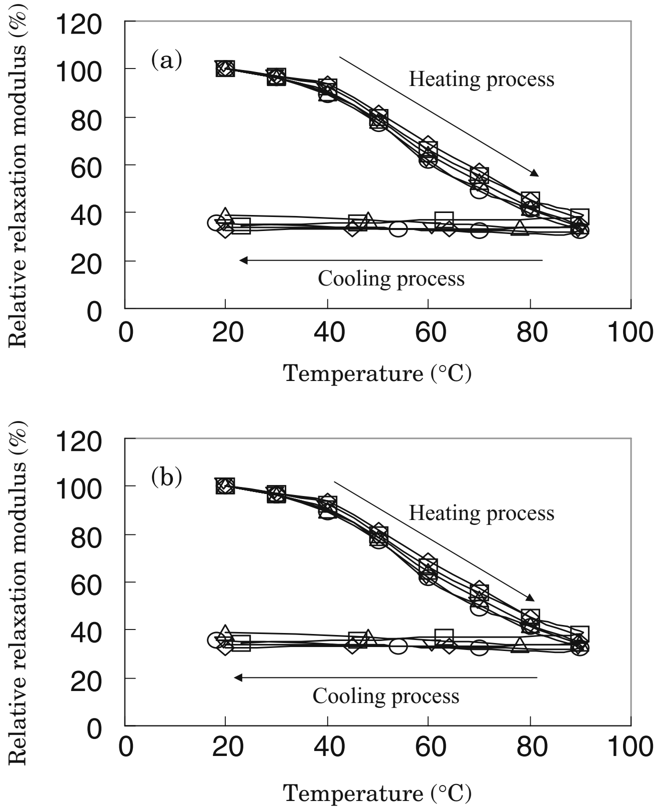

Fig. 3a, b. Effect of bamboo age on thermal-softening properties in heating and cooling processes. **a** Loaded on the epidermis side; **b** loaded on the endodermis side. *Diamonds*, 1 year, *squares*, 3 years; *triangles*, 4 years; *crosses*, 5 years; *circles*, 7 years

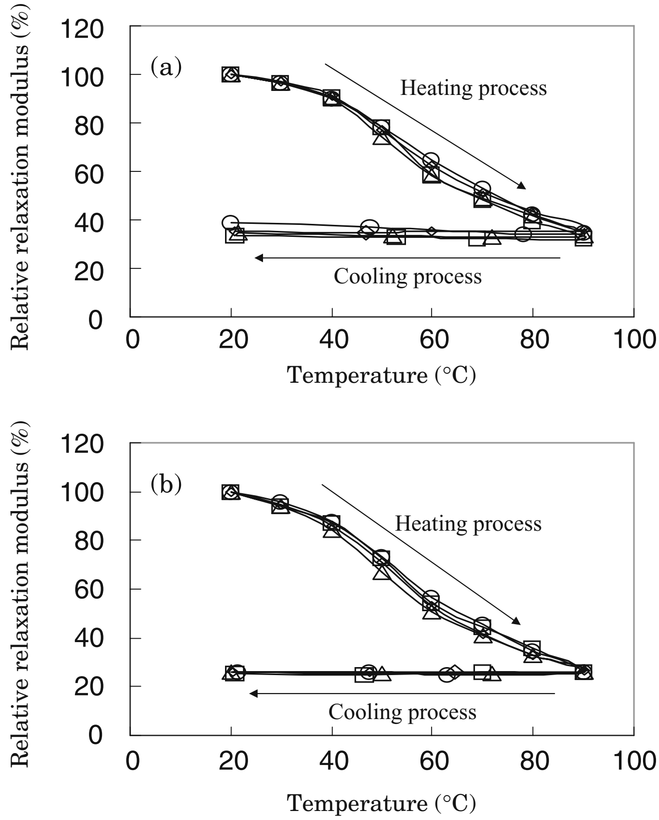

Fig. 4a, b. Effect of culm height from the ground on thermal-softening property. **a** Loaded on the epidermis side; **b** loaded on the endodermis side. *Diamonds*, 400–1400 mm; *squares*, 1400–2400 mm; *triangles*, 2400–3400 mm; *circles*, 3400–4400 mm

heating process were 20°C and 90°C, respectively, and T_{fin} was controlled at 30°, 40°, 50°, 60°, 70°, 80°, and 90°C.

Results and discussion

Thermal-softening properties and cooling set of bamboo

Figures 3 and 4 show stress-relaxation curves in the heating and cooling processes of bamboo. The effect of age is indicated in Fig. 3, and the effect of culm heights is shown in Fig. 4. In the heating process, for both Figs. 3 and 4, the relative relaxation modulus decreased with increasing temperature regardless of B_{end} or B_{epi}. The relative relaxation modulus of B_{end} and B_{epi} decreased to 25% and 35% at 90°C, respectively. In particular, remarkable decreases in relative relaxation moduli were recognized at around 60°C. Mechanical relaxation in this temperature range under wet conditions is known to be caused by thermal softening of wood lignin.[15–17] Considering that the lignin content of mature bamboo is almost identical to that of wood,[18] these remarkable decreases in relative relaxation moduli were caused by thermal softening due to the micro-Brownian motion of lignin. The steep decrease of elasticity moduli around this temperature and the interpretation almost corresponded with the investigation by Furuta et al.[19] using moso bamboo. However, it should be noted that the shape of the curve changes slightly with heating rate, partially because the decrease of relaxation modulus in this result also includes time-dependent stress relaxation.

On the other hand, no clear change in the relative relaxation modulus was recognized in the cooling process. Similar behaviors were also found by Iida et al.[20,21] They simulated their results with lower elastic moduli and higher fluidities in the cooling process than those at the same temperatures in the heating process. They concluded that the difference in relaxation modulus between the heating process and the cooling process resulted from an unstable state induced in the cooling process after the heating process.

For behavior in heating and cooling processes as a whole, no characteristic trend with age and culm height on thermal-softening properties was found in Figs. 3 and 4. However, it has been reported that rapid changes in chemical constituents or crystallinity occur in the early stages of the growing process, and, moreover, mechanical and physical properties and anatomical characteristics also change with growth.[3]

On the other hand, comparing thermal-softening behavior between B_{end} and B_{epi} in Fig. 5, a larger decrease in relative relaxation modulus in the heating process was found for B_{end}. This difference in thermal-softening behavior between B_{end} and B_{epi} was shown regardless of age and culm height, and considered to be due to the tissue; however, the detailed mechanism has not been clarified at this stage.

After the stress-relaxation measurement in heating and cooling processes, about 75% and 65% of residual deflection was recognized for B_{end} and B_{epi}, respectively. Because the specimen had been in water, it was water-saturated during this experiment, and this fixation of the deformation included no drying set. We named this fixation of the deformation due to temperature change as the cooling set. The results of the residual set measurement for each age and culm height are shown in Table 1. As indicated in Table 1, no clear effect of age and culm height on cooling set was found; that is, regardless of culm age and height, the residual set ratio was about 65% for B_{end} and 75% for B_{epi}. The effect of culm age and height on the set ratio is interesting in relation to the main constituents included in each culm, so this result is discussed in more detail later in the article (effect of temperature). On the other hand, clear differences between B_{end} and B_{epi} for cooling set (such as thermal-softening behavior) were found; that is, a larger set ratio was recognized when the specimen was loaded on the endodermis side. The primary tissue of bamboo culms consists of parenchyma cells, with embedded vascular bundles composed of metaxylem vessels. Moreover, across the culm wall, the percentage of fiber generally decreases from the outside to the inside.[1,2] Considering differences in the mechanical properties between parenchyma cells and vascular bundles,[9] it was deduced that different stress distributions were generated for B_{end} and B_{epi} in bending. In other words, it was deduced that the differences of the residual set ratio between B_{end} and B_{epi} are due to the tissue. This relation should be investigated in more detail in the near future. As described above, no significant influence of age and culm height from the ground was found for both thermal-softening properties and residual set, so 4-year-old bamboo (3400–4400 mm from the ground) was used in the following investigation.

Effect of temperature on cooling set

Thermal-softening behaviors with different maximum temperatures in the heating process are shown in Fig. 6. As described in the previous section, no clear changes in the relative relaxation modulus in the cooling process was found when the T_{max} was 90°C; however, as a noteworthy result, clear differences in the slope in the cooling process were found in Fig. 6. This means that small increases in the relative relaxation modulus were recognized in the cooling processes after heating above 60°C, while the relative relaxation modulus increased clearly by lowering the temperature when the T_{max} was below 60°C. With the relative relaxation modulus being a measure of the repulsion force, the result mentioned above suggests that a larger part of the elastic recovery potential was frozen during the cooling processes after heating to temperatures above 60°C. This

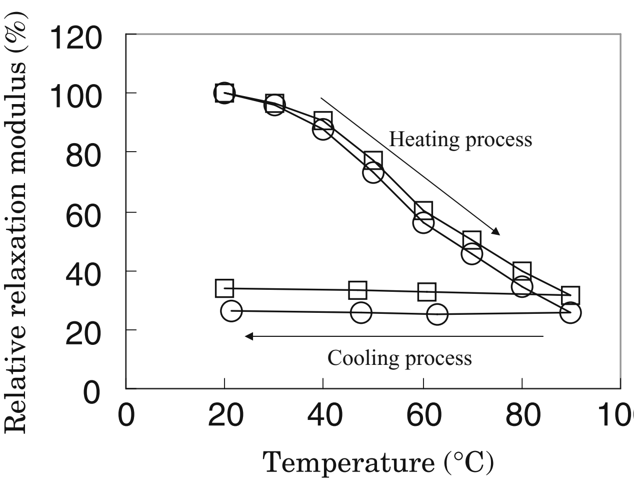

Fig. 5. Comparison of B_{end} (*circles*) and B_{epi} (*squares*) for thermal-softening properties. For both B_{end} and B_{epi}, 4-year-old bamboo specimens from 3400–4400 mm were used

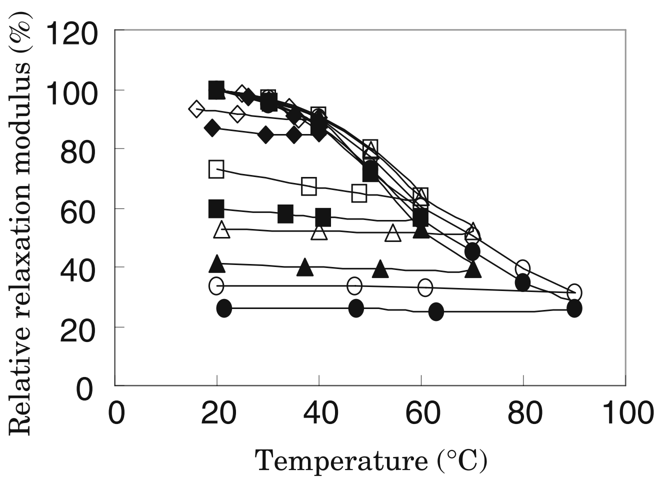

Fig. 6. Effect of T_{max} on thermal-softening property. Specimens were loaded on the epidermis (*open symbols*) and endodermis (*solid symbols*) sides. Maximum temperature: *squares*, 40°C; *crosses*, 60°C; *triangles*, 70°C; *circles*, 90°C

Table 1. Average values of residual set ratio

Sample	Culm height (mm)				Age (years)				
	400–1400	1400–2400	2400–3400	3400–4400	1	3	4	5	7
B_{epi}	63.91 (3.38)	65.73 (2.70)	64.73 (3.24)	62.11 (0.35)	65.94 (3.84)	66.22 (0.56)	62.11 (0.35)	62.11 (3.33)	62.60 (1.51)
B_{end}	74.11 (1.54)	72.94 (2.42)	72.08 (1.66)	75.35 (1.62)	73.78 (3.18)	74.56 (1.23)	75.35 (1.62)	73.68 (0.87)	72.79 (1.81)

Values are averages of three samples for each condition; standard deviations are shown in parentheses
B_{epi}, sample loaded on the epidermis side; B_{end}, sample loaded on the endodermis side

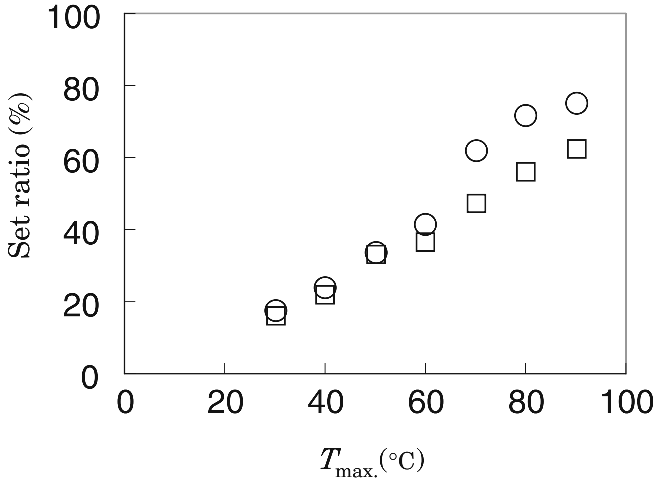

Fig. 7. Effect of T_{max} in the heating process on cooling set. Specimens were loaded on the epidermis side (*squares*), and endodermis side (*circles*)

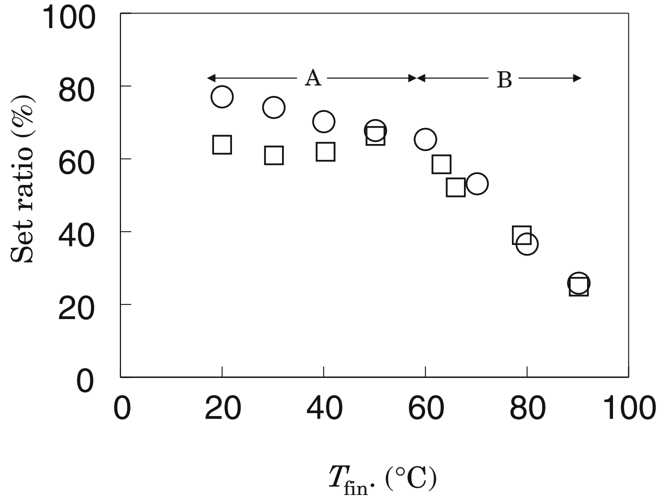

Fig. 8. Relationship between residual set ratio and T_{fin}. Specimens were loaded on the epidermis side (*squares*), and endodermis side (*circles*). *A*, plateau region; *B*, steep slope region

means that lignin was fixed in a new conformation deformed by heating.

Figure 7 shows the effect of T_{max} on residual set. In this examination, T_{fin} was 20°C. In Fig. 7, the residual set ratio increased with increasing T_{max} in the heating process for both B_{end} and B_{epi}. According to the results in Figs. 6 and 7, heating bamboo over the glass transition temperature is quite important to fix the deformation of bamboo; moreover, this is important in connection with the fixation mechanism of the deformation by cooling set. The fact that a difference in the increasing rate of the set ratio with T_{max} between B_{end} and B_{epi} was found regardless of the same initial deflection is also interesting in connection with the characteristic tissue of bamboo. The cooling set for bamboo is mainly related to thermal softening due to micro-Brownian motion of lignin; however, the effects of other factors such as tissue should also be investigated in the future.

Figure 8 indicates the effect of the temperature at which the specimen was unloaded during the cooling process on the residual set. In this examination, T_{max} was controlled at 90°C, and T_{fin} was changed. In Fig. 8, two regions with different slopes should be noted: a plateau region (A) and a steep slope region (B). In the steep slope region, in particular, little residual set was found when the specimen was unloaded at 90°C with no cooling process. Under such high temperature, lignin is still in the rubber state, or there is little restriction of the elastic recovery of cellulose microfibrils; accordingly, most of the bending deformation recovered by unloading. This means that lowering the temperature is important to fix the deformation of bamboo. On the other hand, in the plateau slope region, in the case of T_{fin} below 60°C, no large change in the set ratio was seen. This temperature corresponds well to the steep decrease of the relative relaxation modulus in the heating process and the slight increases in the relative relaxation modulus in the cooling process when the maximum temperature was below 60°C. These results showing the effects of T_{max} and T_{fin} suggest that the cooling set of bamboo is closely related to the thermal-softening properties of lignin; moreover, freezing micro-Brownian motion by lowering the temperature below the glass transition temperature of lignin is important to fix their deformation. Furthermore, there are some reports in which there was no clear change of lignin contents in mature bamboo with age and little unevenness in the distribution of the main constituents among different culm heights.[3] These reports correspond well to the results obtained in this study that thermal-softening behavior and residual set ratio were not influenced by age and culm height.

Comparing bamboo and wood

In plastic working of wood, the deformation is generally considered to be fixed by drying set, as shown in compressed wood and wood bending. Iida et al.[13] indicated that complete recovery of compressed wood was not caused by only moisture treatment. In other words, this suggests that the effect of cooling set is also included in the compression set of wood. However, little investigation of the cooling set for wood has been reported, so comparing the effects of cooling on fixation of the deformation between bamboo and wood is not only important for plastic working of bamboo but also wood.

Thermal-softening properties of bamboo and wood are compared in Fig. 9, and their differential curves are shown in Fig. 10. In Fig. 9, the thermal-softening behavior of wood initially appears similar to that of bamboo, but the relative relaxation modulus for wood decreased steeply at a slightly higher temperature than that for bamboo. This is indicated more clearly in Fig. 10. As described above, it should be noted that the shape of the curve changes slightly with heating rate. Olsson and Salmen[22] showed that hardwood lignins have lower softening temperatures than softwood lignins, and explained that the difference in softening temperature was caused by differences in cross-linking between softwood and hardwood. Furuta et al.[23] deduced that the

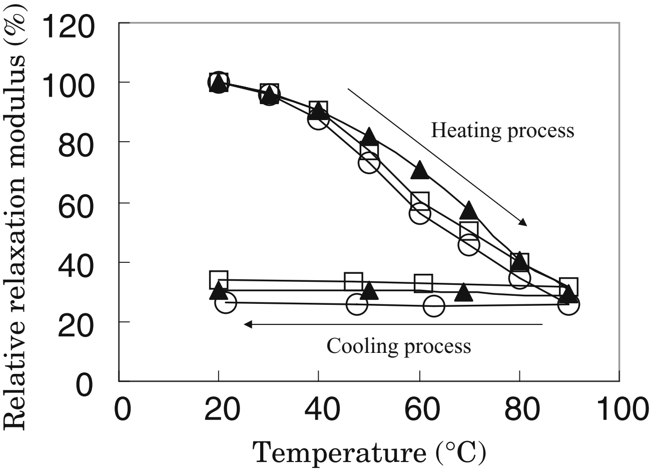

Fig. 9. Comparison of thermal-softening properties between bamboo (*open symbols*) and wood (*solid symbols*). *Squares*, epidermis side; *circles*, endodermis side; *triangles*, wood

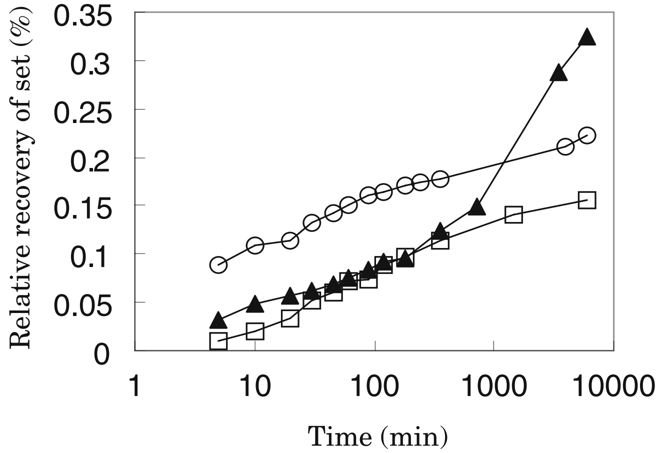

Fig. 11. Recovery of the deformation with time for bamboo (*open symbols*) and wood (*solid symbols*). *Squares*, epidermis side; *circles*, endodermis side; *triangles*, wood

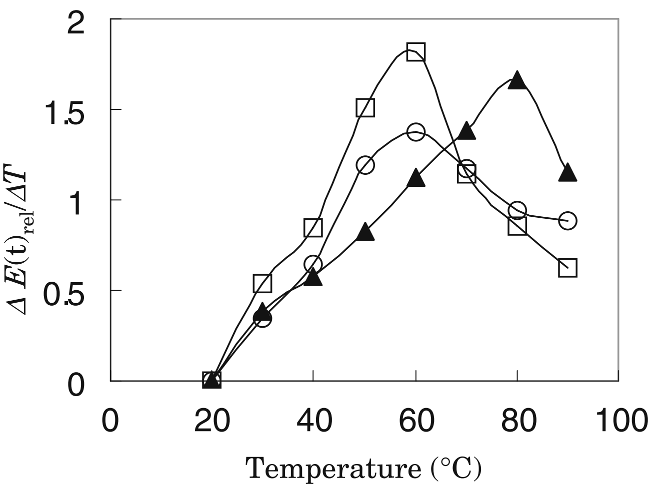

Fig. 10. Comparison of peak temperature of thermal softening between bamboo (*open symbols*) and wood (*solid symbols*). *Squares*, epidermis side; *circles*, endodermis side; *triangles*, wood; $E(\mathrm{t})_{\mathrm{rel}}$, relative relaxation modulus; T, temperature

differences in the thermal-softening temperature region between softwood and hardwood depended on the condensation levels of lignin. Under these considerations, the difference in the thermal-softening temperature between bamboo and wood is thought to be based on the differences in condensation level or degree of cross-linking for lignin. However, as described above, it should be noted that these peaks do not strictly mean thermal-softening temperature, and, moreover, other factors such as the cell wall structure between bamboo and wood[1–3] should also be investigated in the near future.

On the other hand, about 75% of residual set was recognized for wood. This value is almost the same as bamboo sample B_{end}, and, moreover, it indicates that cooling set of wood is caused by glass transition of lignin from the rubbery to the glassy state. However, as shown in Fig. 11, clear differences in recovery of the deformation with time between bamboo and wood were recognized, especially after 500 h; that is, larger recovery of deformation was found a long time after 500 h for wood, while no remarkable recovery was seen after 500 h for bamboo. It is generally considered that bamboo and wood have a time distribution for the recovery of deformation due to various factors such as tissue, cell wall structure, or chemical constituents. This result is most important to explain the differences between wood and bamboo in connection with actual plastic working. It is considered that the deformation of wood was fixed by drying, while that of bamboo was fixed by cooling set. However, the reason why the recovery behaviors are different between wood and bamboo is not clear at present, and should be investigated in more detail in the near future.

Conclusions

Thermal-softening properties and cooling set of water-saturated bamboo were investigated in comparison with wood, and the results are summarized as follows.

1. For bamboo, a steep decrease in the relative relaxation modulus due to thermal softening of lignin was found around 60°C in the heating process. On the other hand, no clear change in the relative relaxation modulus was recognized in the cooling process. After the cooling process, about 65% and 75% of residual set remained when the specimen was loaded on the epidermis and endodermis side, respectively.
2. Residual set depended on the maximum temperature reached in the heating process and the unloaded temperature in the cooling process. From these results, it was deduced that the glass transition of lignin from the rubbery to glassy state is important to fix the deformation.

3. Comparing thermal-softening behaviors between bamboo and wood, the relative relaxation modulus of wood decreased steeply at a higher temperature than for bamboo, and 75% of residual set of wood similar to bamboo was found after the cooling process. However, the recovery of the deformation after a long period was larger in wood than in bamboo.

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