

ORIGINAL ARTICLE

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The effect of lignin on the bending properties and fixation by cooling of wood

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Abstract To clarify the effects of lignin on the fixation of bending deformation by cooling, cooling set for delignified woods with various lignin residues were investigated to compare with mechanical and dynamic viscoelastic properties. Bending tests showed that steep reductions occurred in the modulus of elasticity and modulus of rupture with delignification during the initial stage of delignification. The dynamic viscoelastic measurements revealed that the peak temperature of $\tan \delta$ due to micro-Brownian motion of lignin was reduced with delignification, and the peak disappeared in the temperature range of 5°–100°C for the specimens that had lost more than 21% of their weight. On the other hand, no clear change in residual set was found in the range of 0%–15% of weight loss in spite of a marked reduction in lignin content. Subsequently, set decreased steeply for the specimens delignified beyond 15% of weight loss. It was suggested that cooling set is not determined solely by lignin content but is influenced by changes in the quality of lignin due to delignification. Lignin quality affects the balance of the elastic potential to recover from deformation and its viscosity, which is an indication of resistance against flow.

Key words Lignin · Plastic working · Cooling set · Thermal softening · Delignification

Introduction

Thermal softening of wood has been studied in connection with plastic working and pulping.^{1–4} In our previous studies,^{5–7} a close relationship between cooling set and the thermal softening of lignin was found for bamboo from stress-relaxation measurements during heating from 20° to 90°C and from thermal-recovery measurements for the cooling set in this temperature range. This suggests that cooling set is principally caused by freezing of the micro-Brownian motion of lignin caused by lowering the temperature below the thermal-softening temperature before unloading. Furthermore, cooling set was also seen in wood although there were some differences in the level of set, probably resulting from differences in the higher order structures of wood and bamboo.⁶ In any event, it can be considered that lignin is an important factor for cooling set, but the details of the mechanisms of cooling set have not been clarified.

To obtain new information regarding the effect of lignin on cooling set, delignification is an effective method. Some properties of delignified wood such as change in quality of lignin and thermal-softening temperature have been reported. Minato et al.⁸ investigated the acetylation of woods that were delignified to different levels and found that the apparent activation energy of acetylation decreased up to moderate delignification and subsequently increased with further delignification. From this result, they suggested that during the delignification process, the remaining lignin may change to some complicated chemical and/or physical structure, that is, a qualitative change of lignin. A similar trend was seen for a reaction using vaporous formaldehyde.⁹ Fushitani¹⁰ examined the temperature dependence of stress relaxation of delignified hinoki (Japanese cypress, *Chamaecyparis obtusa*), and a decrease in the relaxation modulus at 35°–40°C was found. Furuta et al.¹¹ investigated the thermal-softening properties of delignified wood, and they showed that no clear peak of $\tan \delta$ in the range of 5°–100°C was found for wet delignified wood. In contrast, nondelignified wood showed an obvious $\tan \delta$ peak in this temperature range.¹¹ Thus, it can be considered that delig-

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nification causes drastic changes in the thermal-softening properties of wood. Wang et al.¹² measured weight loss with delignification for block specimens of different thickness (longitudinal direction; below 4 mm), and revealed that lignin was uniformly eliminated throughout a block of wood by a modified version of Klauditz's method (45°C, less than 72 h). Furthermore, they showed the relationship between weight loss by delignification and lignin residue in the specimen after delignification and suggested that the residual amount of lignin could be controlled by varying the reaction duration.¹² Whiting and Goring¹³ reported that the topochemical effect, such as the difference in the delignification rate between the secondary wall and middle lamella tissue, was small for acid-chlorite pulping. According to the above results, it is possible to obtain delignified wood with various lignin residues and uniformity on some level, and, moreover, investigate the relationship between the thermal-softening properties of lignin and cooling set in more detail. In this study, delignified woods with various amounts of lignin residue were employed to clarify the effects of lignin on cooling set, and their dynamic viscoelastic properties, bending properties, and the residual set caused by cooling were investigated.

Materials and methods

Materials

The specimens used for the bending test and residual set measurement are shown in Fig. 1. Cross-sectional wood specimens were cut successively in the longitudinal direction around the outer region of the heartwood with a straight grain from a log of hinoki (Japanese cypress *Chamaecyparis obtusa*). This was because the mechanical properties of wood are most characteristically represented in the longitudinal direction. The dimensions of the specimens used for the bending test were: 120 mm (radial direction, R) × 15 mm (tangential direction, T) × 4 mm (longitudinal direction, L). The specimens for the dynamic viscoelastic measurement were cut similarly, and their dimensions were 1.0 mm (L) × 1.5 mm (T) × 40 mm (R). All specimens were extracted with hot water for 3 h and with ethanol–benzene mixture (1:2 v/v) for 8 h, followed by ethanol for 8 h.

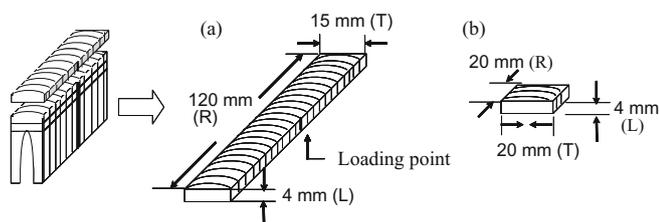


Fig. 1a, b. The shape of specimens used for **a** the bending test and residual set measurements, and **b** weight loss measurement after delignification

Delignification

To eliminate the lignin from the specimens for the bending test (4 mm thickness) and those for the dynamic viscoelastic measurement (1 mm thickness), Klauditz's method was employed: 4% acidified sodium chlorite solution was impregnated into the specimens under vacuum and the specimens were treated at 45°C for 0, 4, 14, 24, 32, 48, 72, or 120 h. The specimens used for weight-loss measurement are also shown in Fig. 1. According to Wang et al.,¹² uniformly delignified wood with various lignin contents can be obtained by this treatment, and, moreover, the influence of the thickness (i.e., fiber length direction) of specimens on the elimination of lignin is almost negligible.

Measurements

Bending test

A material testing instrument (Toyo Measuring Instruments, Tensilon UTM-4L) was used. The specimen was supported on a stand with an 80-mm span in water at 20°C.

Residual set measurement

The same apparatus used in the bending test was employed for residual set measurement. As described in our previous study,⁵ constant deflection within proportional limits was applied to the center of the span. Then the water temperature was elevated to 90°C at a rate of 1°C/min and was successively annealed to 20°C without unloading. After the cooling process, the specimen was unloaded, and then the residual deflection was read from a chart. It should be noted that the deformation fixed by cooling reduces with time after unloading, and the residual deformation is characteristic of the value measured after a long period. For example, in our previous study,⁷ it was found that the residual set measured at 6000 min after unloading (Set_{6000}) was quite different between parenchyma-rich bamboo and fiber-rich bamboo, although that measured immediately after unloading (Set_0) was almost the same for both specimens. Considering this, representative data for Set_{6000} were employed for the following discussion and the set ratio was defined as the percentage of residual deflection measured at 6000 min after unloading to the applied initial deflection.

Dynamic viscoelastic measurement

The temperature dependence of the dynamic elastic modulus (E') and loss modulus (E'') in the radial direction 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 5°–100°C for water-saturated specimens at a rate of 1°C/min. The frequencies for the measurement were 0.05, 0.5, 1, 5, and 10 Hz; the span was

20 mm in the radial direction; and the displacement amplitude was 5 μm .

Results and discussion

Delignification

Figure 2 shows how the weight loss varied with reaction time. A steep decrease in the weight was seen in the early stage of the reaction, and the values leveled off at around 30% weight loss after 72 h. Wang et al.¹² showed that the residual amount of lignin decreased more steeply than indicated by the weight loss of the specimens in the initial stage of delignification. This result indicates that some lignin that was decomposed by delignification remained in the specimens and was not detected in the determination of lignin contents.

The specimens with a weight loss of around 30% that had a little defect (deformation or fragmentation) due to intensive removal of lignin were excluded. On the other hand, it is doubtful whether intensively delignified specimens could keep the structure of original wood even if the specimens did not cause isolations. However, it is thought that these specimens are informative in this study because the data is essential to investigate the role of the lignin for the occurrence of cooling set. Therefore, the data for the specimens that did not cause isolations in spite of intensive delignification were used in the following discussions.

Bending test

The load–deflection diagram at 20°C for the water-saturated woods that had been delignified to various levels or left untreated is shown in Fig. 3. The effects of the delignification on the modulus of elasticity (MOE), modulus of rupture (MOR), and breaking strain are shown in Fig. 4. As shown in Figs. 3 and 4, the MOE and MOR did not decrease

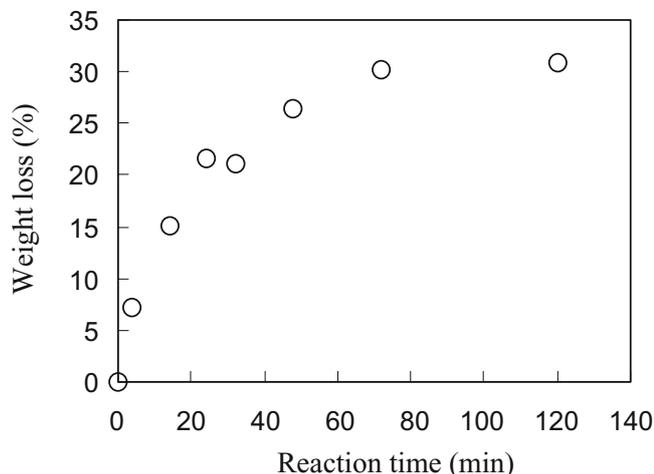


Fig. 2. The relationship between reaction time and weight loss due to delignification by Klaudivitz's method at 45°C

linearly. Also, they decreased more steeply in the early stage of the reaction than lignin content with weight loss, as determined by Wang et al.¹²

It is known that lignin in water-saturated wood is in a glassy state at around room temperature and that the mechanical properties of wood in the radial direction depend not only on the quantity but also the quality of lignin.^{14,15} Hence, the steep decreases in MOE and MOR suggest that the decomposition of lignin in the early stage influenced the rigidity and strength of the wood.

On the other hand, Fig. 4c shows that the breaking strain increased with delignification up to 26% weight loss and then decreased. As described above, it is considered that the increase in breaking strain with delignification is due to the elimination of glassy lignin, that is, an increase in fluidity due to plasticizing at room temperature. The brittle nature induced by the glassy state was therefore modified. For the specimens delignified with a weight loss of more than 26%, it is considered that the decrease in breaking strain was caused by a reduction in cohesive power in the intercellular lamella brought about by intensive delignification. In any event, the above results show that the effects of delignification on the mechanical properties of wood in the radial direction are quite different at each reaction stage.

Dynamic viscoelastic properties

Figure 5 shows temperature dispersion curves for E' , E'' , and $\tan \delta$ at 1 Hz for delignified wood after various amounts of delignification as well as for untreated wood. The frequency was selected because the most noiseless patterns were obtained at 1 Hz among the frequencies measured, although similar trends were seen for all frequencies.

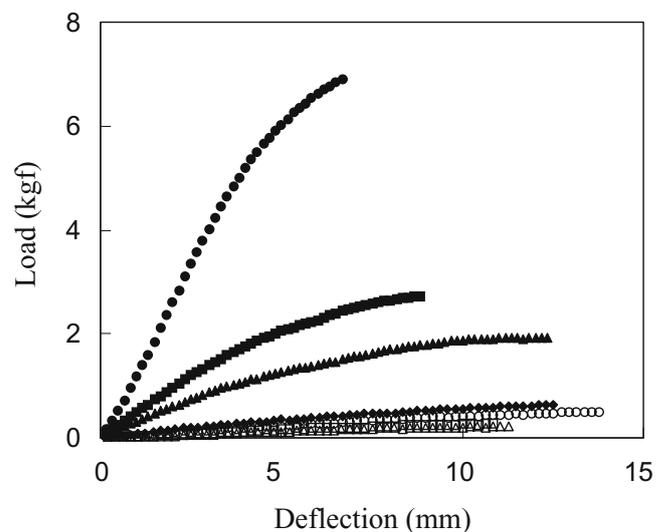


Fig. 3. Load–deflection diagram for water-saturated wood delignified to various levels and untreated wood at 20°C. *Filled circles*, untreated; *filled squares*, 7.2% weight loss (reacted for 4 h); *filled diamonds*, 15.2% (14 h); *filled diamonds*, 21.6% (24 h); *open circles*, 21.1% (32 h); *open squares*, 26.5% (48 h); *open triangles*, 30.2% (72 h)

Fig. 4a–c. Variation in **a** modulus of elasticity (*MOE*), **b** modulus of rupture (*MOR*), and **c** breaking strain with delignification at 20°C

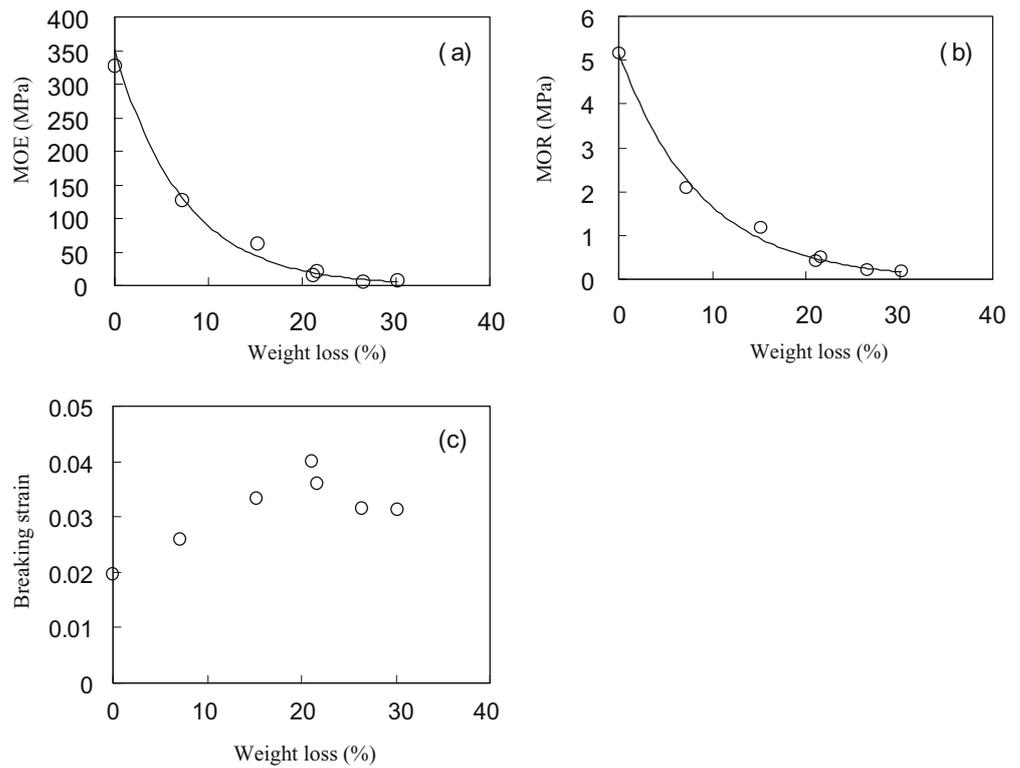
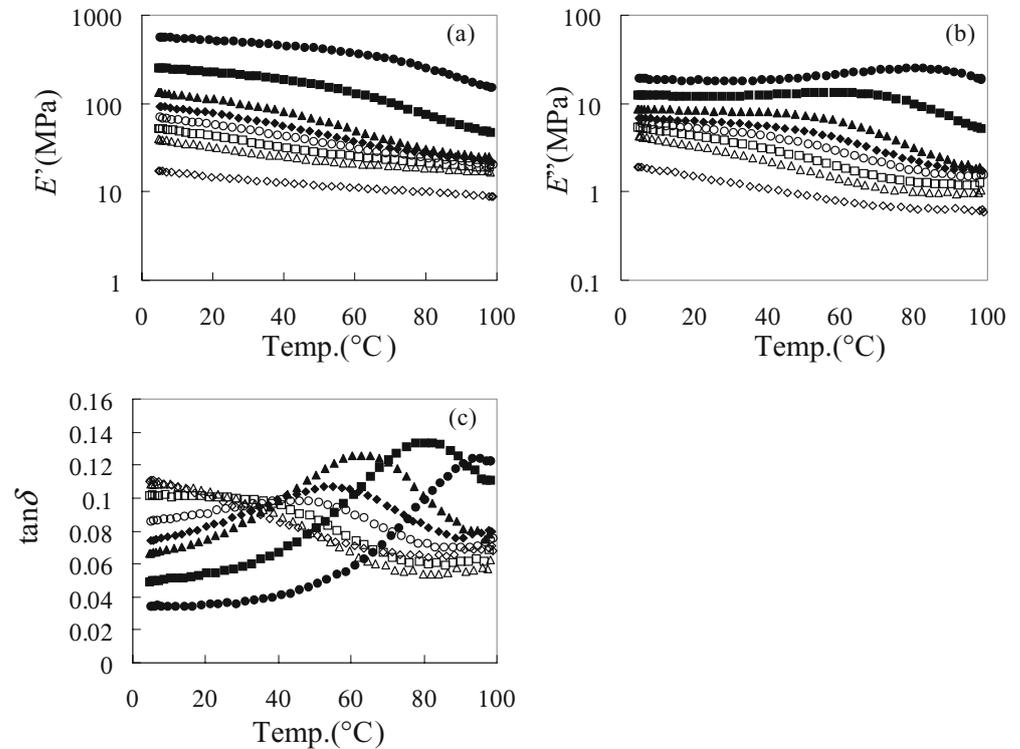


Fig. 5a–c. Temperature dispersion of **a** E' , **b** E'' , and **c** $\tan \delta$ at 0.05 Hz for water-saturated wood delignified to various levels and untreated wood. Symbols are as defined for Fig. 3



E' at room temperature decreased with delignification, and marked decreases in E' were similarly found in the early stage of the reaction as seen in Figs. 3 and 4. Furthermore, a steep decrease in E' at room temperature was found for the specimen at the latest stage of reaction. E' also

decreased with heating, and the temperature ranges that showed the steep decrease in E' varied with delignification level.

E'' had the peaks up to 7.2% of weight loss, and then decreased with temperature without a peak for the speci-

mens delignified above 15.2% of weight loss. E'' at around room temperature also markedly decreased with delignification in the early and latest stage of the reaction.

The peak of $\tan \delta$, which is attributable to the thermal softening of lignin, was detected for delignified wood up to 20% of weight loss. The peak temperature gradually decreased and the shape of the peak became broader as delignification progressed, before the peak finally disappeared after more than 20% of weight loss. The disappearance of the peak for the intensively delignified wood corresponds well with the results obtained by Furuta et al.¹¹ These results demonstrate that delignification causes changes in the quality of lignin, such as breakage of its three-dimensional network and/or lowering of its molecular mass. Moreover, the quality of the lignin is different at each delignification level. As mentioned in the Introduction, Fushitani¹⁰ investigated the temperature dependence of stress relaxation for delignified wood, and a decrease in the relaxation modulus at 35°–40°C was found. It can be considered that the decrease in relaxation modulus corresponds to the shift in the $\tan \delta$ peak toward lower temperatures as delignification progresses. From the dynamic viscoelastic measurements, it was clear that qualitative changes in lignin occurred and that decreases in the elastic modulus and softening occurred at room temperature with the progress of delignification.

Residual set

Figure 6 shows the relationship between weight loss and Set_{6000} (set ratio measured at 6000 min after unloading). From the results of the bending test, it can be considered that the reactions that cause the steep reductions in MOE and MOR occur in the early stage of delignification. However, as shown in Fig. 6, only a slight decrease in Set_{6000} due to delignification was found up to 15% of weight loss, and then it decreased drastically with further delignifica-

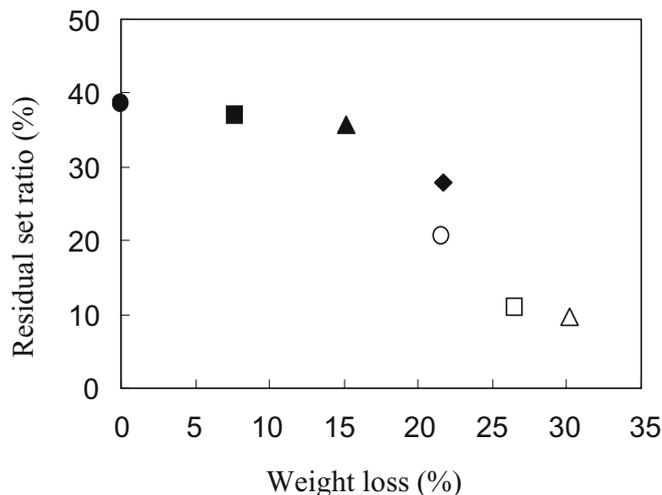


Fig. 6. Residual set (Set_{6000}) of water-saturated wood delignified to various levels and that of untreated wood. Symbols are as defined for Fig. 3

tion. This reduction in residual set suggests that cooling set is not determined only by lignin content.

In the dynamic viscoelastic measurement in the temperature range of 5°–100°C and in bending tests, $\tan \delta$ peaks due to the micro-Brownian motion of lignin were found and the mechanical properties such as MOE decreased drastically in the early stage of delignification. However, in the later stage of delignification (beyond 20% of weight loss), the $\tan \delta$ peak disappeared. This suggests that cooling set is not determined only by lignin content but also strongly depends on the glass transition due to the micro-Brownian motion of lignin.

For occurrence and maintenance of cooling set, temperature changes that induce a transition from a glassy state to a rubbery state in the heating process and from a rubbery state to a glassy state in the cooling process with loading are important. For example, the residual set ratios for 21.6% and 21.1% of weight loss are quite different in spite of the fact that their weight loss levels are almost the same. For this reason, differences in the thermal-softening behavior of the two specimens shown in the Fig. 5 are suggested (in the range of 5°–100°C). Although the weight loss of the two specimens is almost the same, the treatment time is quite different between the two specimens, and the peak temperature of $\tan \delta$ at 21.1% of weight loss is lower than that for 21.6%.

With regard to the variation in the residual set with the progress of delignification, the following consideration is applicable. When the specimen is deformed at room temperature and the temperature rises above the glass transition point, conformational changes occur in the microstructure due to breakages of hydrogen bonds and specimens deform with respect to the applied stress. Then hydrogen bonds reform at new binding positions according to the lower temperature, and so the deformation should hold; cooling set occurs. The amount of deformation retained (the residual set) is determined by a balance between elastic elements, which are a source of elastic potential to recover from the deformation, and viscous elements, which function as a resistance to recovery from the deformation. Therefore, higher fluidity gives less resistance. The fluidity should be enhanced by softening with increasing temperature and the progress of delignification in the present case. Therefore, the slight decrease in Set_{6000} due to delignification up to around 15% of weight loss, and drastic decreases with further delignification, suggest that the effect of decreases in the elastic modulus balance with decreases in resistance against flow (i.e., increases in fluidity), up to around 15% of weight loss. Thereafter, the effect of the increase in fluidity appears to exceed that of the decrease in the elastic modulus due to further delignification.

Conclusions

The cooling set of woods with various lignin contents were investigated to compare with the mechanical and dynamic viscoelastic properties of the same wood. The results were as follows:

1. The bending test showed a steep decrease in MOE and MOR with delignification in the early stage of the reaction.
2. In the dynamic viscoelastic measurement, it was found that the $\tan \delta$ peaks, which are attributable to the micro-Brownian motion of lignin, shifted in the early stage of delignification, and the peak disappeared in the temperature range of 5°–100°C for the specimens that had lost more than 21% of their weight.
3. No clear change in residual set was found for the specimens with up to 15% delignification in spite of intensive weight loss, and residual set markedly decreased for the specimens delignified beyond 15% of weight loss.

From these results, it is clear that cooling set is not determined solely by lignin contents. These results can be explained by changes in the quality of lignin due to delignification that affect the balance of the elastic potential of a particular wood to recover from the deformation and its viscosity, which is an indication of its resistance against flow.

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