



Temperature dependences of the dynamic viscoelastic properties of wood and acetylated wood swollen by water or organic liquids

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Abstract

In this study, to summarize the changes of thermal-softening behaviors of wood and acetylated wood due to differences in the kinds of swelling liquids, the following measurements were conducted. Untreated and acetylated wood samples were swollen by various liquids and the temperature dependences of the dynamic viscoelastic properties were measured after the heating and cooling histories were unified among the samples. The results obtained are as follows. Untreated samples swollen by high-polarity liquid had lower peak temperature of $\tan\delta$, however acetylated samples had higher peak temperature of $\tan\delta$ than those of untreated wood. On the other hand, untreated wood samples swollen by low-polarity liquid had higher peak temperature of $\tan\delta$, however acetylated samples had lower peak temperature of $\tan\delta$ than those of untreated wood. The amount of swelling is determined by interaction between wood and liquid due to proton-accepting power and molar volumes of liquid and so on, therefore the peak temperature of $\tan\delta$ and degree of reduction in dynamic elastic modulus (E') with increasing temperature were corresponded to the amount of swelling.

Keywords Organic liquid · Temperature dependence · Dynamic viscoelastic property · Acetylated wood · Glass transition temperature

Introduction

The mechanical properties of materials such as metals and plastics are changed by cooling rate from higher temperature and aging temperature. Some of the mechanisms of these phenomena have been determined scientifically and applied to technologies. For example, when the cooling rate in polyethylene terephthalate (PET) from molten state is too fast, arrangement of the molecules cannot transit to those in the equilibrium state. Then, PET in amorphous state has different appearance and mechanical property from those in crystalline state [1]. Therefore, the properties of a material greatly change due to structural changes in molecular level caused by quenching or annealing.

On the other hand, it has been revealed that elastic modulus decreases and fluidity increases in water-saturated wood by quenching and drying history [2–14]. The mechanism of these phenomena is considered as follows. In the case of wood placed in an environment for a long time, molecules remain in the stable state in the humidity and temperature. However, when environment changes rapidly like quenching or drying, molecule arrangements cannot follow a new environment and become in a thermodynamic unequilibrium state (unstable state). Changes in mechanical properties caused by quenching have been reported in many studies on water-saturated wood [3–10]. In these studies, elastic modulus decreased largely in some cases that wood was cooled rapidly from the temperature higher than a glass transition temperature of lignin to lower temperature [5, 11]. That is, the degree of destabilization introduced by quenching is considered to be affected by the range of cooling temperature across the glass transition temperature.

From these results, molecules of wood constituents would be in more thermodynamic unequilibrium state if the quenching treatment is carried out in the wider temperature range across the glass transition temperature of lignin. However, studies for the thermodynamic unequilibrium state of

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molecules of wood constituents generated by quenching have been conducted only for water-saturated wood [3–10]. The relationship between range of quenching temperature and destabilization of wood is not researched for the wood with higher or lower glass transition temperature of lignin than that when swollen by water. According to previous studies, the glass transition temperature of wood is largely changed by changing the kinds of swelling liquids [15] or swelling rate [16]. In addition, thermal-softening behavior is also changed by chemical treatment because molecular mobility is changed due to introduction of functional group or generation of crosslinking [17]. Therefore, it is considered that the thermal-softening behavior of wood can be changed by changing swelling liquids or conducting chemical treatment. Furthermore, it is also interesting to research the destabilization caused by quenching in each swelling condition from the viewpoint of the basic study for highly controlling of wood properties. To promote the use of wood and wood-based materials, research and development of technology should be conducted taking structural change in molecular level into consideration as with other materials.

In this study, to summarize the changes of thermal-softening behaviors of wood and acetylated wood due to differences in the kinds of swelling liquids, the following measurements were conducted. Untreated and acetylated wood samples were swollen by various liquids and the temperature dependences of the dynamic viscoelasticity of these samples with the same heating and cooling histories were measured. In particular, dynamic elastic modulus (E') and $\tan\delta$ were determined because of many previous studies in water-saturated wood. Based on these results, we will study in detail the changes of dynamic viscoelasticity immediately after quenching or in the swelling process of samples swollen by various liquids in the next report.

Materials and methods

Samples

The samples used for measurement were hinoki (*Chamaecyparis obtusa*). Blocks (40 mm in the radial direction and 3 mm in the tangential direction) were cut from almost the same growth ring band. From each block, end-grain samples with 1 mm thickness were obtained continuously in longitudinal direction. The average of the annual ring width was 0.73 mm, and there were few variations between samples. The shape of samples is shown in Fig. 1.

The samples were extracted for 9 h using methanol, then were oven-dried and impregnated with acetic anhydride under reduced pressure, and then treated for 8 h in an oil bath at 120 °C. After treatment, they were rinsed for 1 week under flowing water at room temperature,

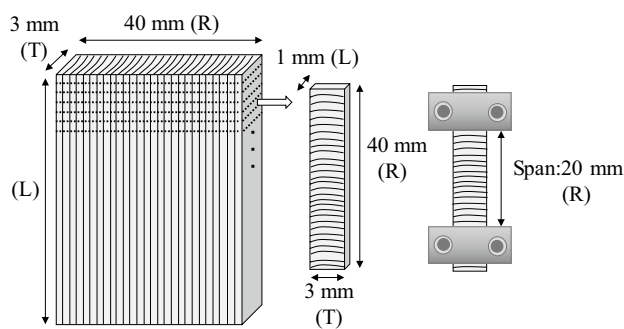


Fig. 1 The shape of samples and schematic diagram of the sample attached to the forced-vibration dynamic viscoelastometer

and oven-dried under vacuum for 40 h at 25 °C. Weight increase due to acetylation was 24%. The untreated samples were dried for 2 weeks in a desiccator with phosphorus pentoxide until constant weight, and were then oven-dried in oven for 10 h at 105 °C. To avoid moisture adsorption of the dried samples, they were immediately sealed in sample jars and impregnated with the liquids under vacuum. The sealed samples were left for 1 month or more, and subjected to dynamic viscoelasticity measurements.

Organic liquids

Distilled water and the 10 organic liquids listed in Table 1 were used. Ethanol (EtOH), 2-propanol (PrOH), 1-butanol (BuOH), acetone (Act), methyl ethyl ketone (MEK), ethylene glycol (EG), formamide (FA), and dimethyl sulfoxide (DMSO) and methanol (MeOH) and toluene (Tol) were used and basic properties for these liquids are as listed in Table 1.

Dynamic viscoelastic measurement

A forced-vibration dynamic viscoelastometer (DMS6100, Seiko Instruments, Chiba, Japan) was used. The samples swollen by the organic liquids and distilled water were measured in each liquid at a temperature range of – 20 to 95 °C. If the freezing and boiling points were within this temperature range, measurements were taken in a range of 10 °C above or below the freezing and boiling points of the liquids. The heating and cooling rate was 1 °C/min. Results were obtained in the second heating process to uniform the heating and cooling histories. The direction of load was set as tensile, and the span of 20 mm, $\pm 5 \mu\text{m}$ forced vibration was applied in the radial direction using combined waves. Results were obtained for 0.05 Hz through Fourier transform.

Table 1 Properties of the used liquids and relative swelling ratios of the wood swollen by those liquids

| | Liquids | Structural formula | Molar volumes (cm ³ /mol) | P.A.P.Δv ^a (cm ⁻¹) | H-bonding properties | C.E. ^d (cal/cm ³) | Relative swelling ^e (%) |
|---------------------|---------|--|---|--|-------------------------|--|--|
| Methanol | MeOH | CH ₃ OH | 40.7 | 187 | AD ^b | 204 | 89.7 |
| Ethanol | EtOH | C ₂ H ₅ OH | 58.5 | 187 | AD | 166 | 82.5 |
| 2-Propanol | PrOH | (CH ₃) ₂ CHOH | 75.0 | 187 | AD | 144 | 73.6 |
| 1-Butanol | BuOH | CH ₃ CH ₂ CH ₂ CH ₂ OH | 91.8 | 187 | AD | 128 | 63.0 |
| Acetone | Act | CH ₃ COCH ₃ | 74.0 | 64 | A ^c | 96 | 68.0 |
| Methyl ethyl ketone | MEK | CH ₃ CH ₂ COCH ₃ | 90.2 | 57 | A | 86 | 56.0 |
| Toluene | Tol | C ₆ H ₅ CH ₃ | 106.4 | 45 | A | 79 | 0.9 |
| Ethylene glycol | EG | HOCH ₂ CH ₂ OH | 55.8 | 206 | AD | 266 | 111.2 |
| Formamide | FA | HCONH ₂ | 39.7 | | AD | 317 | 116.8 |
| Dimethyl sulfoxide | DMSO | (CH ₃) ₂ SO | 70.9 | 141 | A | 166 | 133.0 |
| Water | Water | H ₂ O | 18.0 | 390 | AD | 552 | 100.0 |

^aProton accepting powers : the data are cited from a table of Kagiya et al. [18], Crowley and others [19] and Ishimaru and others [20].

^bLiquid having both proton-accepting and donating properties for hydrogen bonding

^cLiquid having only proton-accepting properties for hydrogen bonding

^dCohesion energy : the data are calculated from the solubility parameter values in a table by Hansen [21]

^eRelative swelling compared with that in water : the data are cited from a table of Sakai and others [22] and Ishimaru and others [23]

Results and discussion

Wood swollen by water or high swelling organic liquids

Figure 2 shows the temperature dependences of relative E' and $\tan\delta$ of wood swollen by water or high swelling

organic liquids. Relative E' represents the relative value of E' at the lowest temperature in the measured temperature range.

First, for the untreated sample swollen by water, although no clear peak for $\tan\delta$ was found within the measurement range, the behavior suggesting that $\tan\delta$ was approaching a peak at around 90 °C. For the untreated sample swollen by EG and FA, peaks for $\tan\delta$ were observed at lower

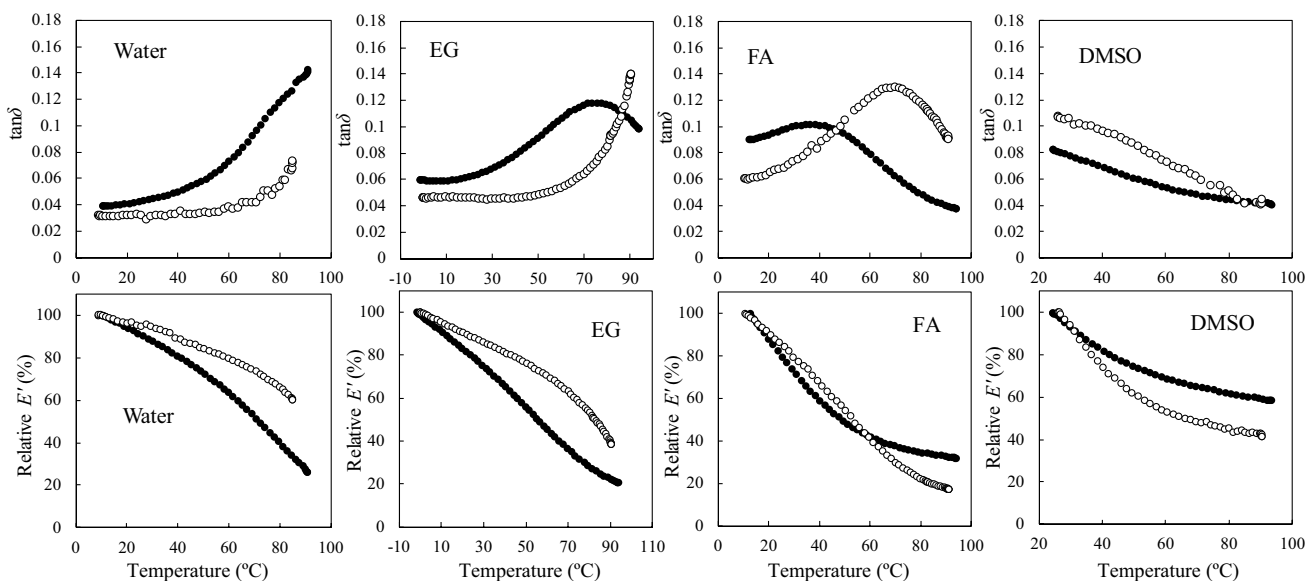


Fig. 2 Temperature dependences of relative E' and $\tan\delta$ in radial direction of untreated or acetylated hinoki swollen by water or organic liquids having high swellability. Filled circles, untreated; open circles, acetylated

temperatures than that of the sample swollen by water, and these temperatures were about 70 and 40 °C for EG and FA, respectively. The cross-sectional relative swellings of wood swollen by these liquids were 111% for EG and 117% for FA against 100% for water, so a higher swelling rate corresponds to a lower $\tan\delta$ peak temperature. Meanwhile, in the untreated sample swollen by DMSO, $\tan\delta$ decreased with increasing temperature.

According to previous studies, DMSO was adsorbed strongly to lignin in particular among the constituents of wood compared to the other organic liquids [24, 25]. In addition, cross-sectional swelling of cell wall swollen by DMSO is much larger than that by water [26]. Therefore, the bending elastic modulus and strength are both lower than those of water-saturated wood [15]. It has also been reported that when wood is delignified, the decrease in elastic modulus due to swollen by DMSO is significantly reduced as a result of untreated wood [27]. Based on these results, we interpret the condition of wood swollen by DMSO as follows.

When wood is swollen by DMSO, the DMSO is preferentially adsorbed on the adsorption sites of lignin and increasing the distance between lignin molecules. This means that the movement of the main and side chains of lignin molecules becomes less constrained, and lignin softens at a much lower temperature than that of water-saturated wood. In short, the results obtained in this study are considered to show the behavior above the peak temperature of $\tan\delta$, which is attributable to micro-brown motion of lignin. Furthermore, the absolute values of E' at the highest temperature are about 100 MPa for the untreated sample and about 50 MPa for the acetylated sample. E' had nearly reached a minimum value in both samples and so these results are considered to show the state that lignin had softened to the utmost limit.

Next, the E' of the untreated sample is discussed. It was found that a lower peak temperature for $\tan\delta$ corresponded to a lower degree of reduction in relative E' . This is thought to be because E' had already decreased greatly at the lower temperatures, and even when the temperature was increased, the reduction in E' was not promoted further.

For the acetylated sample, the temperature at which $\tan\delta$ began to increase was higher than that in the untreated sample for all of the liquids. Obataya et al. [28] reported that the swollen volume of untreated wood is larger than that of acetylated wood when those are swollen by high-polarity liquids such as EG and water. On the other hand, the swollen volume of acetylated wood is larger than that of untreated wood when those are swollen by low-polarity liquids such as Tol. In the result shown in Fig. 2, swollen by high-polarity liquids, the cause that the peak temperatures of $\tan\delta$ were shifted to the higher temperature due to acetylation is considered as follows. When the wood is acetylated, the functional groups of the constituents are hydrophobized. Then, as

the adsorbability of high-polarity liquid to wood constituents declined, the swelling ratio decreased and the wood becomes hard to soften.

Next, focusing on the E' for acetylated sample, the degree of reduction of relative E' was smaller than that for untreated sample swollen by water or EG, and the degree of reduction of relative E' was larger than that for untreated sample swollen by FA or DMSO.

Wood swollen by low-swelling organic liquids

Figure 3 shows the temperature dependences of relative E' and $\tan\delta$ for samples swollen by alcohols (MeOH, EtOH, PrOH, and BuOH), which have high hydrogen-bonding capacities and both proton-accepting and -donating ability.

Looking first at the results for untreated sample, regardless of the swelling liquids, $\tan\delta$ increased and relative E' decreased with increasing temperature. For all of the alcohols, no $\tan\delta$ peak was found within the measured temperature range, however, $\tan\delta$ increased rapidly at higher temperatures, so a $\tan\delta$ peak is considered to exist at the higher temperatures of the measured temperature range.

In the acetylated sample, for all of the swelling liquids, the temperatures at which $\tan\delta$ began to increase were shifted to lower temperature compared to untreated sample and the degree of reduction in relative E' increased with increasing temperature. Especially for samples swollen by PrOH and BuOH, $\tan\delta$ peaks appeared in the measurement temperature range, which were not observed for untreated samples. The peak temperatures differed depending on the kinds of alcohols, which were about 80 °C by PrOH and about 70 °C by BuOH. Relative E' also decreased greatly with increasing temperature for the wood swollen by PrOH and BuOH. These results show that acetylated wood swollen by alcohols softens at a lower temperature than untreated wood.

Figure 4 shows the temperature dependences of relative E' and $\tan\delta$ of sample swollen by ketones (Act, MEK) which have proton-accepting ability only and Tol which has the ability to accept protons weakly. Focusing on the results for untreated sample, regardless of the swelling liquid, the increase of $\tan\delta$ and the decrease of relative E' were also low. However, in the acetylated sample, $\tan\delta$ increased for all of the liquids. It increased slightly with increasing temperature for the sample swollen by Act, and increased slightly to a maximum and then began to decrease for the sample swollen by MEK. For the sample swollen by Tol, $\tan\delta$ showed the same behavior for both untreated and acetylated sample until 20 °C, and then for acetylated sample increased rapidly between 20 and 60 °C and reached an almost constant value. Relative E' decreased greatly for acetylated samples, regardless of the swelling liquids.

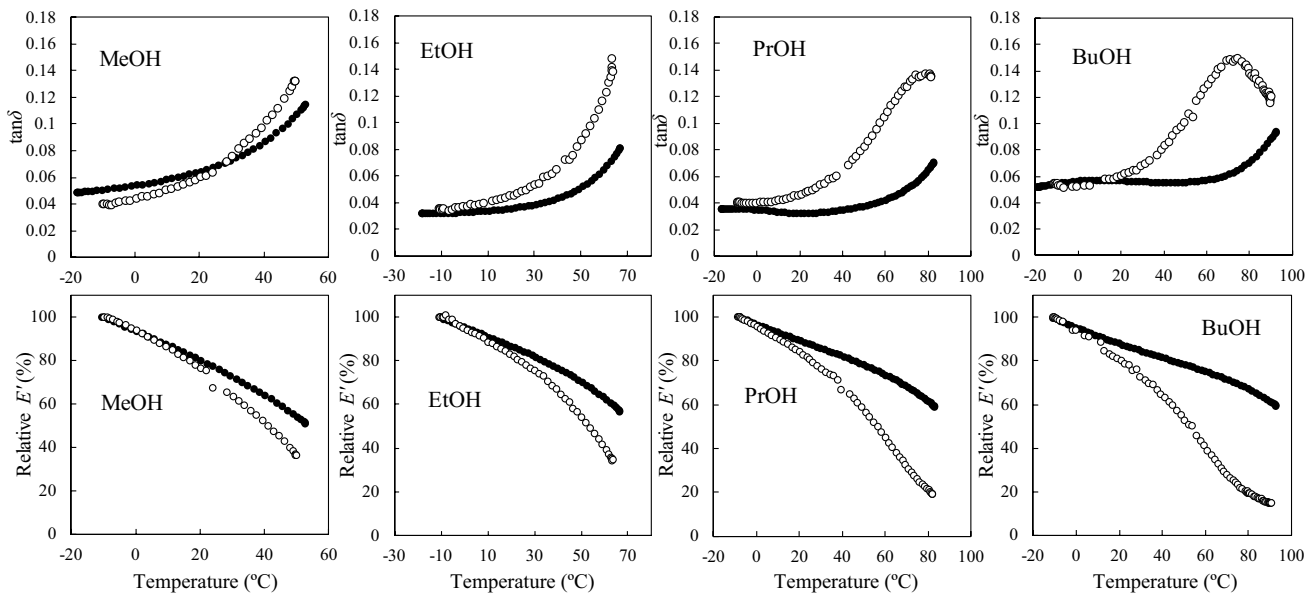


Fig. 3 Temperature dependences of relative E' and $\tan\delta$ in radial direction of untreated or acetylated hinoki swollen by alcohols. Filled circles, untreated; open circles, acetylated

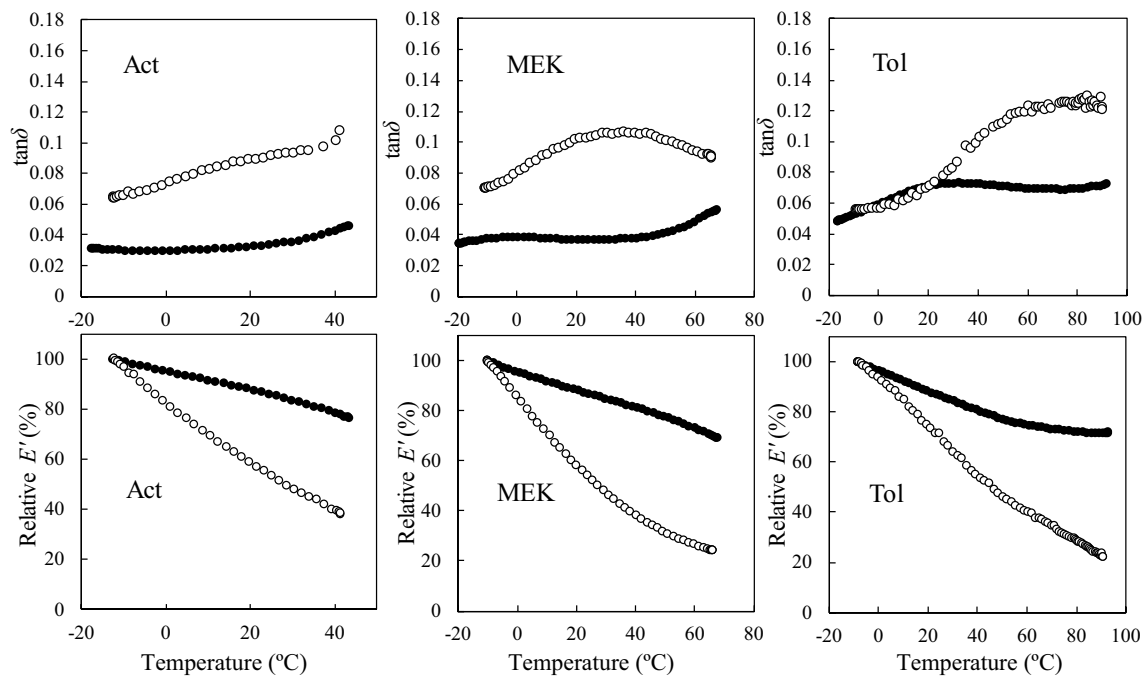


Fig. 4 Temperature dependences of relative E' and $\tan\delta$ in radial direction of untreated or acetylated hinoki swollen by organic liquid of ketone or toluene. Filled circles, untreated; open circles, acetylated

Obataya et al. [28] reported that the swollen volume of untreated wood swollen by Tol was about 5%, that in the case of acetylated wood is about 20%, and a similar tendency was found in wood swollen by Act, MeOH, EtOH, PrOH, and BuOH. The cause is considered as follows. The low-polarity acetyl groups are introduced to the wood constituents due to

acetylated treatment. Then, adsorption of non-polar liquid is facilitated and the energy required to break the internal hydrogen bonds among the wood constituents is reduced. Considering the study mentioned above, it is thought that the liquid molecules with low adsorption to wood became easy to adsorb to the acetylated wood due to introduction of the

hydrophobic acetyl groups and the swelling ratio increased. The distance between molecules increased, the movement of the main and side chains became less confined and molecular movement became easier. For these reasons, the peak temperatures of $\tan\delta$ decreased and the reduction of relative E' with increasing temperature became larger in acetylated samples.

Conclusions

Temperature dependences of the dynamic viscoelastic properties of untreated and acetylated wood samples swollen by water or various organic liquids were revealed after the heating and cooling histories were unified among the samples. From the results, untreated samples swollen by high-polarity liquid had lower peak temperature of $\tan\delta$, however, acetylated samples had higher peak temperature of $\tan\delta$ than those of untreated wood. On the other hand, untreated wood samples swollen by low-polarity liquid had higher peak temperature of $\tan\delta$, however, acetylated samples had lower peak temperature of $\tan\delta$ than those of untreated wood. The amount of swelling is determined by interaction between wood and liquid due to proton-accepting power and molar volumes of liquid and so on, therefore, the peak temperature of $\tan\delta$ degree of reduction in E' with increasing temperature was corresponded to the amount of swelling. However, $\tan\delta$ showed different behaviors depending on the kinds of swelling liquids, so the thermal-softening properties of wood are considered to be influenced not only by swelling ratio but also by properties of liquids itself, for example, the cohesive force of the liquid and the temperature dependence of adsorbability to wood.

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