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## Compression behaviors of acetylated wood in organic liquids. Part II. Drying-set and its recovery

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**Abstract** Unmodified and acetylated cedar wood specimens were swollen in various liquids and dried under radial compression. Two stress relaxation processes were observed during drying, and the second process observed below the fiber saturation point was responsible for the drying-set and the temporary fixation of compressive deformation. The fixed shape of acetylated wood was partly recovered by soaking it in water and toluene and completely recovered in acetone. The effective shape fixation and recovery of toluene-swollen samples implied that the intermolecular hydrogen bonding was not necessary for the drying-set of acetylated wood. The degree of shape recovery was not explained by initial softening, while the acetylated wood always exhibited greater recoverability than unmodified wood. Although 85% stiffness was lost after large compression set and recovery of unmodified wood, such a stiffness loss was limited to 39% when the acetylated wood was processed with organic liquids. This indicated that the swelling of the hydrophobic region in the acetylated wood was effective in preventing mechanical damage due to large compressive deformation.

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### Introduction

Thus far, we have dealt with the mechanical properties of acetylated wood in various organic liquids as part of an attempt to fabricate a high-performance wood-based composite. In part I of this paper, we reported the characteristic effects of acetylation and organic liquids on the shape recovery of wood after large radial compression (Obataya and Yamauchi 2005). In contrast with the water-swollen unmodified wood, acetylated wood swollen in organic liquids exhibited greater shape recovery despite its higher stiffness. Although the

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intrinsic mechanism of shape recovery is still debatable, such recoverability might be an advantage of acetylated wood.

In order to use acetylated wood for elements of a composite, its mechanical behavior in non-equilibrium conditions is equally important. During the formation process of a composite, the wooden elements are often pressed under non-equilibrium conditions in which moisture and various solvents are removed. In this case, the deformation of wood is unusually enlarged due to the mechano-sorptive effect, and a part of the deformation is fixed while drying. Such a fixation is termed as drying-set (Tiemann 1951); a similar phenomenon is generally observed in hygroscopic natural fibers (Schulz 1961; Feughelman and Haly 1962). Due to its practical importance in various wood processing, a lot of investigations have been carried out on the mechanism of drying-set and recovery in a wood–water system (Armstrong and Christensen 1961; Gibson 1965; Eriksson and Norén 1965; Takahashi and Schniewind 1974; Iida et al. 1984; Norimoto and Gril 1989; Tokumoto 1991), and the rheological aspect of these phenomena has been reviewed by earlier authors (Schniewind 1968; Grossman 1976). In several cases, the reformation and scission of hydrogen bonds among amorphous wood polymers have been regarded as the dominant mechanisms of drying-set and recovery. In these cases, it is expected that acetylated wood shows an incomplete drying-set because the possibility of intermolecular hydrogen bonding is reduced to an extent by the substitution of active hydroxyl groups with acetyl groups. However, the compressive deformation of acetylated wood was effectively fixed while drying, and its fixed shape was more stable than that of unmodified wood in cold water (Inoue et al. 1992). This fact requires the reconsideration of the role of hydrogen bonds in the set and recovery of acetylated wood.

Our final goal is to fabricate an acetylated wood-based composite that possesses excellent dimensional stability and durability even under severe wet–dry cycling. For this purpose, gradual shape recovery, i.e., the release of drying-set, is a serious problem. On the contrary, the drying-set may enable an easier modification of the shape and density of wooden parts if the fixed shape is sufficiently stable in humid conditions. However, there is only a scarce amount of information available on the drying-set of acetylated wood, whereas the unmodified wood has been extensively investigated. Thus, for a more comprehensive understanding of the acetylated wood, this paper describes the compressive stress relaxation of acetylated wood while drying and its shape recovery in various liquids.

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## Materials and methods

### Wood specimens

Sapwood from the Japanese cedar (*Cryptomeria japonica* D. Don.) was cut into cubes of dimensions  $15 \times 15 \times 15 \text{ mm}^3$  (longitudinal  $L \times$  radial  $R \times$  tangential  $T$ ). In order to remove the natural extractives, the specimens were previously leached with methanol (1 week) and subsequently cold water (1 week). These extracted specimens were then oven-dried at  $105^\circ\text{C}$  and their weight and dimensions were measured. Half the specimens were soaked overnight in acetic anhydride under vacuum and then heated for 8 h at  $120^\circ\text{C}$ . The treated specimens were im-

mersed in cold ethanol, dried at room temperature, and then rinsed in running water for 2 weeks to remove the remaining chemicals. The leached specimens were oven-dried at 105°C to measure their weight and dimensions. The weight percent gains due to acetylation ranged from 19.8% to 20.7%.

### Compression tests

First, the compressive Young's modulus ( $E$ ) of oven-dried specimens along the  $R$  direction was determined. The specimens were then soaked in water (Wt), acetone (Ac), or toluene (Tol) under vacuum until the dimensional equilibrium (1–4 weeks), and their  $E$  values were measured again. In order to prevent the loss of solvents during the measurements, the specimens were wrapped with a thin polyvinylidene chloride (PVDC) film in the same manner as that described earlier (Obataya and Yamauchi 2005). The PVDC film was subsequently removed and the specimens were compressed by 5 mm ( $\varepsilon = 32\%–33\%$ ) along their  $R$  direction at 1 mm/min crosshead speed. The compressed specimens were then dried at 23°C–25°C and 52%–56% RH while observing their stress relaxation. In order to evaluate the change in mass of the compressed specimens, three conditioned samples were placed beside the testing machine and weighed intermittently. These dummy samples had been previously pressed and fixed by aluminum jigs. The additional three samples were dried without compression to measure their radial shrinkage.

### Recovery test

The compressive deformation of wood specimens was almost completely fixed during the stress relaxation measurements described above. In order to measure their absolutely dry weight and dimensions, these *set* specimens were oven-dried at 105°C without any mechanical restriction. The specimens were then dried with dehydrated silica gel (D), soaked in Wt, Ac, or Tol for 40 days at 20°C, while intermittently measuring their dimensions. The Wt-soaked specimens were subsequently boiled for 1 h, cooled in cold water, and their dimensions were then measured. After the recovery treatments, the specimens were air-dried for approximately 1 week and oven-dried at 105°C to determine their weight and dimensions. All the specimens were then soaked in Ac (1 week), Wt (1 week), and boiled for 1 h to complete the possible shape recovery. The recovered specimens were finally oven-dried and their  $E$  values were measured.

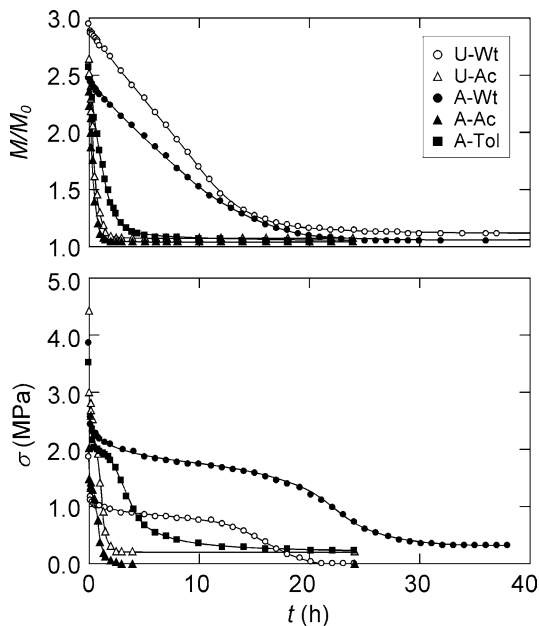
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## Results and discussion

### Stress relaxation during drying-set

Figure 1 shows the changes in the relative mass ( $M/M_0$ ) and compressive stress ( $\sigma$ ) of wood specimens while drying. The mass ( $M$ ) of specimens was normalized by that in the oven-dried condition ( $M_0$ ). With the elapse of time, the mass of the specimens decreased almost linearly and then leveled off to attain equilibrium. The organic solvents (Ac and Tol) were removed rapidly within a few hours, while the evaporation of water (Wt) required almost an entire day. Corresponding to the drying rate, the stress relaxation was faster in Ac- and

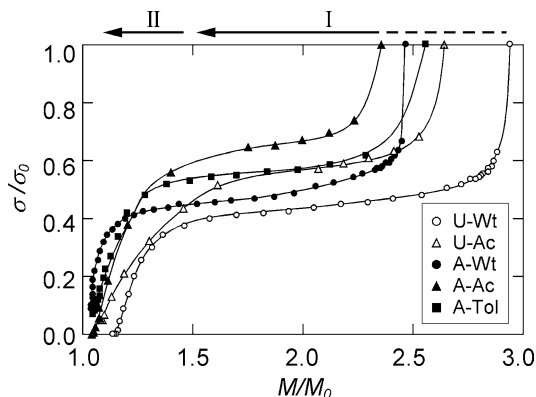
**Fig. 1** Changes in mass ( $M/M_0$ ) and compressive stress ( $\sigma$ ) of unmodified (U) and acetylated (A) wood specimens while drying at constant strain. The abbreviations indicate water (Wt), acetone (Ac), and toluene (Tol) used for the initial swelling of wood



Tol-swollen specimens than that observed in Wt-swollen specimens. Figure 2 shows a plot of the relative stress against the relative mass. The relative stress ( $\sigma/\sigma_0$ ) was defined as the relaxed stress at  $t$  ( $\sigma$ ) divided by the initial instant stress ( $\sigma_0$ ). Two separate stress relaxation processes were obtained, irrespective of the treating conditions. In the beginning of drying, the stress dropped by 40%–60% and then leveled off (relaxation I). At approximately  $1.5 M/M_0$ , the stress began to decrease again and finally disappeared (relaxation II).

During the initial stage of drying, the solvents were removed from the cell cavities while most of the cell walls remained completely swollen. As exhibited in Fig. 3, no apparent shrinkage was detected in the range of  $M/M_0$  corresponding to relaxation I. Therefore, relaxation I is attributable to the viscoelastic rearrangement of wood polymers that remain completely swollen with solvents. Relaxation I enabled a 40%–60% reduction in stress, but a complete

**Fig. 2** Plots of relative stress ( $\sigma/\sigma_0$ ) versus relative mass ( $M/M_0$ )



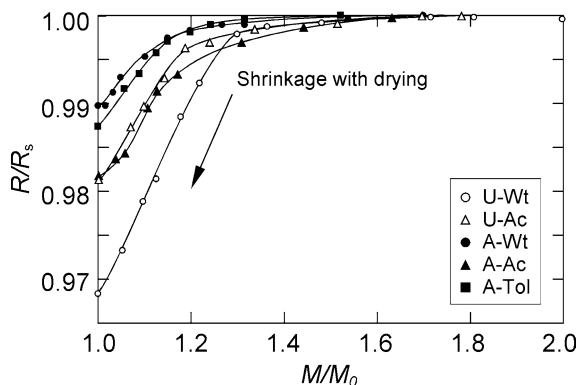
drying-set was not achieved. The result of a preliminary test also suggested a slight fixation effect of relaxation I: the shape of the specimen was almost completely recovered upon removal of the load at the end of relaxation I ( $M/M_0 = 1.8\text{--}2.0$ ). On the other hand, relaxation II resulted in a complete drying-set. Although relaxation II involves both the shrinkage of wood and structural changes in wood components, the shrinkage itself did not appear to be a dominant factor in the completion of the drying-set. As shown in Fig. 3, the radial shrinkage of uncompressed wood was 3% at most. Since the initial compression resulted in an increase of approximately 50% in density, and the shrinkage of wood generally increases in proportion to its density, possible shrinkage is estimated at or below 5%. Further, as stated above, the initial deformation was barely fixed at the end of relaxation I. Thus, the possible shrinkage of compressed wood ( $< 5\%$ ) is much smaller than the potentially remaining strain (32%–33%) at the beginning of relaxation II. This serves an indirect evidence suggesting a slight contribution of wood shrinkage in shape fixation during relaxation II.

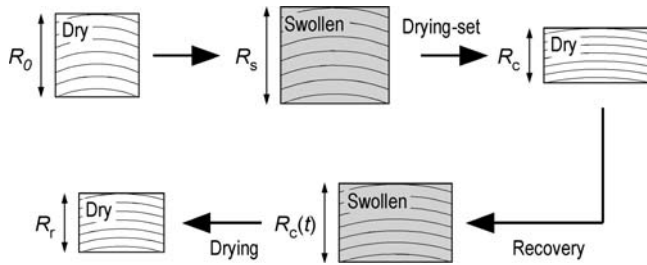
It is worth noting that the compressive deformation of Tol-swollen acetylated wood was almost completely fixed. According to extensive investigations carried out by earlier authors, Tol scarcely penetrates into the wood cell wall, where tight hydrogen bonds are formed between the amorphous wood polymers, because it has little proton attracting power (Nayer and Hossfeld 1949; Ishimaru and Adachi 1988). On the other hand, acetylated wood is remarkably swollen in various organic liquids such as Tol (Obataya and Gril 2005). It is possible that these aprotic liquids penetrate the hydrophobic region in the acetylated wood cell wall, where either few or very weak hydrogen bonds are formed. This implies that the introduction and removal of Tol seldom involves the drastic scission and reformation of hydrogen bonds among acetylated wood polymers. Thus, the effective stress relaxation of the A-Tol specimen suggests that intermolecular hydrogen bonding is not necessary for the drying-set of acetylated wood. This speculation is consistent with the results of the recovery tests, which will be described later.

### Recovery of drying-set

Figure 4 illustrates the changes in the shape of a wood specimen through the drying-set and recovery processes. In order to evaluate the gradual recovery of

**Fig. 3** Radial shrinkage of uncompressed wood specimens as a function of relative mass ( $M/M_0$ ). The radial dimension ( $R$ ) of a specimen was normalized by that in the swollen state ( $R_s$ )

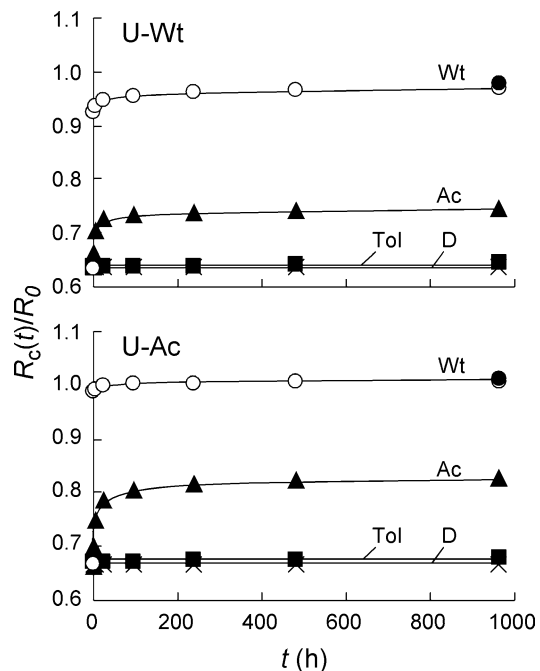




**Fig. 4** Changes in the shape of wood specimens through the drying-set and recovery processes

the radial dimension, we use the recovered dimension ( $R_c(t)$ ) divided by the uncompressed and oven-dry dimension ( $R_0$ ). Figure 5 shows the changes in  $R_c(t)/R_0$  of unmodified wood under different conditions. No recovery was observed in Tol and dry air. This indicates that the drying-set is not released when the wood cell wall remains unswollen. On the other hand, in Wt, the shape of unmodified wood was fairly recovered within a day, and it remained almost unchanged after additional boiling. The shape of wood was also recoverable in Ac, but this recovery was less than that achieved by Wt-soaking. Figure 6 exhibits the shape recovery of acetylated wood. No recovery was observed in dry air. In contrast with the unmodified wood, acetylated wood exhibited a rapid and complete recovery in Ac, whereas the recovery was incomplete in Wt even after boiling for 1 h. The most interesting result was a marked recovery in Tol. When the acetylated wood was set with organic liquids, the effect of Tol-soaking was rather larger than that of Wt-soaking. As stated in the previous

**Fig. 5** Changes in the radial dimension ( $R_c(t)/R_0$ ) of compressed unmodified wood in water (Wt), acetone (Ac), toluene (Tol), and dry air (D) with the elapse of time ( $t$ ). U-Wt, set with water; U-Ac, set with acetone; filled circles, boiled in Wt



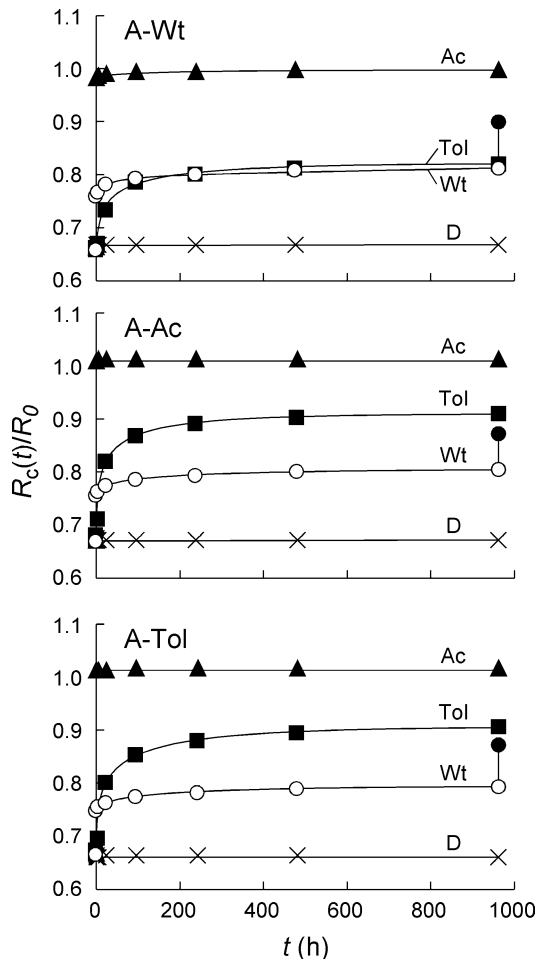
section, Tol has little potential in breaking the intermolecular hydrogen bonds. Thus, the significant shape recovery in Tol indicates that a part of the hydrophobic wood polymers is responsible for the shape fixation and recovery of acetylated wood without the reformation and scission of intermolecular hydrogen bonds.

$R_c(t)/R_0$  includes the swelling of the wood cell wall as well as the recovery of cell shape. In order to exclude the former effect, we defined the strain recovery index (SR) indicated by the following equation

$$SR(\%) = 100 \times \frac{R_r - R_c}{R_0 - R_c},$$

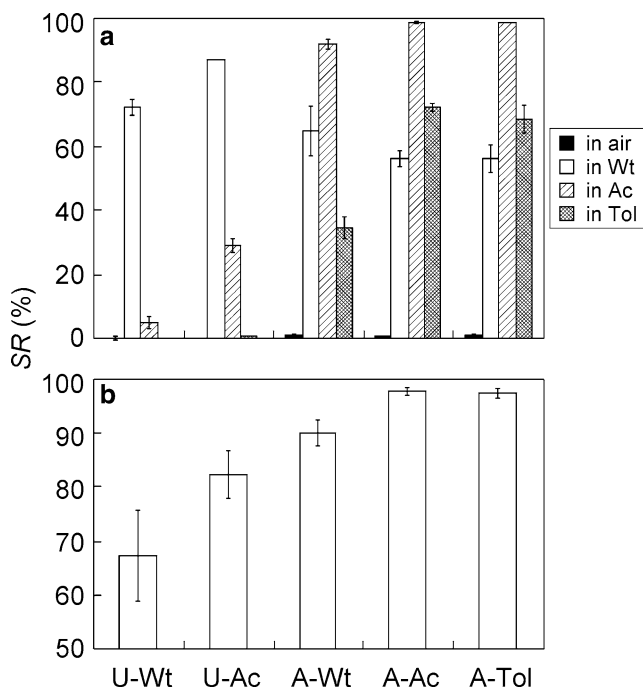
where  $R_0 - R_c$  and  $R_r - R_c$  represent the initial drying-set and its recovery, respectively. The SR should be 0% if no recovery occurs, while 100% SR indicates complete recovery. Figure 7a shows the SR values of wood specimens recovered under different conditions. The Wt-soaking and subsequent boiling was effective in recovering the shape of unmodified wood (U-Wt and U-Ac),

**Fig. 6** Changes in the radial dimension ( $R_c(t)/R_0$ ) of compressed acetylated wood in water (Wt), acetone (Ac), toluene (Tol), and dry air (D) with the lapse of time ( $t$ ). A-Wt, set with water; A-Ac, set with acetone; A-Tol, set with toluene; filled circles, boiled in Wt



but the SR values were limited to 85% or below. On the other hand, when organic liquids were used for its setting (A-Ac and A-Tol), the shape of acetylated wood was almost completely recovered by soaking in Ac. In these sample sets, the recovery in Tol was greater than that in Wt. Figure 7b shows the maximum SR values of wood specimens achieved by soaking in Ac and boiling in Wt. The recovery of unmodified wood was still incomplete (SR < 82%) whereas the SR of acetylated wood reached 98%.

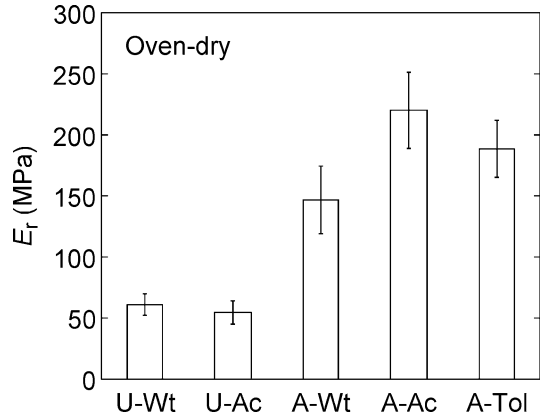
Figure 8 shows the compressive Young's modulus ( $E_r$ ) of the oven-dry wood specimen that was subjected to large compression and recovery. It should be noted that the incomplete shape recovery yields a slight increase in the density of wood. Therefore, the  $E_r$  value of unmodified wood, especially of the U-Wt specimen, would be smaller than that exhibited in Fig. 8, if its shape was completely recovered. With regard to this densification effect, it can be said that the behavior of  $E_r$  (Fig. 8) is generally similar to that of SR (Fig. 7b). This suggests that both SR and  $E_r$  reflect the irreversible damage in the structure of wood induced by the initial large compression. Since Young's modulus of the oven-dry uncompressed specimens was almost 360 MPa, it was evaluated that 83%–85% stiffness was lost during the compression and recovery of unmodified wood. On the other hand, when the acetylated wood was processed with organic liquids, the stiffness loss was limited to 39%. This indicates that the recoverability of wood is greatly enhanced by acetylation and the additional swelling in organic liquids.



**Fig. 7** Strain recovery index (SR) of wood specimens. **a** Recovered in different conditions; **b** recovered by soaking in acetone and subsequently boiling in water. The bars indicate standard deviations



**Fig. 8** Compressive Young's modulus ( $E_r$ ) of oven-dry wood specimens after the drying-set and recovery of large compression. The bars indicate standard deviations



In general, sufficient wetting and softening are required for a large deformation of wood with less mechanical damage. In fact, dry wood specimens often exhibited checks and cracks under large compression, whereas no such visible failure occurs in Wt-swollen specimens. For additional softening, hot water is generally used in the manufacture of bentwood and compressed wood, because the hygro-thermal softening of amorphous wood components enables an easier and larger deformation in wood. In this sense, the degree of recovery is considered to depend on the stiffness of wood in its initial swollen state. Table 1 lists the compressive Young's modulus ( $E_0$ ) of wood specimens in their initial swollen and uncompressed conditions. Despite the most remarkable softening in its initial state ( $E_0 = 76$  MPa), the U-Wt specimen recorded the smallest SR (67%, in Fig. 7b) and a very low  $E_r$  (61 MPa, in Fig. 8). Additionally, the A-Tol specimen exhibited complete recovery (SR=98%) and large remaining stiffness ( $E_r = 190$  MPa) despite the high initial stiffness ( $E_0 = 240$  MPa). Table 1 also lists the radial swelling ( $\Delta R$ ) of wood specimens due to initial conditioning. The small SR and  $E_r$  values of U-Wt specimens and the relatively large SR value of U-Ac specimens were not consistent with their initial swelling levels (4.0% and 1.9%, respectively). These results indicate that when acetylation and organic liquids are involved, the recoverability of wood is not merely determined by its initial softening condition.

According to Inoue and coauthors, the compression set of acetylated wood is not recovered in cold water, but is completely recovered by boiling in water (Inoue et al. 1992). They explained that the thermal softening of wood components was responsible for the completion of recovery. In the present case, however, the recovery of acetylated wood was not completed in Wt even after 1 h of boiling. In addition, the degree of recovery did not correspond to that of initial softening, as discussed previously. Thus, the interpretation provided by Inoue should be slightly modified in order to explain the phenomena observed in this study.

We now reconsider the different roles of hydrophilic and hydrophobic regions in acetylated wood. From among the various swelling agents, aprotic liquids such as Tol barely penetrate the unmodified wood cell wall, whereas they can easily access the hydrophobic region formed in acetylated wood. As discussed earlier, the swelling of the hydrophobic part is considered to exert less influence on the stiffness of wood than the water-swelling of the hydrophilic

**Table 1** Compressive Young's modulus ( $E_0$ ) and radial swelling ( $\Delta R$ ) of wood specimens in their initial uncompressed conditions

Condition	$E_0$ (MPa)		$\Delta R$ (%)	
	Unmodified	Acetylated	Unmodified	Acetylated
Wt	76 (8)	201 (21)	4.0 (0.3)	3.8 (0.5)
Ac	270 (37)	107 (16)	1.9 (0.3)	3.8 (0.5)
Tol	–	240 (29)	–	3.4 (0.4)
OD	355 (69)	363 (35)	0.0	2.3 (0.5)

Values in parentheses indicate standard deviations.  $\Delta R$  of acetylated wood includes bulking due to acetylation Wt soaked in water; Ac soaked in acetone; Tol soaked in toluene; OD oven-dried

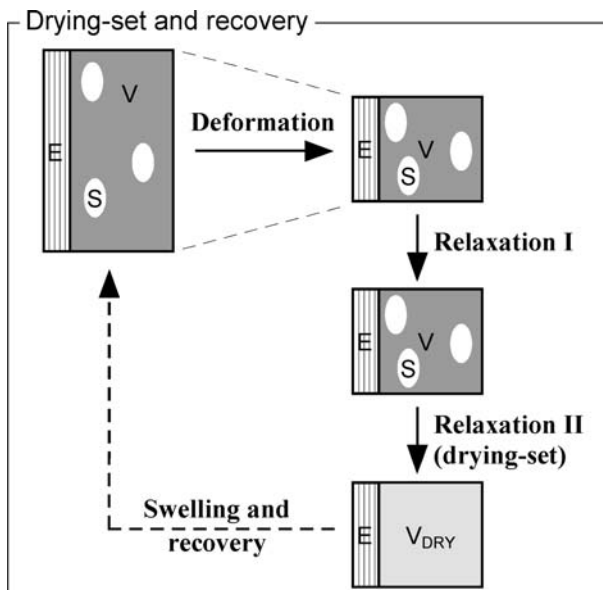
part (Obataya and Yamauchi 2005; Ishimaru and Minase 1992). This serves a reason for the Tol-soaking resulting in a lesser reduction in the Young's modulus of acetylated wood than Wt-soaking. Further, it is possible that the swelling of the hydrophobic region enables a greater viscoelastic deformation of wood (Obataya and Yamauchi 2005). Therefore, it is considered that hydrophobization due to acetylation and the swelling of hydrophobic components in organic liquids are effective in preventing irreversible damage with less softening of wood. This idea accounts for the excellent recoverability and greater remaining stiffness of acetylated wood, and is also consistent with the results obtained for unmodified wood: the U-Ac sample exhibited greater recovery than the U-Wt sample despite its higher stiffness and lesser swelling. Although further experiments are necessary for quantitative interpretation, the extended hydrophobic region may take an important role in the large compression of acetylated wood.

#### Qualitative interpretation for the drying-set and recovery of acetylated wood

Generally, drying-set is a recoverable, i.e., reversible phenomenon with respect to dimensional change, whereas a large deformation possibly induces irreversible deterioration in the structure of wood (Grossman 1976; Iida et al. 1984; Norimoto and Gril 1989). For a qualitative interpretation of reversible dimensional changes, it is convenient to use a parallel model, as shown in Fig. 9. This model explains that the deformation of wood is fixed at the viscoelastic part (V) with the removal of solvents (S), while the elastic part (E) stores sufficient energy for shape recovery. Although this model does not reflect the complicated anatomical structure of wood, the E and V parts approximately represent the roles of cellulosic microfibrils and amorphous matrix substances in the wood cell wall, respectively. The wood cell wall is a fiber-reinforced composite in which cellulosic microfibrils are embedded in amorphous matrix substances such as lignin and hemicelluloses. The wetting of wood induces a marked softening of the matrix, whereas the microfibrils remain unaffected. Matrix softening is particularly remarkable at high temperatures at which a part of the matrix components shift from the glassy state to the rubbery state. Accordingly, the softened matrix permits the relative displacement of microfibrils under loads. At the beginning of drying, the stress is partly relaxed with the viscoelastic rearrangement of matrix polymers (relaxation I); however, a slight shape fixation occurs at that time because the matrix is still swollen and soft.

Below the fiber saturation point, the matrix stiffens with the reformation of intermolecular hydrogen bonds and the polymer conformation is fixed in its new rearranged state. This process is detected as relaxation II and is responsible for the completion of drying-set. The *freezing* of matrix polymers may also be effective in shape fixation when the wood is deformed at high temperatures, cooled, and then dried. In any case, the initial deformation of wood is set while drying and remains un-recovered as far as the matrix is in a dry glassy state. By rewetting, however, the matrix is softened again with the scission of intermolecular hydrogen bonds. Matrix softening is enhanced by heating because of its glass–rubber transition. As a result, the elastic energy stored in microfibrils is released to recover the shape of the wood. These are interpretations for the drying-set and recovery of the wood–water system given by the model shown in Fig. 9. Additionally, a part of the matrix components such as cross-linked lignin might also contribute to the storage of elastic energy; however, the evidence for this entropy-elastic contribution is scarce. On the other hand, X-ray measurements have suggested that the drying-set and recovery of wood were accompanied by the set and release of strain in the cellulose crystallite (Doi et al. 1978, 1980). This indicates that the elastic microfibrils certainly store the elastic energy required for the shape recovery of wood.

In the present case, the effects of glass-rubber transition are excluded from the discussion because all the samples were set at room temperature. Therefore, it is logical to attribute the set and recovery of Wt-swollen unmodified wood to the reformation and scission of intermolecular hydrogen bonds, as suggested by several researchers (Gibson 1965; Eriksson and Norén 1965; Schniewind 1968; Grossman 1976; Norimoto and Gril 1989). Regarding the drying-set of acetylated wood, however, the intermolecular hydrogen bonds appear to be less



**Fig. 9** An interpretation for the drying-set and recovery of wood. E, elastic part; V, viscoelastic part; S, swelling agent

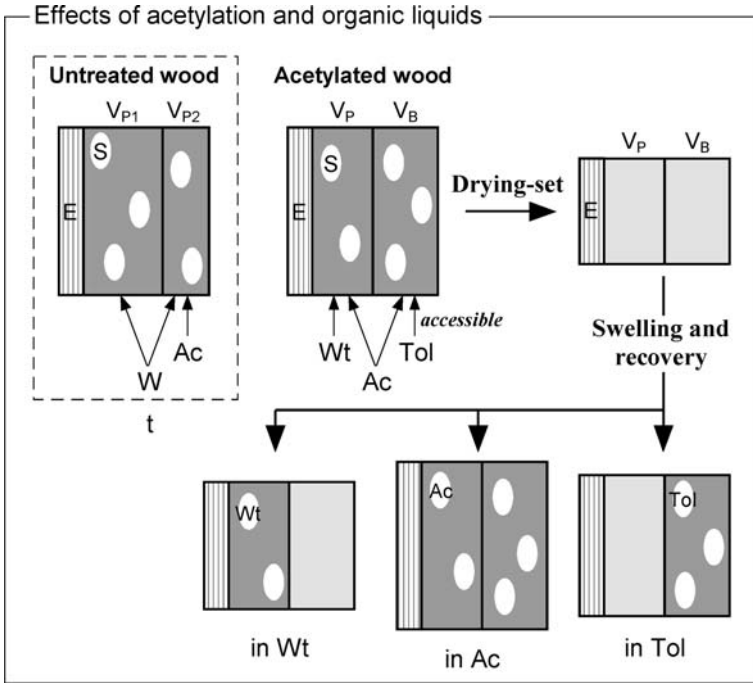
important, as indicated by the effective drying-set of the Tol-swollen sample and its significant recovery in Tol. It is possible that the hydrophobized matrix polymers in the acetylated wood are sufficiently rigid to fix the shape of the wood cells without tight hydrogen bonding, whereas they readily swell and are easily rearranged in aprotic organic liquids such as Tol. The bulky nature of acetyl groups may be responsible for the immobilization of wood polymers in the dry glassy state. In fact, the Young's modulus of wood ( $R$  direction) is significantly enhanced with the introduction of glucose pentaacetate ( $M_w = 390$ ), without any chemical bonds between the adduct and the wood components (Obataya et al. 2003).

Another argument is the effect of the initial setting condition on the recovery of drying-set. The deformation of wood that is set at high temperatures is not completely recovered in cold water (Iida et al. 1984). The setting humidity also affects the recovery of wood. Tokumoto discovered that the recovery of wood is remarkable at particular moisture contents corresponding to the humidity conditions employed for setting (Tokumoto 1991). He suggested that such a *memory* of hygro-thermal history could be explained by different viscoelastic units aligned in series. However, such a series model does not account for the behaviors of acetylated wood, particularly, when organic liquids are used for setting and recovery. If the effective recovery is achieved during the initial setting condition, as predicted by the series model, the acetylated wood set with Wt (A-Wt) would exhibit less recovery in Tol. In the same sense, the recovery of acetylated wood in Wt should be very small when it is set with Tol (A-Tol). However, as shown in Fig. 6, both the A-Wt and A-Tol samples showed moderate recovery in Wt and Tol. Thus, we propose a parallel model shown in Fig. 10, which is designed for interpreting the behaviors of an acetylated wood–organic liquid system. Due to acetylation, a part of the amorphous region bulks with hydrophobic acetyl groups. Hydrophobization permits a marked swelling of wood in aprotic liquids such as Tol, instead of the exclusion of Wt from the cell wall. Therefore, it is supposed that the Wt-accessible hydrophilic part ( $V_P$ ) and the Tol-accessible hydrophobic part ( $V_B$ ) are largely distinct in the acetylated wood cell wall, even though they may partly overlap. Irrespective of the liquids used, the initial deformation of acetylated wood is fixed while drying, i.e., the polymer conformation in part V is fixed in its rearranged state regardless of the initial swelling conditions. The swelling and softening of part  $V_P$  results in gradual shape recovery when the set wood is soaked in Wt. However, this recovery is retarded and limited by part  $V_B$ , which remains unaffected in Wt. Similarly, part  $V_P$  resists the recovery of acetylated wood in Tol. Consequently, both Wt and Tol permit a moderate recovery of acetylated wood irrespective of the liquids used for setting. On the other hand, Ac enables the rapid and complete recovery of acetylated wood because it can access both the parts  $V_P$  and  $V_B$ . Although the physical and anatomical meanings of parts  $V_P$  and  $V_B$  are still debatable, they should be aligned in parallel rather than in series, in order to explain the drying-set and recovery of acetylated wood.

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## Conclusions

The compressive drying-set and recovery of acetylated wood were observed in various liquids. Based on the results, the following is concluded:



**Fig. 10** An interpretation for the recovery of acetylated wood in different liquids.  $V_P$  and  $V_B$  indicate the hydrophilic and hydrophobic parts in the amorphous matrix, respectively

1. Two stress relaxation processes were observed during the compressive drying-set. The first relaxation was observed at the beginning of drying and the second occurred below the fiber saturation point. Shape fixation was achieved during the second relaxation process.
2. Toluene-swollen acetylated wood exhibited an effective drying-set. In addition, the acetylated wood exhibited a significant shape recovery in toluene. These facts suggested that hydrogen bonds are insignificant in the drying-set of acetylated wood. Irrespective of the initial conditions, the drying-set of acetylated wood was completely recovered in acetone, which can access both the hydrophilic and hydrophobic regions in the acetylated wood cell wall.
3. Following large compression and recovery, the compressive Young's modulus of acetylated wood was four times greater than that of unmodified wood, whereas their original Young's moduli were almost identical. These facts indicated that the irreversible damage in acetylated wood due to the initial large compression was lesser than that in unmodified wood, particularly, when it was swollen in organic liquids.

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