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Wood Physics/Mechanical Properties

Yuka Miyoshi* and Yuzo Furuta

Effect of the interaction between wood constituents and swelling liquid on the creep properties of wood during drying

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Abstract: This study aimed to clarify the effect of the interactions between the swelling liquid and wood constituents on the creep behavior during drying. Creep tests were conducted during drying of four sample groups (untreated, acetylated, delignified, and hemicellulose-extracted samples) that were swollen using water, one organic liquid, or water-organic mixtures. The largest creep deformation was measured for the hemicellulose-extracted samples, followed by delignified, untreated, and acetylated samples. Apart from the acetylated samples, all treated samples tended to have large creep deformation in water-organic mixtures. For the acetylated samples, the creep deformation was small, except in case of acetone. These differences in the creep deformation behavior are mainly due to the differences in the glass-transition temperature of lignin as a result of the interaction between the wood constituents and the swelling liquid. The considerable increase in creep deformation due to hemicellulose-extraction suggests that hemicellulose, which interacts with lignin and cellulose, reduces the fluidity of the wood due to liquid desorption during creep measurements.

Keywords: acetylation; delignification; hemicellulose-extraction; mechano-sorptive creep; organic liquid.

1 Introduction

Creep deformation measured during moisture absorption or desorption is considerably larger than that measured under constant-moisture conditions (Armstrong and Kingston 1960). This phenomenon is called mechano-sorptive (MS) creep and is due to the effect of a simultaneous moisture change and applied load on wood (Grossman 1976). Various studies have been conducted to elucidate the mechanisms of MS creep (for example, Hanhijärvi and Hunt 1998; Hoffmeyer and Davidson 1989; Hofstetter and Gamstedt 2009; Hunt and Shelton 1987; Mukudai and Yata 1988; Nakano 2022; Salmén and Olsson 2016; Svensson and Toratti 2002; Takemura 1968; Tokumoto 2001). One of them investigates the mechanism of MS creep in terms of the phenomenon of wood destabilization due to changes in moisture content. Takahashi et al. (2004; 2005; 2006) revealed that creep deformation was greater in a sample measured immediately after drying than that measured over a long time under each relative humidity, despite the measured samples having almost the same moisture content. Hunt and Gril (1996) reported the relationship between the logarithmic decrement and moisture content of wood during sorption and desorption, with equilibrium values reported for comparison. The logarithmic decrement measured during the adsorption/desorption process were different from the equilibrium logarithmic decrement but approached equilibrium during aging after adsorption/desorption. Therefore, the large difference in the creep deformation between samples with very similar moisture contents suggests that MS creep is caused by the destabilization of the molecules of the wood constituents due to water desorption. MS creep was also measured with single or mixed liquids using water, methanol and ethanol (Kojiro et al. 2012) and the creep deformation of the samples swollen by the different liquids differed during drying. Therefore, the destabilization of wood constituents due to liquid desorption depends on the interactions between the liquid and wood constituents during swelling.

Some studies reported that wood swollen using different organic liquids exhibits different mechanical properties (for example, Ishimaru and Minase 1992; Ishimaru et al. 1996; Miyoshi et al. 2016). Recently, the temperature dependence of the dynamic viscoelasticity of untreated and acetylated wood swollen using various liquids was reported (Miyoshi et al. 2018; Miyoshi et al. 2020). For liquids that interact with

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***Corresponding author: Yuka Miyoshi**, Department of Wood Properties and Processing, Forestry and Forest Products Research Institute, Matsunosato 1, Tsukuba, Ibaraki 305-8687, Japan,
E-mail: ymiyoshi@ffpri.affrc.go.jp
Yuzo Furuta, Division of Environmental Sciences, Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Hangi-cho, Shimogamo, Sakyo-ku, Kyoto 606-8522, Japan, E-mail: furuta@kpu.ac.jp

wood constituents, such as water, ethylene glycol, and formamide, the glass-transition temperature (T_g) of lignin is below 90 °C at the frequency of 0.05 Hz measured in the previous paper (Table 1) because the molecular motion of wood constituents is activated by a swelling liquid (Miyoshi et al. 2018). However, for wood hydrophobized via acetylation treatment, the T_g values of the acetylated samples swollen by water, ethylene glycol, or formamide were higher than those of untreated samples swollen by the same liquid because the affinity between the wood constituents and liquids was low (Miyoshi et al. 2018). Moreover, the adsorption capacity of wood constituents (such as cellulose, hemicellulose, and lignin) toward liquids depends on the type of liquid (Nakatani et al. 2006). This is due to the fact that liquid molecules are adsorbed by the areas containing wood constituents with a high affinity for the specific liquid, which can alter the mechanical properties of the wood.

Based on the literature discussed above, it was considered that changing the interaction between the wood constituents and liquid using different swelling liquids as well as modifying the wood constituents would be effective in understanding the detailed mechanism of the increase in creep deformation during drying. Herein, the MS creep behaviors of the samples in which the interaction between wood constituents and liquid was changed were measured. In addition, the relationship between the microstructural state of the wood cell wall and the creep behavior was investigated. Acetylation, delignification, and hemicellulose extraction were used to modify the wood to clarify the role of each wood constituent on the MS creep behavior. Various swelling liquids were used, including water, three organic liquids, and binary liquid mixtures of water and one of the organic liquids. If the conditions that increase the creep deformation of wood can be clarified, the findings could be used to develop new wood-processing technology.

2 Materials and methods

2.1 Samples

Cross-sectional samples were obtained in the longitudinal direction from the outer region of heartwood with a straight grain obtained from a log of Japanese bigleaf magnolia (*Magnolia obovata*). For extracting hemicellulose before extracting lignin, hardwood is more suitable than softwood in terms of the distribution of chemical components in the cell wall (Magara 2010). In addition, relatively homogeneous samples can be obtained because the anatomical features of Japanese bigleaf magnolia are diffuse-porous and the growth ring boundaries are indistinct. Finally, Japanese bigleaf magnolia was chosen as an experimental sample because it is easily available in Japan. The dimensions of the samples for the static bending and creep tests were 100 mm (radial) × 15 mm (tangential) × 4 mm (longitudinal). This study aimed to observe the change in the morphology of the amorphous region of the cell walls, because this has a dominant effect on the mechanical properties associated with the adsorption and

Table 1: Glass transition temperature (T_g) values cited in the literature.

T_g of liquid-swollen untreated and acetylated wood samples measured at a the frequency of 0.05 Hz[a]			T_g of wood samples swollen by water-ethanol mixtures measured at a frequency of 0.5 Hz[b]			T_g of lignin and hemicellulose extracted water-swollen wood samples measured at a frequency of 0.05 Hz[c]			
Species	**Cypress**			**Cypress**	**Beech**	**Japanese bigleaf magnolia**			
Sample type	**Untreated**	**Acetylated**		**Untreated**	**Untreated**	**Delignified**		**Hemicellulose-extracted**	
Liquids	T_g (°C)	T_g (°C)	Mole fraction of ethanol	T_g (°C)	T_g (°C)	Weight-loss rate after delignification (%)	T_g (°C)	Weight-loss rate after hemicellulose extraction (%)	T_g (°C)
Water	90	Not observed up to 90	0	98	72	0	76	0	76
Ethylene glycol	72	Not observed up to 90	0.2	50	40	0.3	60	3.8	75
Formamide	38	70	0.4	50	41	0.8	55	14	75
Ethanol	Not observed up to 78	Not observed up to 78	0.6	60	50	5.2	46	23.7	78
2-Propanol	Not observed up to 80	76	0.8	70	68	7.6	42	33.6	95
Acetone	Not observed up to 40	Not observed up to 40	1	Not observed up to 78	Not observed up to 78	12.8	26		

The peak temperature of tanδ measured in the radial direction of the samples is defined as T_g. The data marked [a,b,c] are cited from the studies of Miyoshi et al. (2018), Tanaka (2019), and Furuta et al. (2010), respectively.

desorption of liquids. Therefore, samples cut in the radial direction, in which the earlywood and latewood are arranged in series, were used to prepare cross-sectional samples.

To measure the changes in the liquid content of the samples during drying, cross-sectional samples 40 mm (radial) × 20 mm (tangential) × 4 mm (longitudinal) were also obtained in the longitudinal direction from the same log. After water injection under vacuum, the samples were soaked overnight at approximately 20 °C. The water-swollen samples were boiled for 1 h and left in the hot water until they cooled, and then air-dried at approximately 20 °C. Methanol was injected into the dried samples under vacuum and then the samples were soaked in methanol at approximately 20 °C overnight. The samples were heated in methanol at 50 °C for 6 h and then air-dried at room temperature. The dried samples were treated under one of the four conditions shown in Figure 1 to produce four sample groups. The weight-loss ratio after hot water and methanol extraction was 5.5%. The weight change for all sample types were calculated based on the oven-dried weight of the original sample in all case.

The acetylated samples were prepared using the following procedure. The air-dried samples after hot water and methanol extraction were soaked in acetic anhydride overnight for impregnation under vacuum at approximately 20 °C, and then heated at 120 °C for 8 h. After heat treatment, the samples were rinsed for one week under running water at room temperature. The weight-increase ratio due to acetylation was 12.3%.

The delignified samples were prepared using the Klaudiz method (Klaudiz 1957). The air-dried samples were impregnated with a 4% sodium chlorite aqueous solution adjusted from pH 3.8 to 4.0 by adding acetic acid. Then, the samples were soaked overnight in an aqueous solution at approximately 20 °C, and heated at 45 °C for 24 h. After the heat treatment, the samples were rinsed under running water at room temperature for one week. The weight-loss ratio due to delignification was 16.1%.

The hemicellulose-extracted samples were prepared based on a previous method (Wang et al. 2006). The air-dried samples were impregnated with 0.1% NaOH aqueous solution and soaked overnight at room temperature, followed by heating at 120 °C for 4 h in a pressure vessel. After the heat treatment, the samples were rinsed for 1 week under running water at room temperature. The weight-loss ratio due to hemicellulose extraction was 13.9%.

If a wood sample is heated before measurement of its physical properties, the test results will depend on the cooling rate of the sample immediately before testing (Furuta et al. 2008; Kojiro et al. 2008). Therefore, the pretreated samples were soaked in water and boiled for 1 h, followed by natural cooling in the same vessel to unify the cooling rate before mechanical measurement. The untreated and acetylated samples were dried at approximately 20 °C and then soaked in each test liquid (as described in Section 2.2) for 3 months. The liquid was changed twice for solvent exchange. Because the delignified and hemicellulose-extracted samples could shrink due to cell collapse during drying, the excess water was simply wiped off the sample surfaces. These samples were also soaked in the test liquids for 3 months, and the liquid was changed seven times. Based on the results of the bending tests performed in this study and a previous study of solvent exchange in wood (Ishimaru and Yamada 1997), it was determined that the solvent-exchange period used in this study was sufficient.

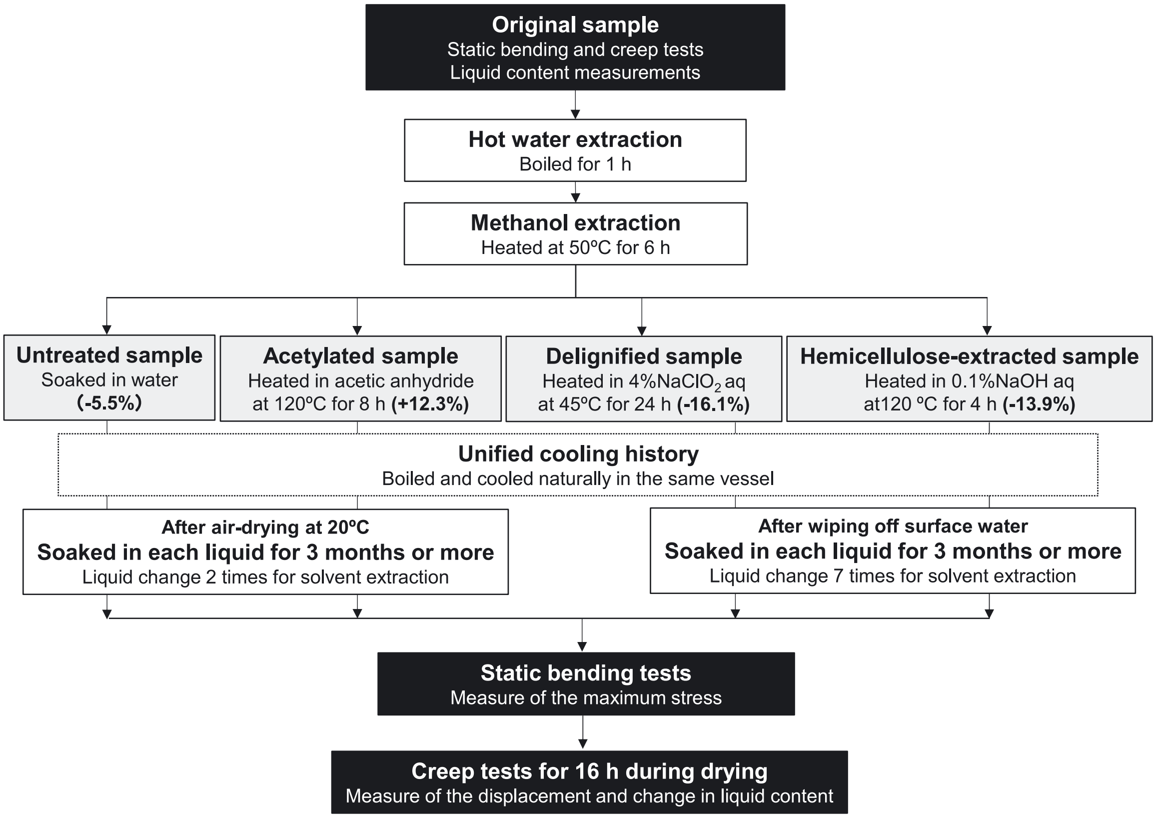

Figure 1: Conditioning procedures used to treat the samples.

2.2 Liquids

Distilled water, three organic liquids, and three different binary liquid mixtures were used as the test liquids. The basic properties of water, ethanol (EtOH), 2–propanol (PrOH), and acetone (Act) are listed in Table 2. The water-organic mole fraction of the three binary liquid mixtures (water–EtOH, water–PrOH, and water–Act) was 0.8:0.2. The three binary liquid mixtures were chosen because the activities of both constituents exhibit a significant positive deviation in partial pressure compared to the ideal behavior based on the law of mixing (Ishimaru and Sakai 1988). The swelling ratio of wood was shown to be higher when soaked in a water-organic liquid mixture with a 0.8:0.2 ratio compared to that obtained after soaking in a single liquid (Sakai and Ishimaru 1989).

2.3 Static bending test

Three-point bending tests were conducted using a tabletop material tester (EZ test EZ–SX 500N, Shimadzu) placed in an environmentally controlled room (20 °C and 65% relatively humidity (RH)). The span was 80 mm, and the crosshead speed was 8 mm/min. The dimensions of each sample were measured before the tests, and the tests were continued until the samples broke. All operations were performed quickly before the samples began to dry. The average values of the maximum stress and modulus of elasticity (MOE) at each measurement condition were measured for each group of samples (n = 5). In a preliminary test, the load of the creep test was set as 25% of the maximum stress recommended for the wood creep test. However, some samples could not be measured owing to their large deformation. Therefore, 10% of the maximum stress was used as the creep load for each group of samples.

2.4 Creep tests and liquid content during drying

Creep tests and measurements of the liquid content were conducted in a closed box placed in an environmentally controlled room (20 °C and 65% RH) (Figure 2). All samples were tested in a radial direction for 16 h. This measurement time was chosen based on the drying time of the water-swollen sample, which had the slowest drying rate among the various samples and took approximately 16 h to change from a saturated state to a single-digit moisture content. For creep tests, a span of 80 mm was used, with a point load in the center of the sample. The creep load was 10% of the maximum stress for each sample type. The displacement was measured using a laser displacement sensor (IL–S100, Keyence). N_2 gas flowed into the box with a flow rate of 2.5 L/min adjusted using a flowmeter, and air in the box was removed (2.5 L/min) using a pump. To investigate the change in the liquid content of the sample during drying, the weight of the sample was measured using an electronic force balance. Similar creep behavior was observed for the samples under identical conditions, so the results for only one sample from each group are discussed here.

2.5 Determination of creep compliance and liquid content

The creep compliance (J_t, m^2 N^{-1}) was determined using the following equation.

$$J_t\,(\mathrm{m^2N^{-1}}) = 4bh^3P^{-1}l^{-3}\,(\omega_t - \omega_0)$$

where b is the width (tangential direction) and h is the height (longitudinal direction) of the samples, p (N) is the load, l (m) is the span and ω_0 and ω_t are the deflections without instantaneous deformation measured at 0 and t min after the start of the creep measurement, respectively.

In this experimental system, the creep of the wood samples was measured during the process of liquid desorption from the liquid-saturated state. Therefore, it should be noted that the calculated J_t includes both viscoelastic creep above the fiber-saturation point (FSP) and MS creep below the FSP. The liquid content (LC,%) was determined using the following equation:

$$LC = 100\,(W_t - W_0)/W_0$$

where W_0 and W_t are the weights of the sample after oven drying and after swelling by the test liquid, respectively.

3 Results

3.1 *LC* and creep behavior of the conditioned samples during drying

The drying rate of the wood depends on the liquid used during swelling. The changes in *LC* during drying of the various samples are compared in Figure 3. The decrease in

Table 2: Properties of the liquids and the relative swelling ratio of the samples swollen by those liquids.

Liquid	Structural formula	Molar volume (cm^3/mol)	P.A.P.Δν[a] (cm^{-1})	H-bonding properties	C.E.[d] (cal/cm^3)	Relative swelling fraction[e] (%)
Ethanol (EtOH)	C_2H_5OH	58.5	187	AD	166	82.5
2-Propanol (PrOH)	$(CH_3)_2CHOH$	75.0	187	AD	144	73.6
Acetone (Act)	CH_3COCH_3	74.0	64	A[c]	96	68.0
Water	H_2O	18.0	390	AD	552	100.0

[a]Proton accepting powers: the data are cited from a table in Kagiya et al. (1968), Crowley et al. (1966), and Ishimaru (1981). [b]Liquid having both proton accepting and donating properties for hydrogen bonding. [c]Liquid having only proton accepting properties for hydrogen bonding. [d]Cohesion energy: data calculated from the solubility parameter values in a table in Hansen (1967). [e]Relative swelling ratio compared with that in water: data cited from a table in Sakai and Ishimaru (1989) and Ishimaru and Minase (1992).

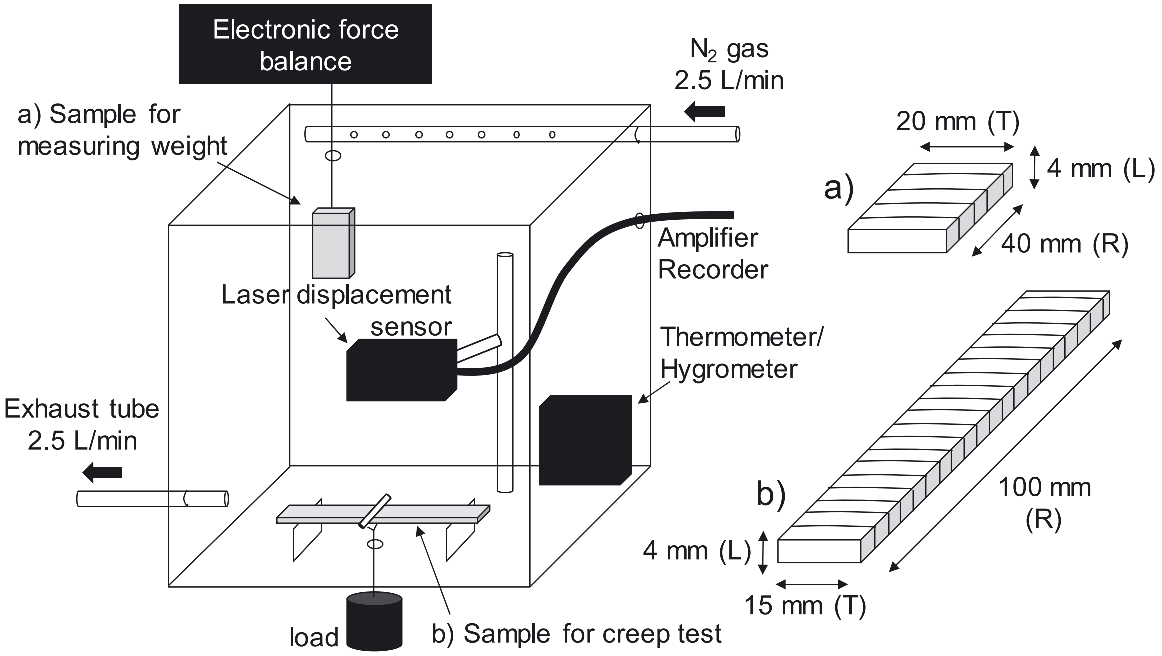

Figure 2: Schematic of the creep test and liquid-content measurements of the wood during drying.

LC (i.e., drying) was faster for the samples treated in organic liquids than in water. The samples treated in binary liquid mixtures showed an intermediate drying rate between those of the samples treated in Act and water. The mole fraction of the desorbed binary liquid mixture may not be uniform during drying as an inflection point was observed for the

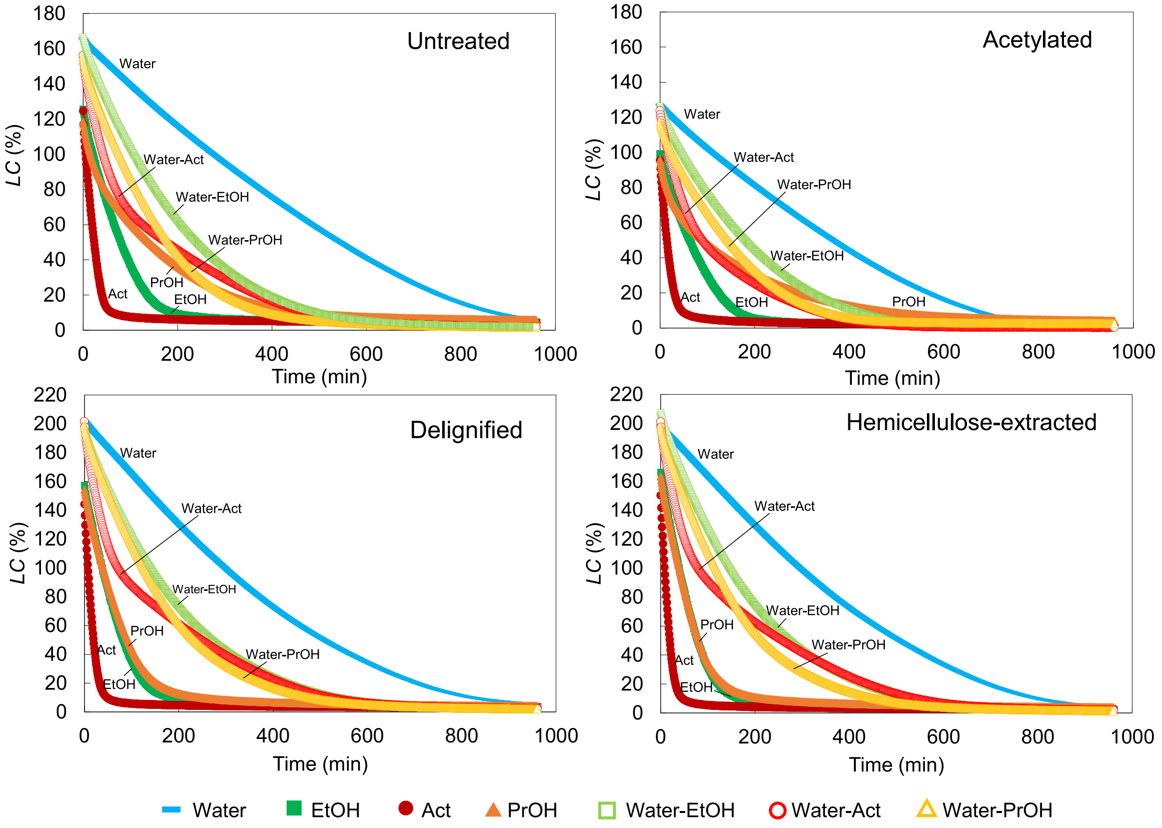

Figure 3: Change in the liquid content (*LC*) of the four groups of conditioned samples during drying.

water–Act sample at around 100 min. The *LC* behavior of each liquid, except PrOH, was similar among the four conditioned samples.

The creep behavior is shown in Figure 4. The magnitude of creep measured for the delignified and hemicellulose-extracted samples was significantly greater than that of the untreated and acetylated samples, with a 10-fold difference between the maximum and minimum J_t values. For the untreated samples, the J_t values measured after 960 min were quite small for the samples treated in organic liquids and large for those treated in the binary liquid mixtures. The time at which J_t increases differs between liquids. The J_t of the samples swollen in Act (with the fastest drying rate) increased immediately after the measurement was started, while that of the sample treated in water (with the slowest drying rate) increased gradually. However, the J_t values obtained after 960 min were larger for the samples treated in water than those of the samples treated in Act. Therefore, factors other than the drying rate of the liquid affect J_t after 960 min. Comparing the J_t after 960 min for the samples treated in organic liquids, the EtOH samples showed the largest values, followed by the Act and PrOH samples. The actual swelling ratio in this experiment could not be measured because the hardness of the sample varies with the treatment conditions of the samples. Therefore, literature values for the swelling ratio of the samples in organic liquids relative to that in water are listed in Table 2, where the swelling ratio decreased in the order of water, EtOH, PrOH, and Act. If the swelling ratios of our samples are equal to the literature values, this implies that the swelling ratio is not proportional to the J_t values at the end of drying. The J_t values after 960 min for the samples treated in binary liquid mixtures, decreased in the order of water–PrOH, water–Act, and water–EtOH. The activities of both constituents in the three mixtures exhibit an appreciable higher activity from the ideal behavior, where the activities of water–Act and water–PrOH are larger than those of water–EtOH (Sakai and Ishimaru 1989). The J_t after 960 min varies depending on the activity of both constituents in the mixtures.

The creep behavior of the acetylated samples was different from that of the untreated samples, and the J_t values were lower for these samples compared to the untreated ones for most liquids, except Act, which exhibited a higher J_t than the equivalent untreated sample. The decrease in J_t measured for the samples swollen in water–Act was

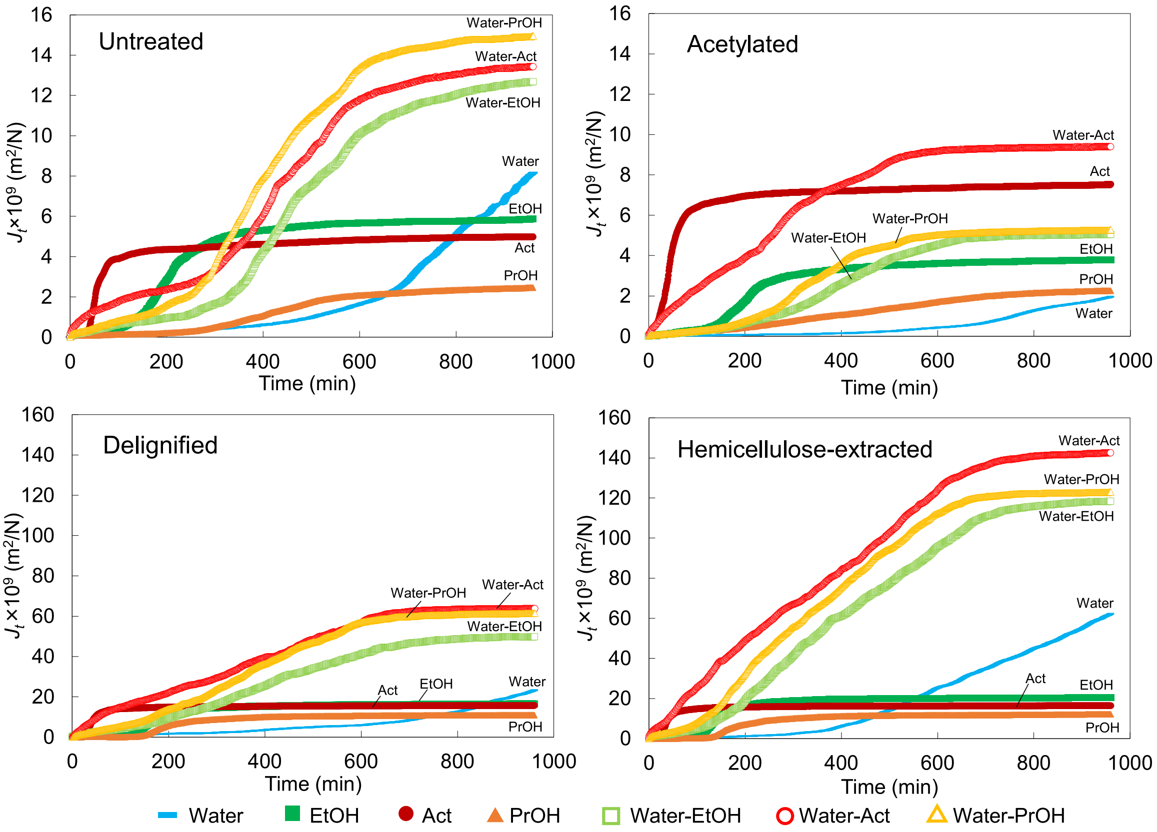

Figure 4: Creep compliance of the four groups of conditioned samples during drying.

smaller than four the samples treated in other binary liquid mixtures. In acetylated wood, the hydrophilic hydroxyl groups of the wood constituents are substituted by hydrophobic acetyl groups. According to the previous reports examining the swelling rates of raw and acetylated wood, the volume swelling due to the organic liquids increases, while the volume swelling due to water decreases after acetylation (Obataya and Gril 2005). Stronger interactions between the wood constituents and liquid result in larger volume swelling of the wood. The decrease in the J_t for samples treated in water may be a result of weaker interactions between the wood constituents and water. However, the slightly lower J_t after acetylation observed for the sample swollen in PrOH does not correspond to the change in the volume swelling via acetylation reported previously (Obataya and Gril 2005). Thus, to discuss the relationship between the wood constituents/liquid interactions and creep behavior, it is necessary to consider the changes in the dimensions and volume of the samples as well as the molecular mobility of the wood constituents that can be analyzed using dynamic viscoelasticity measurements.

In the delignified and hemicellulose-extracted samples, the J_t values were large compared to those of the untreated and acetylated samples. The weight-loss ratios of the delignified and hemicellulose-extracted samples were about 16% and 14%, respectively. Although this difference is small, the observed difference in J_t is large. The J_t values were larger in the hemicellulose-extracted samples than in the delignified samples swollen in water.

3.2 Relationship between *LC* and J_t during drying

To discuss the relationship between the desorption of the liquids and creep behavior, the relationship between the *LC* and J_t is shown in Figures 5 and 6. The creep behavior of the samples swollen with EtOH, Act, and PrOH was similar, and the delignified and hemicellulose-extracted samples showed a larger J_t than that of the other conditioned samples. On the other hand, the creep behavior of the water-swollen samples differed from that observed for those swollen in organic liquids. The J_t of the hemicellulose-extracted samples was much larger than that of the delignified samples. A similar trend is observed for the samples swollen by the binary liquid mixtures (Figure 6). The J_t values of the samples swollen with the binary liquid mixtures were double those of the samples swollen with water. In Figure 5, the four groups of conditioned samples swollen with EtOH, Act, and PrOH showed a large increase in J_t when the *LC* was below 30%. As mentioned in the introduction, the increase in MS creep is caused by the destabilization of the microstructure of wood owing to the desorption of liquid from the wood cell walls. The FSP of water in untreated wood is approximately 30%. Thus, water volatilizes from the cell lumen in the moisture content range above 30%, and water desorbs from the cell wall when the moisture content is below 30% during drying. Although the FSP of the wood modified and/or swollen by the organic liquids in this study is unknown, it is considered that the increase in J_t is related to the desorption of liquid from the wood cell wall below the FSP. However, in Figures 5 and 6, the four conditioned samples swollen with water or binary liquid mixtures showed a linear increase in J_t with decreasing *LC* in the *LC* range above 30%. For the water-swollen wood, drying of the samples begins at the surface, and a moisture gradient is present between the surface and inside the sample for a long time. Therefore, a decrease in the moisture content below the FSP at the surface of the sample resulted in creep at a high moisture content. The change in the *LC* of the samples does not provide sufficient insight into the creep behavior observed for the samples swollen with water and binary liquid mixtures. Therefore, further experiments were required to clarify the observed phenomena, such as observing the changes in shrinkage due to drying.

3.3 Relationship between the elastic modulus and fluidity

Static bending tests were conducted to determine the creep load and MOE of each sample. The relationship between the MOE and J_t after 960 min is shown in Figure 7. The data points for the untreated and acetylated samples are distributed along a similar curve, while the data points for the delignified and hemicellulose-extracted samples are distributed along curves slightly above the untreated and acetylated samples (higher J_t values) in the MOE range of 600–900 $\mathrm{Nm^{-2}}$. However, in the range of lower MOE values, the delignified and hemicellulose-extracted samples show a sharp increase in J_t with decreasing MOE. In the MOE range of 100–200 $\mathrm{Nm^{-2}}$, the J_t values after 960 min of the hemicellulose-extracted samples were larger than those of the delignified samples. The weight-loss ratios of the delignified and hemicellulose-extracted samples were similar (16.1% and 13.9%, respectively), and the MOE values of these samples were also similar. If creep deformation during drying occurs via the same mechanism in both samples, the J_t values after 960 min should be distributed in the same range. Therefore, the observed differences in J_t values between the different sample

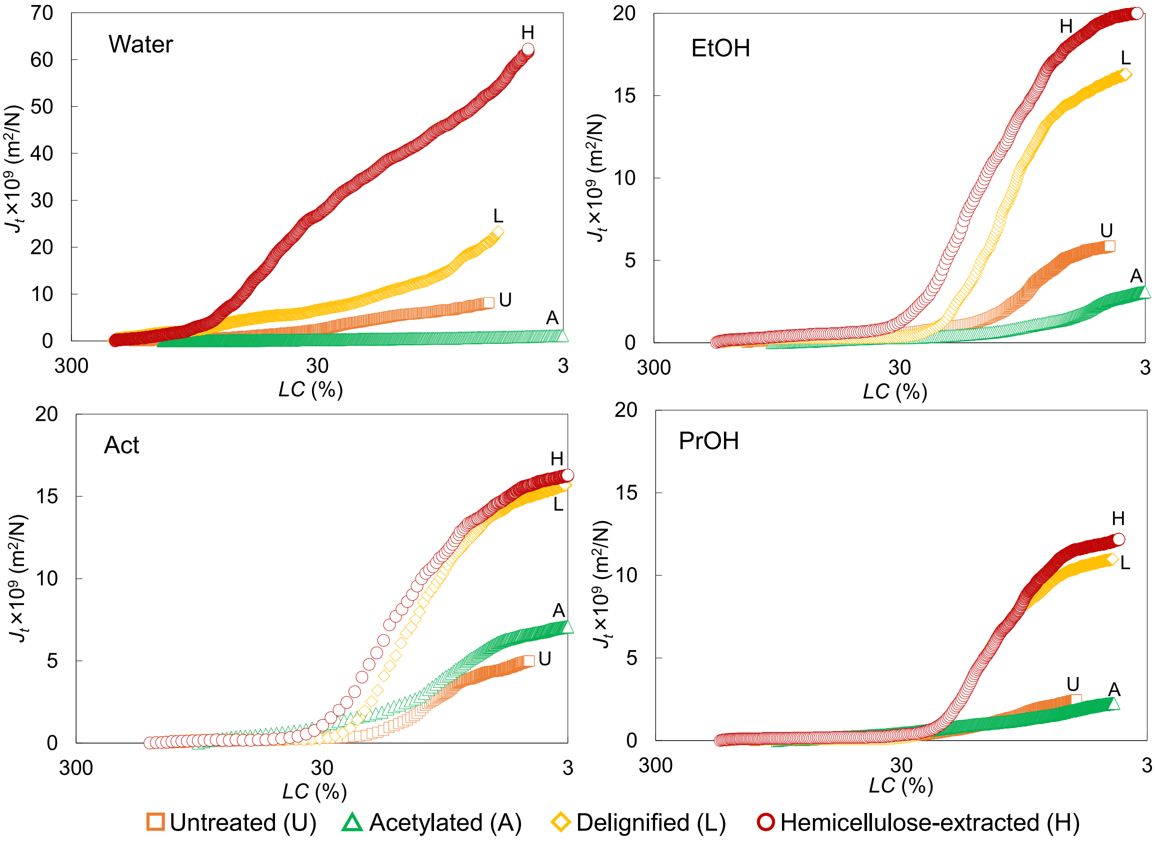

Figure 5: Relationship between creep compliance (J_t) and liquid content (*LC*) of samples swollen by water or organic liquids during drying.

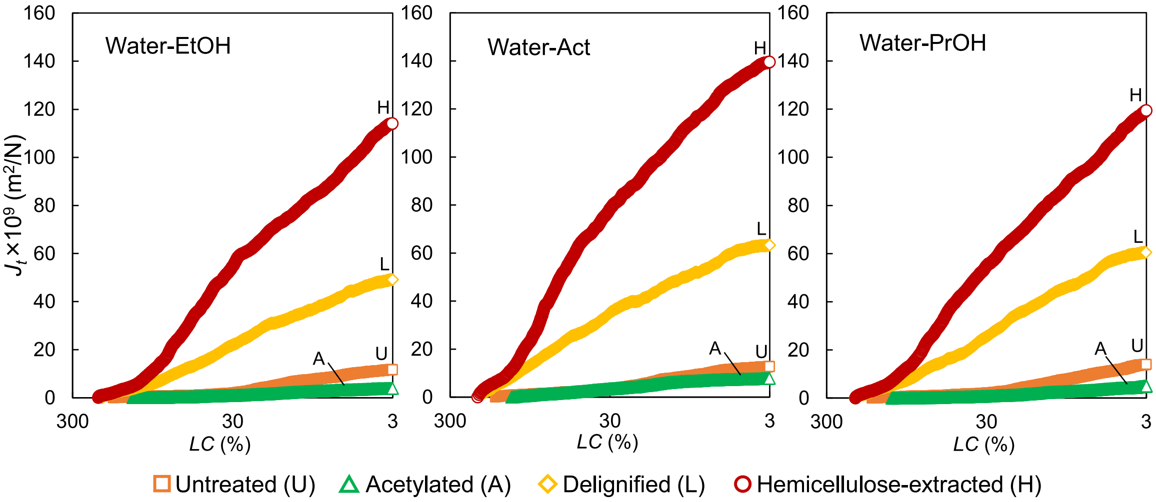

Figure 6: Relationship between creep compliance (J_t) and liquid content (*LC*) of samples swollen by binary liquid mixtures during drying.

groups may indicate a distinct MC creep mechanism in the hemicellulose-extracted sample. Based on the results presented above, the dependence of the observed creep behaviors on the wood-treatment conditions is discussed in the next section.

4 Discussion

Based on the dynamic viscoelastic properties of wood, the relaxation processes attributed to the motion of methylol groups, polysaccharides (hemicellulose) in the swollen

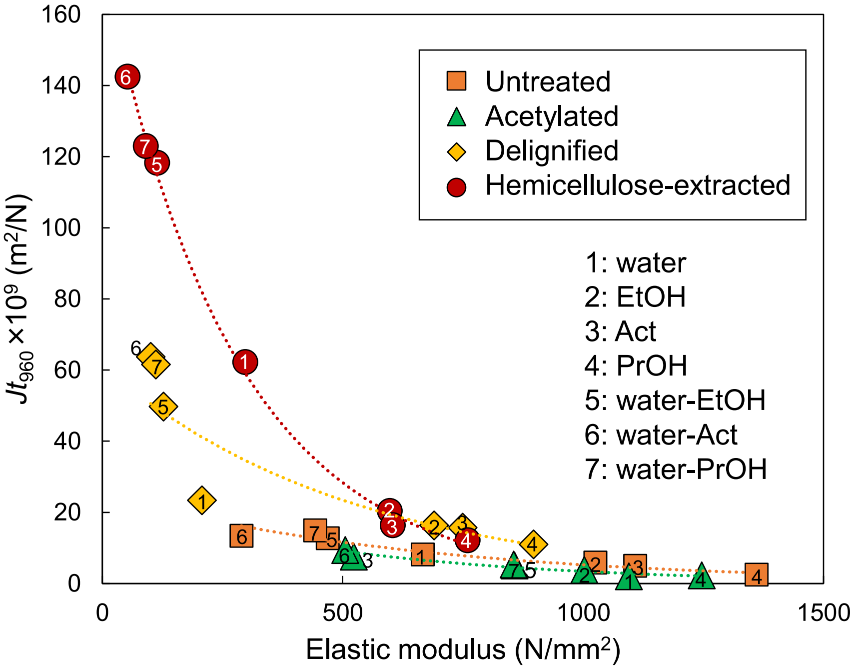

Figure 7: Relationship between creep compliance (J_t) after 960 min and the elastic modulus measured by a static bending test. Abbreviations for liquids are as follows: ethanol, EtOH; 2-propanol, PrOH; acetoneAct. Water:organic liquid mole fraction = 0.8:0.2 for the three binary liquid mixtures (water–EtOH, water–PrOH, and water–Act).

state, and lignin in the swollen state were observed at −100 °C, −40 °C, and 80 °C, respectively (Obataya et al. 1996; Furuta et al. 2001). The relaxation at around 80 °C observed in water-swollen wood is recognized as the lignin T_g (for example, Furuta et al. 2001; Kelley et al. 1987; Salmén 1984). Although the thermal softening temperatures of isolated hemicellulose and lignin increase with decreasing moisture content (Goring 1963; Takamura 1968), the increase of creep deformation during drying measured in this study was significant, even when the moisture content range was above the FSP. Therefore, the results are discussed below in terms of the T_g of each wood constituent in the swollen state.

Based on the temperature-dependent dynamic viscoelasticity measured using untreated Japanese cypress, which is a softwood with a T_g higher than that of hardwood, a T_g of around 90 °C was measured for a water-swollen sample (Miyoshi et al. 2018). However, for the samples swollen by EtOH, PrOH, and Act, a T_g could not be observed (Table 1) and it was concluded that the T_g points were above the measured temperature range (Miyoshi et al. 2018). A comparison of the thermal softening behavior of untreated cypress swollen with water, EtOH, PrOH, and Act (Miyoshi et al. 2018) showed that only the water-swollen sample began to soften gradually above around 20 °C, the temperature at which creep was measured in this study. Meanwhile, Tanaka et al (2019) measured the temperature dependences of the dynamic viscoelasticities of beech and cypress samples swollen by a binary water–EtOH mixture. The relationship between the mole fraction of ethanol and the T_g is shown in Table 1. The T_g of the water-swollen beech sample was observed at 72 °C. However, the T_g of the sample swollen by EtOH could not be observed up to 78 °C. The T_g of the beech sample swollen by the binary liquid mixture shifted to lower temperature with increasing EtOH content in the mixture, and the sample showed the lowest T_g of 40 °C at a water:ethanol molar fraction of 0.8:0.2, which is the condition chosen for the creep tests in this study. Based on the findings of previous studies, there is a correspondence between T_g and J_t after 960 min in untreated wood. It is suggested that a lower T_g of lignin in the swelling equilibrium is related to a larger J_t during drying because the T_g of the hemicellulose in the swollen state is below 0 °C (Furuta et al. 2001). However, for a detailed discussion of the relationship between the creep behavior during drying and the molecular mobility of the wood constituents, it is necessary to study the viscoelastic properties in the non-equilibrium state because the thermal softening temperature of lignin and hemicellulose depend on liquid content.

In the acetylated wood sample, hydrophobic acetyl groups fill the cell wall. The T_g of the acetylated wood is above room temperature for both dry and water-swollen samples (Sugiyama and Norimoto 1996). Therefore, acetyl groups introduced into the cell wall may not act as plasticizers at room temperature. If the interactions between the wood constituents and the liquid are not strong, creep deformation will decrease with decreasing free volume owing to the presence of acetyl groups. The J_t after 960 min was decreased by acetylation for almost all the samples, except for the Act-swollen acetylated samples, which showed an increase in J_t after this treatment. The decrease in J_t after 960 min for the acetylated sample swollen by water–Act was smaller than that of the samples swollen by the other mixtures. A similar tendency was observed for the acetylated sample swollen by PrOH. A comparison of the T_g values of the acetylated samples in the swelling equilibrium state (Table 1) shows the lowest value for PrOH except for Act among the liquids used in the creep tests (Miyoshi et al. 2018). The T_g was unclear in the acetylated sample swollen by Act; however, its tanδ value was much larger than that of the untreated sample swollen by Act from −10 to 40 °C (Miyoshi et al. 2018). The wood constituents in an amorphous region swollen by Act may be in the rubber state, even at 20 °C where the creep tests were conducted. In the acetylated sample, both the decrease in free volume due to acetylation and the change in T_g based on the affinity between the acetylated wood constituents and the liquid are expected to control creep deformation.

In the delignified sample swollen by water, the T_g is lower than that of the untreated sample (Furuta et al. 2010). The relationships between the weight-loss ratio of the delignified and hemicellulose-extracted samples and the T_g measured by Furuta et al. (2010) are shown in Table 1. A decrease in the T_g is observed even when the weight-loss ratio due to the delignification is only approximately 0.3% (Furuta et al. 2010). In the Furuta et al. (2010) report, it is considered that the crosslinking density of lignin decreases even with a mild delignification treatment; the T_g decreases due to the loosening of the lignin network. The order of the J_t values after 960 min were similar for the delignified and untreated samples. According to Figure 4, the samples swollen with the three binary liquid mixtures showed the highest creep values, followed by water, EtOH, Act, and PrOH. Therefore, the decrease in T_g due to the delignification treatment affects the increase in creep deformation. The mechanism of MS creep for the delignified samples is expected to be the same as that for the untreated samples.

It has been reported that in hemicellulose-extracted samples, the T_g derived from lignin does not change significantly, even if the extraction treatment causes a weight-loss ratio of approximately 20% (Furuta et al. 2010). This report suggests that the hemicellulose extraction treatment does not change the structure of lignin. Thus, when the hemicellulose-extraction is performed, hemicellulose is removed while lignin is maintained. In the wood cell wall, hemicellulose is linked to cellulose chains and lignin by hydrogen and chemical bonds, respectively (Fukushima 2011). If the hemicellulose connected to lignin and cellulose is removed, it is assumed that the interface is prone to displacement when liquid molecules enter the gap between lignin and cellulose molecules or when external forces are applied that change the distance between the constituent molecules. In addition, Figures 5 and 6 show that the increase in J_t of the hemicellulose-extracted sample is significant for samples swollen with water and binary liquid mixtures. This behavior may occur owing to the reduction of the resistance to fluidity deformation, because polar water adsorbs on the hydroxyl groups on the surface of the cellulose chain, increasing the intermolecular distance between cellulose and hemicellulose/lignin. The above results showed that; the hemicellulose-extracted samples exhibited large Jt values owing to a different deformation mechanism compared to that of other samples.

5 Conclusions

Creep tests were performed during the drying of the four groups of conditioned samples (untreated, acetylated, delignified, and hemicellulose-extracted samples), which were swollen using the water, organic liquids, and binary liquid mixtures thereof. The creep mechanisms were discussed in terms of the interactions between the wood constituents and swelling liquids. The following conclusions are proposed obtained.

In the untreated samples, creep deformation tended to be large for the wood samples swollen by high-swelling liquids. However, a clear relationship between the swelling rate and creep deformation could not be confirmed. For the untreated samples, a lower T_g of lignin at swelling equilibrium was related to higher creep deformation during drying. The creep deformation of acetylated samples was small during drying of most liquids. Both the decrease in fluidity due to bulking by hydrophobization and the change in T_g based on the affinity between the acetylated wood constituents and the liquid are thought to control the creep deformation. Significantly higher creep deformation was observed for the delignified samples than the untreated samples. It was expected that the lower T_g of lignin under swollen conditions of delignified samples would result in increased creep deformation. However, even larger creep deformation was observed for the hemicellulose-extracted samples than for the delignified samples. The enhanced creep of the hemicellulose-extracted samples was attributed to a creep mechanism different from that of other samples, because the weight-loss ratio and reduction in

MOE after extraction were similar to those of the delignified samples, and the T_g of lignin in the swollen state did not decrease after hemicellulose-extraction. It was assumed that the interface is prone to displacement when polar liquid molecules enter the gap between lignin and cellulose and external forces are applied because the hemicellulose connected to lignin and cellulose was removed.

Abbreviations

Act	acetone
EtOH	ethanol
J_t	creep compliance
LC	liquid content
PrOH	2-propanol
T_g	glass transition temperature

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