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Solute diffusion into cell walls in solution-impregnated wood under conditioning process II: effect of solution concentration on solute diffusion

Soichi Tanaka[1] · Masako Seki[2] · Tsunehisa Miki[2] · Ichinori Shigematsu[2] · Kozo Kanayama[1]

Abstract This study focused on solute diffusing into cell walls in solution-impregnated wood during conditioning, process of moderate drying of solvent. To clarify the effect of solution concentration on the diffusion during the conditioning, weight percent gain (WPG) and relative swelling of the wood sample impregnated with an aqueous solution of polyethylene glycol (PEG) polymers at a concentration of 10, 20, 30, 40, or 50 mass% were examined during the conditioning and subsequent drying processes. The relation between the concentration and the relative swelling after all processes, an indicator of the amount of the polymers in cell walls, exhibited a concave-downward curve with a maximum value at 20 mass%. The estimated mass of the polymers in cell walls just before conditioning increased with the concentration. This indicates that the distribution of the polymers changed during conditioning. The estimated mass just before conditioning and the relative swelling after all processes were normalized to the packing ratios of the polymers in cell walls. The ratio after all processes subtracted by that just before conditioning was larger than the ratio just before conditioning, and increased with the concentration up to 20 mass%; after which it decreased. This indicates that the majority of the polymers in cell walls increased during conditioning, and that the

amount of the polymers that diffused into cell walls was at the maximum at concentration of 20 mass%. This was explained by two factors: the decrease in the diffusivity into cell walls and in the concentration difference of the polymers between cell walls and cell cavity with the concentration, based on the behavior of WPG during conditioning; and the estimated minimum concentration at which the solution contains the least amount of polymers to fill the cell walls.

Keywords Impregnated wood · Conditioning · Relative humidity · Solute diffusion · Solution concentration

Introduction

Wood is chemically treated to control its physical properties, such as its dimensional stability and mechanical properties [1]. The chemical treatment here refers to treatment that does not destroy the crystalline structure of the cellulosic microfibrils in wood cell walls [2]. In such a treatment, the physical properties of wood are controlled by manipulation of the hydroxyl groups and surrounding chemical bonds. The treatment is classified into several types, including heat treatment, acetalization, esterification, etherification, formations of wood-plastic composite (WPC) and wood-inorganic composite (WIC), and treatments with phenol formaldehyde resin, polyethylene glycol (PEG), etc. [2]. All these types of treatments involve either effect of crosslinking, hydrophobic, or bulking, or the combination of these effects. The bulking effect is especially important because it contributes to the majority of chemical treatments, except heat treatment and formalization.

✉ Soichi Tanaka
soichi_tanaka@rish.kyoto-u.ac.jp

1 Research Institute for Sustainable Humanosphere, Kyoto University, Uji 611-0011, Japan

2 Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan

The bulking effect prevents intrusion of water into the amorphous region by introducing the bulking agent into the region and swelling it. When the chemical substance is hydrophobic, solid, has high viscosity, or has high molecular weight, however, the substance itself may not easily impregnate into the amorphous region. In such cases, the chemicals are often dissolved in a solvent with a high ability to swell the amorphous region. The solvent is usually removed once the impregnation is completed. Both the solvent and the substance are present in the amorphous region, and thus after the solvent is removed, the region contains space that can absorb water. To treat wood completely with the chemical substance, this space has to be also filled with the substance. Therefore, we focused on the mechanism whereby a non-volatile substance diffuses into cell walls during the conditioning, or process of moderate drying of solvent, of wood impregnated with a solution of the substance, as suggested by Stamm [3].

Figure 1a–c show the treatment process including impregnation and conditioning, the phenomena at the cellular level during the process [3], and the state of the amorphous region during the process, respectively. For impregnation (Fig. 1a), the wood is soaked in a solution of a non-volatile chemical substance (solute), then placed under a vacuum (or subjected to pressure) while in contact with the treatment solution. For conditioning (Fig. 1a), the impregnated wood is placed under an atmosphere. For both processes, migration of the solute and solvent occurs at the cellular level (Fig. 1b):

- During impregnation, the solution uniformly permeates the cell walls and cell cavities.
- During conditioning, a greater amount of solvent evaporates from the cell cavities than from the cell walls, which increases the concentration of solute in the cavities compared to the walls. This concentration difference causes the solute to diffuse from the cavities to the walls [3].

The solute permeability during impregnation has been studied by many researchers using PEG polymer as a solute [3–14], which was summarized in our previous paper [15]. The mechanism of a solute diffusing into cell walls during conditioning has, however, never been verified. The amount of the solute in the cell walls will increase if the diffusion of the solute is promoted during the conditioning, but will not increase if the diffusion is not promoted (Fig. 1b). The solute will fill the amorphous regions in the former case, while in the latter it will be present in only part of the regions (Fig. 1c). Therefore, there exists the possibility of maximizing the amount of the solute in the cell walls, or of filling the amorphous region with the solute more rapidly by optimizing the conditioning.

Fig. 1 a Treatment process, b phenomena at the cellular level, and c state of amorphous region, for wood treated with a non-volatile chemical substance (solute)

a Treatment process
(1) Untreated (2) Impregnation (3) Conditioning (4) After all processes

b Phenomenon at the cellular level

c State of amorphous region in cell wall
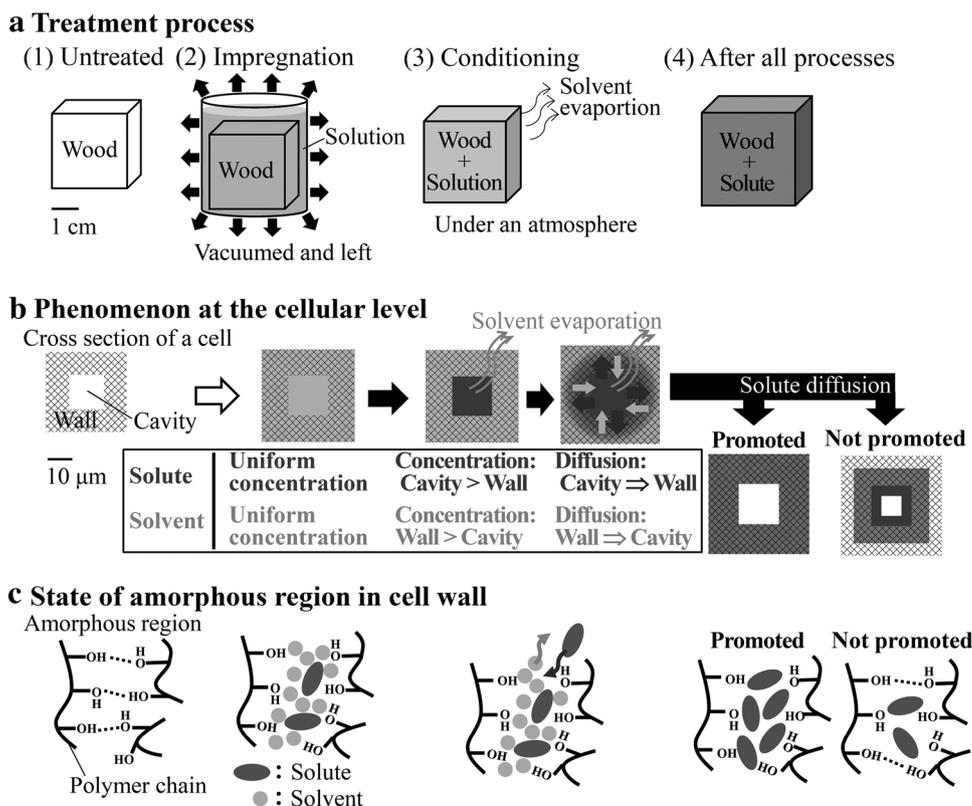
The objective of this study is to determine the conditions that maximize the amount of the solute diffusing into the cell walls of solution-impregnated wood during the conditioning process in a short time. First, it is necessary to choose a method to evaluate the amount of the solute in the cell walls. Previous studies have shown that the mass and dimensions of wood samples impregnated with solution are related to the amount of the solute and solvent, if PEG and water are employed as the solute and solvent, respectively [3, 4, 9–13]. The solution is able to permeate the permanent pores, or cell cavities, and the transient pores in the amorphous region in the cell walls. The mass and dimensions of wood under treatment may increase with the total mass of the solution in the treated wood and the volume of solution in its transient pores, respectively. After the solvent is completely removed from the treated wood, its mass and dimensions increase with the mass of the solute in it and the volume of solute in its transient pores, respectively. Assuming that the solute itself has a constant density, the amount of the solute in the cell walls is estimated by the dimensions of the treated wood. The variation in mass of the impregnated wood under conditioning indicates evaporation of the solvent. Second, it is necessary to predict the condition that affects the amount of the solute diffusing into the cell walls. This amount is directly determined by:

- Concentration difference of the solute between the cell walls and cell cavities.
- Solute diffusivity.

These two factors are affected mainly by solution conditions such as concentration and type of solute and solvent, material conditions such as wood species and dimension, and atmospheric conditions such as temperature and vapor pressure of the solvent [or relative humidity (RH) when the solvent is water].

In our previous papers [15, 16], focusing on the RH in the atmospheric conditions, the mass and dimensions of wood impregnated with an aqueous solution of PEG polymers with 30 mass% concentration were measured during conditioning at different RHs and after subsequent drying in a vacuum. It was verified that the polymers diffused into the cell walls and substituted water there during the conditioning, and that the amount of the diffused polymers was controlled by the RH, and was maximum at approximately RH = 80 %. In this paper, we focused on the concentration in the solution condition. Previous studies [3, 17] have reported that the amount of the PEG polymers increased with the concentration after all treatment processes. In these studies, however, the RH was not controlled [17] or the concentration was lower than 18 mass% [3], and there was no consideration regarding the effect of the concentration on the polymer diffusing into cell walls during conditioning. Since our previous study

[15, 16] showed that the concentration of the solution present in wood affected the diffusivity and concentration difference of the polymers, the amount of diffusion during conditioning may depend on the concentration of impregnated solution.

The purpose of this paper was to clarify the effect of concentration of impregnated solution on solute diffusing into cell walls during the conditioning process of impregnated wood. The PEG polymers and water were employed as the solute and solvent, respectively, because the dimensions and mass of the impregnated wood in this case reflect the amount of the polymers and water in it. The mass and dimensions of wood samples impregnated with aqueous solutions of PEG polymers at different concentrations were examined during the conditioning and subsequent drying processes, and are discussed with respect to the water evaporation and the amount of the polymers in the cell walls. The mass and volume of the polymers in the cell walls just before conditioning and after all processes, respectively, were estimated and normalized to analyze the amount of the polymers diffusing into the cell walls during conditioning.

Materials and methods

Fifteen cross-cut wood samples, with dimensions of 5 mm × 25 mm × 25 mm in longitudinal (L), radial (R), and tangential (T) directions, respectively, were subsequently prepared from a block of hinoki (*Chamaecyparis obtusa*). The samples were impregnated with deionized water and left in it for more than 2 weeks, and their mass and area in RT cross section (m_A and s_A, respectively) were measured. They were then dried at 105 °C to relatively constant mass m_O, their RT-cross-sectional area (s_O) and volume (v_O) were measured, and their average oven-dry density was estimated to be 0.289 g/cm^3. The three dried samples were impregnated with an aqueous solution of PEG polymers (PEG1540, E.P., Wako) with density $\rho_C = 1.13$ g/cm^3 and concentration $U = 10, 20, 30, 40$, or 50 mass%, and left in the solution to reach relatively constant mass and dimensions.

The impregnated samples were conditioned under an atmosphere at 35 °C with the RH controlled according to the two-term conditioning schedule (Fig. 2). The RH was controlled at 83 % during the 1st term for 2161 h ($=t_1$) using a supersaturated solution of potassium chloride (KCl) [18], and subsequently controlled at 11 % during the 2nd term for 84 h ($=t_2 - t_1$) using a supersaturated solution of lithium chloride (LiCl) [18]. The mass and RT-cross-sectional area of the samples related to the conditioning time t ($m(t)$ and $s(t)$, respectively), were measured. The weight percent gain (WPG), swelling coefficient, and relative
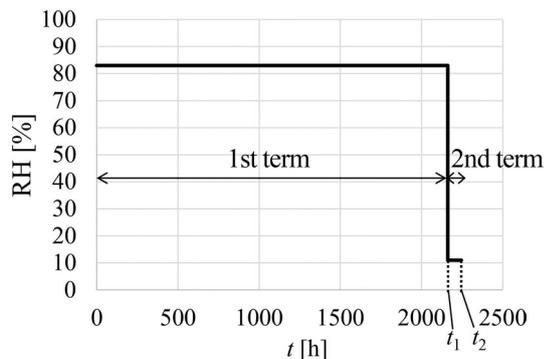
Fig. 2 Conditioning schedule for relative humidity (RH). t conditioning time

swelling as a function of the time t ($W(t)$, $\alpha(t)$, and $r(t)$, respectively) were calculated as follows:

$$W(t) = \frac{100\{m(t) - m_O\}}{m_O} \ [\%], \tag{1}$$

$$\alpha(t) = \frac{s(t) - s_O}{s_O}, \tag{2}$$

$$r(t) = \frac{s(t) - s_O}{s_A - s_O}. \tag{3}$$

The conditioned samples were dried at 35 °C in a vacuum chamber with phosphorous pentoxide (P_2O_5), and then the mass and RT-cross-sectional area (m_V and s_V, respectively) were measured, and the swelling coefficient and relative swelling (α_V and r_V, respectively) were calculated as follows:

$$\alpha_V = \frac{s_V - s_O}{s_O}, \tag{4}$$

$$r_V = \frac{s_V - s_O}{s_A - s_O}. \tag{5}$$

The data employed in the estimation in the Results and discussion section are summarized in Table 1.

Results and discussion

WPG and relative swelling during conditioning

Figure 3a shows the temporal variability of WPG (W) during conditioning with RH schedule according to Fig. 2 for the samples impregnated with different solution concentrations. In the 1st term, the value of W for each concentration decreased during 0–100 h reaching each constant value. In the 2nd term, the value decreased rapidly to be constant soon after the term begun. The decrease in WPG is due to the evaporation of water from the samples. Our previous studies [15, 16] showed that water evaporates from the cell cavities much more readily than from the cell walls, which results in a higher concentration of the PEG polymers in the cell cavities than in the cell walls. Thus, the water evaporation shown in Fig. 3a was thought to cause the concentration difference, which is the driving force behind the diffusion of the polymers into the cell walls. The values of W at the equilibrium points of the 1st and 2nd terms increased with the solution concentration (U) (Fig. 3a), which indicates that the samples impregnated with the solution with lower concentration had higher moisture content at the early stage of the conditioning.

Figure 3b shows the temporal variability of relative swelling (r) during conditioning for different solution concentrations. At all concentrations, the samples swelled during the 1st term, while they shrunk during the 2nd term. The swelling and shrinkage are caused by the PEG polymers diffusing into the cell walls and the water exuding from the cell walls, respectively [15, 16]. Thus, the diffusion of the polymers into the cell walls was promoted, especially during the 1st term.

Relative swelling at each stage of processes

Figure 4 shows the relation of r to U at each stage of the processes. The value of r increased slightly with U just

Table 1 Data for the estimation

Concentration of impregnated solution	Oven-dried samples before treatment		Samples just before conditioning	Samples after all processes
U (mass%)	Mass m_O (g)	Volume v_O (cm^3)	Swelling coefficient for RT[b] cross section $\alpha(0)$ (%)	Mass m_V (g)
10	0.859 ± 0.002[a]	2.972 ± 0.021	6.979 ± 0.149	1.070 ± 0.005
20	0.857 ± 0.001	2.985 ± 0.003	6.850 ± 0.071	1.319 ± 0.001
30	0.856 ± 0.012	2.952 ± 0.033	6.900 ± 0.033	1.577 ± 0.023
40	0.862 ± 0.006	2.989 ± 0.019	6.953 ± 0.062	1.886 ± 0.015
50	0.858 ± 0.008	2.968 ± 0.022	7.191 ± 0.111	2.187 ± 0.012

[a] Standard deviation

[b] Radial-tangential
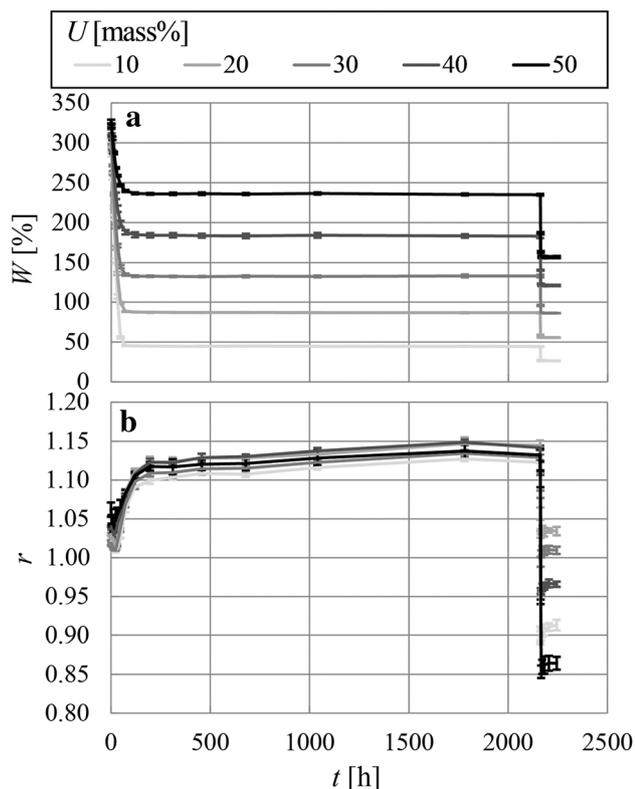
Fig. 3 Temporal variability during conditioning in **a** weight percent gain (W) and **b** relative swelling (r) of samples impregnated with different concentrations of solution (U). *Bars* standard deviations

Fig. 4 Relation of relative swelling (r) to concentration of impregnated solution (U) at each stage of the processes. *Bars* standard deviations

before the conditioning, and was constant for all values of U just after the 1st term. The relation of r to U exhibited a concave-downward curve with a maximum value of r at $U = 20$ mass% just after the 2nd term and after all processes. The value of r after all processes is considered to be proportional to the amount of the PEG polymers in the cell walls, because the samples do not contain any water after drying in a vacuum with P_2O_5. These findings indicate that the relation between the concentration U and the amount of the polymers in the cell walls exhibits a concave-downward curve, with the maximum point at $U = 20$ mass% after all processes. It was, however, unclear when the trend between U and the amount of the polymers in the cell walls develops. The contribution of drying in a vacuum with P_2O_5 to the diffusion of the polymers into cell walls seemed to be small, because the relation of r to U after all processes was similar to that just after the 2nd term (Fig. 4). Thus, this trend was considered to occur during the impregnation and/or conditioning processes. To clarify which processes contributed to this trend, it was necessary to evaluate the amount of polymers in the cell walls just before conditioning.

Estimated amount of polymers in cell walls just before conditioning

The mass of the PEG polymers in cell walls just before the conditioning [$m_W(0)$] was estimated using the following steps. Figure 5a–c show the distribution of solution in wood for the untreated samples in the oven-dry condition, just before conditioning, and after all processes, respectively. The estimation was based on the following assumptions.

1. None of the polymers migrate between the sample and surrounding atmosphere in the processes except during impregnation.
2. The extract with density of ρ_E migrates from the cell walls into the solution during the impregnation, and the mass ratio of the migrated extract to the untreated sample in the oven-dry condition is f_E. The values of ρ_E and f_E are equal to 1 g/cm³ and 0.055 [19], respectively.
3. The concentration of the solution present in the cell cavity just before the conditioning is equal to that of the impregnated solution ($U/100$).
4. The densities of the water, PEG polymers, and extract remain constant regardless of their state or location.
5. The densities of the wood substance and water, ρ_{CW} and ρ_M, are equal to 1.5 [20] and 1.0 g/cm³, respectively.
6. The volume of the cell cavity has a constant value of $v_O - (1 - f_E)m_O/\rho_{CW} - f_E m_O/\rho_E$ over all processes (Fig. 5a–c).

The mass of the PEG polymers in the sample was formulated as $m_V - (1 - f_E)m_O$, based on assumptions 1 and 2.

Fig. 5 Distribution of solution in wood sample at each stage of the processes. Formula in each element represents its mass and/or volume. m_O and v_O, mass and volume of the untreated samples, respectively; f_E, mass ratio of migrated extract to the untreated sample; $\alpha(0)$ and α_V, swelling coefficient just before conditioning and after all processes, respectively; ρ_{CW}, ρ_E, ρ_S, and ρ_C, densities of wood substance, extract, solution, and solute, respectively
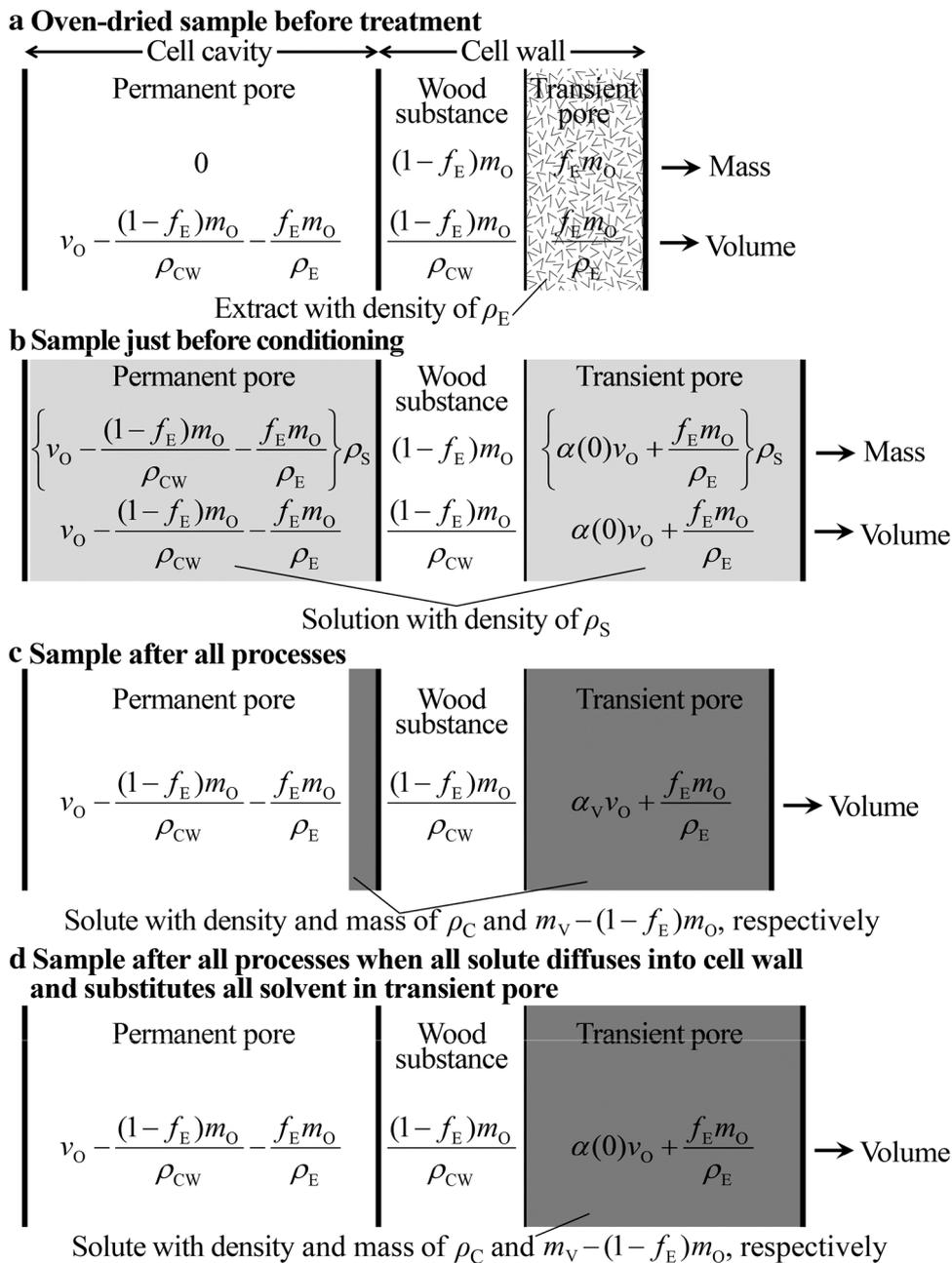
Based on assumptions 3, 4, and 6, the mass of the polymers in the cell cavities was formulated as $\{v_O - (1-f_E)m_O/\rho_{CW} - f_E m_O/\rho_E\}\rho_S U/100$, where ρ_S represents the density of the solution. Using these formulae, $m_W(0)$ was formulated as $m_V - (1-f_E)m_O - \{v_O - (1-f_E)m_O/\rho_{CW} - f_E m_O/\rho_E\}\rho_S U/100$. The density ρ_S was formulated as Eq. (10) (see "Appendix" section); accordingly, $m_W(0)$ was formulated as follows:

$$m_W(0) = m_V - (1-f_E)m_O - \left\{v_O - \frac{(1-f_E)m_O}{\rho_{CW}} - \frac{f_E m_O}{\rho_E}\right\} \times \frac{U\rho_C\rho_M}{(100-U)\rho_C + U\rho_M}.$$

(6)

The value of $m_W(0)$ for each solution concentration U was estimated using Eq. (6), the values in Table 1 and assumptions 2 and 5.
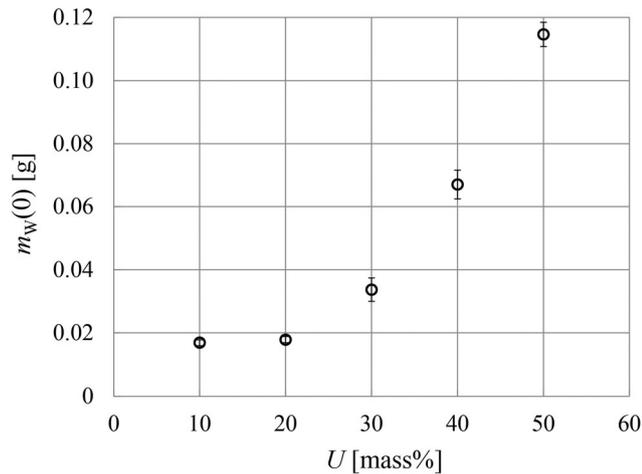
Fig. 6 Relation between impregnated-solution concentration (U) and mass of the polymers in cell walls just before conditioning [$m_W(0)$]. *Bars* standard deviations

Figure 6 shows the relation between U and $m_W(0)$. The value of $m_W(0)$ increased with U, whose trend was clearly different from that for the relation between U and the amount of the polymers in cell walls after all processes (shown by closed circle in Fig. 4). This difference indicates the distribution of the polymers changed during conditioning, which was considered to be caused by the polymers diffusing into the cell walls during the conditioning. The amount of the polymers that diffused during the conditioning, however, remains unclear. To clarify this amount, a normalized indicator is required that represents the amount of the polymers in the cell walls just before conditioning and after all processes.

Amount of diffused polymers during conditioning

As the normalized indicator, the packing ratio of the PEG polymers in cell walls (p) was defined as "the volume ratio of the transient pore filled with the polymers to that created by the solution just before conditioning". The packing ratios of the polymers in cell walls just before the conditioning and after all processes ($p(0)$ and p_V, respectively) were estimated using the following steps. The estimation was based on the following assumptions in addition to assumptions 1–6.

7. The transient pore filled with the extract with volume of $f_E m_O/\rho_E$ before impregnation (Fig. 5a) is filled with the impregnated solution just before conditioning (Fig. 5b).
8. The deformation of the sample in the longitudinal direction is negligible.
9. The swelling of the sample caused by the solution or PEG polymers is sufficiently larger than that caused by the extract.

The mass of the PEG polymers that can theoretically fill the transient pore created by the solution just before conditioning was $\rho_C\{\alpha(0)v_O + f_E m_O/\rho_E\}$ (Fig. 5b) based on assumptions 2–4, 7, and 8. The $m_W(0)$ was just before the conditioning. The volume ratio is equal to the mass ratio when the pore is filled with the same substance (Assumption 4); thereby $p(0)$ was formulated as follows:

$$p(0) = \frac{m_W(0)}{\rho_C\left\{\alpha(0)v_O + \frac{f_E m_O}{\rho_E}\right\}}. \tag{7}$$

Based on assumptions 1, 2, 4, and 8, the packing ratio after all processes (p_V) was the volume ratio of the transient pore after all processes, $\alpha_V v_O + f_E m_O/\rho_E$ (Fig. 5c), to that just before conditioning, $\alpha(0)v_O + f_E m_O/\rho_E$ (Fig. 5b), resulting in the relation $p_V = \{\alpha_V + f_E m_O/(\rho_E v_O)\}/\{\alpha(0) + f_E m_O/(\rho_E v_O)\}$. In this relation, the term $f_E m_O/(\rho_E v_O)$ was negligible compared to α_V and $\alpha(0)$ based on assumption 9, and the ratio of α_V to $\alpha(0)$ was equal to that of r_V to $r(0)$. Therefore, p_V was formulated as follows:

$$p_V \approx \frac{\alpha_V}{\alpha(0)} = \frac{r_V}{r(0)}. \tag{8}$$

The values of $p(0)$ and p_V for each U were estimated using Eqs. (7) and (8), respectively, with the values in Table 1, Figs. 4 and 6, and assumption 2.

Figure 7 shows the relations of $p(0)$ and p_V to U. This figure also shows the relation between U and the difference of the two packing ratios, $p_V - p(0)$, which is approximately equal to the normalized amount of the PEG polymers that diffused during conditioning. The difference, $p_V - p(0)$, was much larger than and similar to $p(0)$ at $U = 10$–40 mass% and 50 mass%, respectively, which
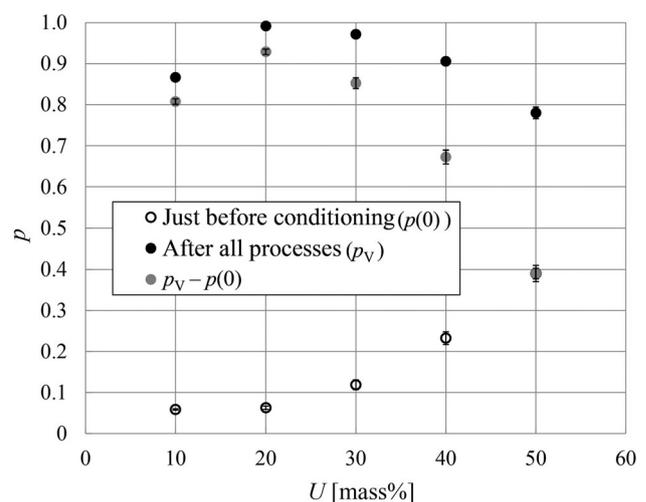
Fig. 7 Relations of packing ratios (p) just before conditioning and after all processes ($p(0)$ and p_V, respectively) to impregnated-solution concentration (U). *Bars* standard deviations

indicates that the majority of the polymers diffusing into cell walls during conditioning if solution concentration was not so high. The relation of $p_V - p(0)$ to U exhibited a concave-downward curve with a maximum value at $U = 20$ mass%. This indicates that the amount of the polymers diffusing into cell walls during conditioning decreased with a more than 20 mass% increase in solution concentration, and that the amount of the polymers in the sample impregnated with the solution with concentration less than 20 mass% might be smaller than the minimum concentration needed for polymers to fill the cell walls. The cause of the former indication and verification of the latter are described in the following sections.

Cause of negative correlation between concentration and amount of polymers diffusing into cell walls

It was verified in our previous studies that the amount of the PEG polymers diffusing into cell walls increased with the diffusivity [15] and the concentration difference [16] of the polymers. From the perspective of these two factors, the effect of the solution concentration on the amount of the diffused polymers is explained as follows.

The diffusivity of the PEG polymers into cell walls is known to increase with the moisture content of the sample [13]. At an early stage of the conditioning, the sample impregnated with the solution with lower concentration was indicated to have higher moisture content (Fig. 3a). This was considered to contribute to the increase in the amount of the diffused polymers with the decrease in the concentration.

The concentration difference between the PEG polymers in cell cavities and cell walls was verified to increase with the amount of water evaporated from the sample in previous studies [15, 16]. The relation between U and the decrease in WPG ($-\Delta W$) during each term is shown in Fig. 8. The value of $-\Delta W$, representing the amount of water evaporated from the samples, during the 1st term was larger than that during the 2nd term and drying in a vacuum. The value during the 1st term decreased as U increased. These findings indicate that the concentration difference occurred especially during the 1st term and decreased with the increase in the solution concentration, which was considered to contribute to the increase in the amount of diffused polymers with the decrease in the concentration.

Estimation of minimum concentration for filling cell walls with polymers

The minimum concentration at which the solution contains the least amount of the polymers required to fill the cell walls was estimated using the following steps. The
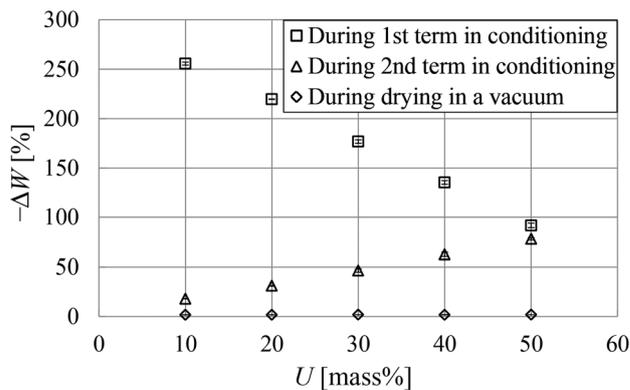
Fig. 8 Relation between impregnated-solution concentration (U) and decrease in weight percent gain ($-\Delta W$) during each term in conditioning and drying. *Bars* standard deviations

estimation was based on the following assumptions in addition to assumptions 1–8.

10. The volume of transient pores in cell walls just before conditioning is equal to that after all processes (Fig. 5b, d).
11. All the PEG polymers in cell cavities diffuse into transient pores in the cell walls during conditioning (Fig. 5d).

The mass of the solution filling both cell cavities and transient pores with volumes of $v_O - (1 - f_E)m_O/\rho_{CW} - f_E m_O/\rho_E$ and $\alpha(0)v_O + f_E m_O/\rho_E$, respectively, was $\{v_O - (1 - f_E)m_O/\rho_{CW} + \alpha(0)v_O\}\rho_S$ (Fig. 5b), based on assumptions 1–4, 6–8, and 10. Based on assumption 4, this solution contained the PEG polymers whose mass was $\{v_O - (1 - f_E)m_O/\rho_{CW} + \alpha(0)v_O\}\rho_S U/100$, which is equal to the mass of the polymers present in the sample just before conditioning. The mass of the polymers that filled the transient pores after all processes was $\rho_C\{\alpha(0)v_O + f_E m_O/\rho_E\}$ (Fig. 5d). Based on assumption 11, the mass of the polymers present in the sample just before conditioning was equal to the mass of the polymers that filled the transient pores after all processes, resulting in the relation $\{v_O - (1 - f_E)m_O/\rho_{CW} + \alpha(0)v_O\}\rho_S U/100 = \rho_C\{\alpha(0)v_O + f_E m_O/\rho_E\}$. By substituting Eq. (10) (see "Appendix" section) for the ρ_S in this relation and then solving for U, the following equation was obtained:

$$U = \frac{100\left\{\alpha(0)v_O + \frac{f_E m_O}{\rho_E}\right\}\rho_C}{\left\{v_O - \frac{(1-f_E)m_O}{\rho_{CW}} - \frac{f_E m_O}{\rho_E}\right\}\rho_M + \left\{\alpha(0)v_O + \frac{f_E m_O}{\rho_E}\right\}\rho_C} \quad [\text{mass}\%].$$

(9)

The minimum concentration was estimated using Eq. (9) with the values in Table 1 and based on assumptions 2 and 5.

The estimated minimum concentration was 10.7 ± 0.2 mass%, which was lower than $U = 20$ mass% at which the

amount of the PEG polymers diffusing into cell walls was at the maximum. This indicates that the polymers remained in the cell walls after all processes if the conditioning processes were controlled. This was because the chemical potential reached the equilibrium point only when some polymers were present in the cell cavity.

Conclusion

To clarify the effect of the concentration of the impregnated solution on the solute diffusing into the cell walls during conditioning, WPG (W), and relative swelling (r), of the wood sample impregnated with an aqueous solution of PEG polymers with $U = 10, 20, 30, 40,$ or 50 mass%, were examined during the conditioning and subsequent drying processes. The relation of r to U after all processes, the indicator of the amount of polymers in cell walls, exhibited a concave-downward curve with a maximum value at $U = 20$ mass%. The estimated mass of polymers in cell walls just before conditioning [$m_W(0)$] increased with U. This indicates that the distribution of the polymers changed during conditioning. The value of $m_W(0)$ just before conditioning and the value of r after all processes were normalized to the packing ratios of the polymers in cell walls, $p(0)$ and p_V, respectively. The difference $p_V - p(0)$ was larger than $p(0)$ and increased with U up to 20 mass% and then decreased. This indicates that the majority of the polymers in cell walls increased during conditioning, and that the amount of the polymers that diffused into cell walls was at a maximum at $U = 20$ mass%. This was explained by two factors: the decrease in the diffusivity into cell walls and in the concentration difference between cell walls and cell cavity of the polymers with the concentration, based on the behavior of W during conditioning; and the estimated minimum concentration at which the solution contains the least amount of the polymers required to fill the cell walls.

Appendix

The relation between the density and concentration of the solution was estimated as follows. Based on assumption 4, the volume of the solution was equal to the sum of the volumes of the solvent and solute, $m_M/\rho_M + m_C/\rho_C$, where m_M and m_C represent the mass of the solvent and solute, respectively, in the solution. The mass of the solution was $m_M + m_C$; thereby the concentration and density of the solution (U and ρ_S, respectively) were formulated as $U = 100m_C/(m_M + m_C)$ and $\rho_S = (m_M + m_C)/(m_M/\rho_M +$

$m_C/\rho_C)$. From these formulae, the following equation was obtained.

$$\rho_S = \frac{100\rho_C\rho_M}{(100 - U)\rho_C + U\rho_M}. \tag{10}$$

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