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A novel method of acetylation of wood using supercritical carbon dioxide

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Abstract Sugi heartwood was acetylated with acetic anhydride in supercritical carbon dioxide (CO₂) (120°C or 130°C, 10–12 MPa). As a result, the weight percent gain increased with increasing acetylation time up to 16%–20% at 1 h and 24%–28% at 24 h. The antismelling efficiency of the acetylated specimens reached 75%–80% at 3–4 h of acetylation. It is supposed that the acetylation in supercritical CO₂ has a high bulking effect compared with liquid-phase and vapor-phase acetylation with uncatalyzed acetic anhydride. The results showed that the acetylation progressed rapidly because supercritical CO₂ and acetic anhydride formed a single phase at more than 90°C, and the acetic anhydride reached the reaction sites in the wood quickly.

Key words Supercritical carbon dioxide · Acetylation · Sugi wood · Antismelling efficiency · Bulking

Introduction

Cellulose, hemicellulose, and lignin, which are the main components of wood, have many hydroxyl groups that adsorb water molecules. Adsorption and desorption of water cause the swelling and shrinkage of wood, which result in various problems such as warping, cracking, and dimension change. Therefore, it is very important to provide wood with dimensional stability against water.

Acetylation is one of the superior chemical modification methods for improving the dimensional stability of wood and, to some extent, acetylation has been put to practical use.¹ Stamm and Tarkow,² Clermont and Bender,³ and Rist and Arseneau⁴ reported that the hygroscopicity of wood

was decreased by acetylation and that dimensional stability against the effects of water was improved. Stamm⁵ and Minato et al.⁶ reported that the bulking effect rather than the decreased hygroscopicity was a major factor in the dimensional stabilization provided by acetylation. In addition, Goldstein et al.⁷ and Rowell et al.^{8,9} reported that acetylated wood has high weathering- and termite-resistant properties, and Norimoto et al.¹⁰ and Sasaki et al.¹¹ reported that the variations of the mechanical, rheological, and acoustical properties of wood that occur under humidity change were suppressed by acetylation.

This study investigated a new acetylation method using supercritical carbon dioxide (CO₂) (critical point: 31°C/7.4 MPa). Supercritical CO₂ diffuses and penetrates as does gas but has solvating properties that approach those of a liquid. Supercritical CO₂ has already been used as a caffeine extraction solvent for coffee beans and as a hop extraction solvent for beer. Its use in the washing of precision machines and semiconductors¹² as well as in dry cleaning¹³ has been investigated. The application of research on supercritical CO₂ treatment of wood includes the following: selective extraction of useful chemical components in wood,¹⁴ removal of heavy metals from chromated copper arsenate (CCA)-treated wood,¹⁵ and preservative treatment of wood-based composites.^{16,17} The authors reported that the water permeability of wood was improved by pretreating the wood with supercritical CO₂ that would remove substances which inhibit the permeation.¹⁸ We also clarified that wood preservatives, such as tebuconazole and 3-iodo-2-propynyl butylcarbamate (IPBC), were caused to penetrate into the core of wood specimens by supercritical CO₂ treatment.¹⁹ It has been shown that ability of supercritical CO₂ to penetrate into the core of wood is useful in extractive and preservative treatments. Therefore, it is expected that the acetylation reagent can be made to penetrate into the core of wood by supercritical CO₂ so that acetylation of wood can take place.

In this study, we aimed to develop a new acetylation method using supercritical CO₂. We acetylated wood in supercritical CO₂ and measured the weight percent gain (WPG), percent increase in oven dry volume (bulking), and

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antiswelling efficiency (ASE). The performance of the acetylated wood was evaluated, and the acetylation mechanism in supercritical CO₂ was investigated.

Materials and methods

Materials

Specimens [5 mm (L) × 20 mm (R) × 20 mm (T)] were prepared from sugi (*Cryptomeria japonica* D. Don) heartwood. The specimens were extracted with ethanol/benzene (v/v = 1:2) for 96 h using a Soxhlet extractor and boiled in water under reflux for 10 h. The mean value of the extractives content was 5.1%.

Acetylation of wood in supercritical CO₂

Schematic diagrams of the supercritical CO₂ treatment apparatus and the inside of the reaction container are shown in Figs. 1 and 2, respectively. Two oven-dried specimens and 3.0 ml acetic anhydride (more than 97.0% purity) (Wako Chemical Industries, Osaka, Japan) were sealed in a batch container (inner diameter, 35 mm; height, 93 mm)

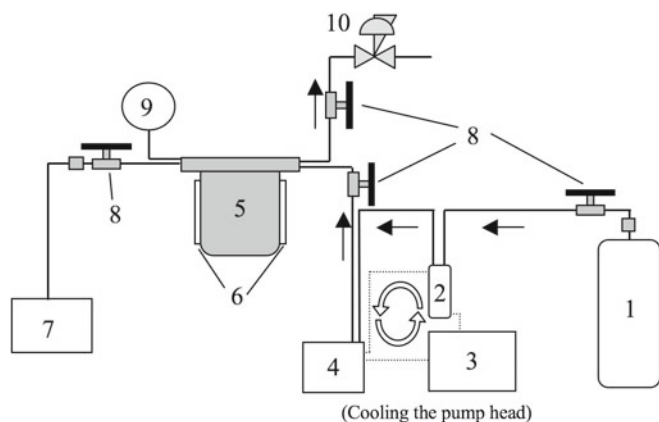
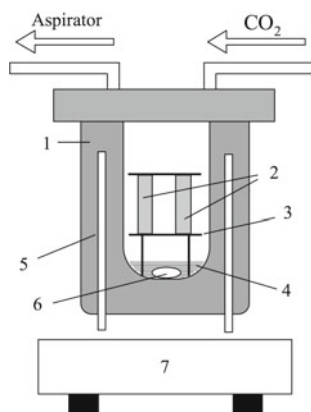


Fig. 1. Schematic diagram of the supercritical CO₂ treatment apparatus. 1, CO₂ cylinder; 2, condenser; 3, cold water circulator; 4, pump; 5, batch container; 6, electric heater; 7, aspirator; 8, valve; 9, pressure gauge; 10, back-pressure regulator

Fig. 2. Schematic diagram of the inside of the reactor container. 1, batch container; 2, wood specimen; 3, table; 4, acetic anhydride; 5, electric heater; 6, stirrer bar; 7, magnetic stirrer



with observation windows made of sapphire glass. The inner part of the container was evacuated using an aspirator and was then filled with CO₂ (>99.9% purity) (Nichigo Nikko, Tokyo, Japan). First, CO₂ was directly transferred from a gas cylinder (inner pressure, 6.5 MPa) to the container. Cooled and liquefied CO₂ was then injected into the container, using a pump to raise the pressure to 7.0 MPa. The temperature was controlled at 120° or 130°C using an electric heater installed outside the container. The internal pressure of the container reached 10.0 MPa when the temperature was increased to 50°–60°C, and then the pressure was maintained in the range of 10.0–12.0 MPa using the back-pressure regulator while the temperature was raised to the target values within 35–40 min. The acetylation time was defined as zero when the internal temperature of the container reached the target values. Acetylation of wood was performed by stirring with a magnetic stirrer (approximately 300 rpm) for 0–63 h.

An experiment to confirm the progress of the acetylation while raising the temperature to the target values was performed. The container was heated from room temperature, and the acetylation was finished when the temperature reached 90° or 110°C. It took 18–23 min or 25–28 min, respectively, for the temperature to increase from room temperature to each target temperature.

Liquid-phase and vapor-phase acetylation

Liquid-phase and vapor-phase acetylation of wood were performed with uncatalyzed acetic anhydride as controls to compare the result of acetylation with that in supercritical CO₂. The experimental devices were prepared separately from the supercritical CO₂ treatment apparatus. The treatment methods were based on the papers of Obataya and Yamauchi^{20,21} and Nishino.²²

In the case of liquid-phase acetylation, two specimens were soaked for 24 h in acetic anhydride (100 ml) at room temperature under vacuum by an aspirator and were then moved to another vessel containing acetic anhydride (200 ml) heated to 120°C beforehand. The acetylation was carried out for 1–120 h.

In the case of vapor-phase acetylation, two specimens and 5.0 ml acetic anhydride were put in a reaction vessel (2 l). The vessel was vacuum-evacuated by an aspirator for 5 min and was then heated in an oven at 120°C for 1–168 h.

Measurement of WPG, bulking, and ASE

Acetylated specimens were leached in running water for 1 week. After air-drying at room temperature, the specimens were oven-dried at 60°C under vacuum for 48 h. The oven-dried weight and dimensions of the specimens were measured, and WPG and bulking were calculated.

The specimens were then immersed in water under vacuum by an aspirator for 1 week, and the swelling coefficient was measured. ASE was calculated from the swelling

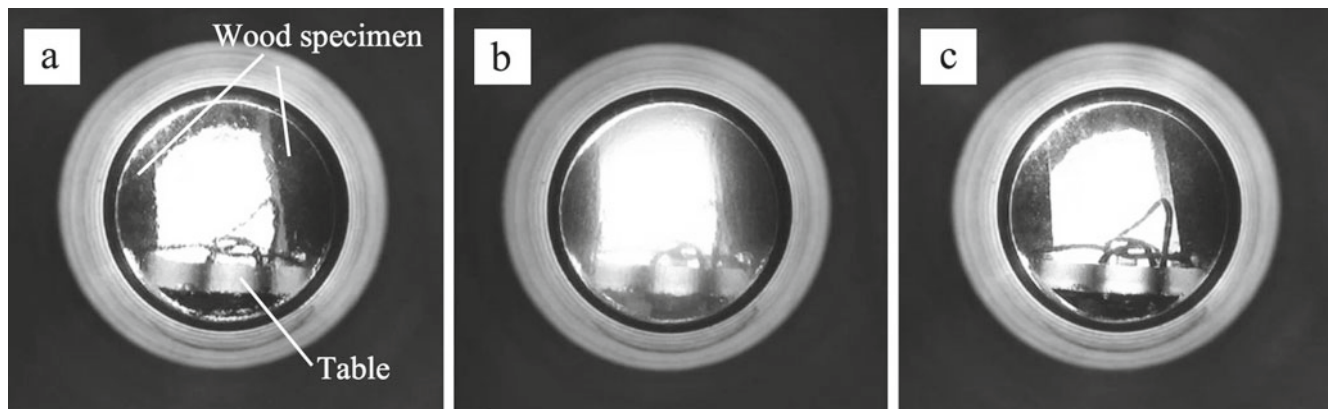


Fig. 3. Changes in the appearance of the inside of the reaction container during the temperature increase. **a** 50°C/10.0 MPa; **b** 70°C/10.7 MPa; **c** 90°C/10.7 MPa

coefficient of untreated (D_0) and treated (D) specimens according to the following equation:

$$ASE (\%) = (D_0 - D) / D_0 \times 100$$

The effect of acetylation method on ASE and bulking was examined by statistical analysis. Analysis of variance was performed using WPG as a covariate. Statistical computation was performed using SPSS (SPSS 17.0 software package; SPSS), and the significance level (P) was determined.

Results and discussion

Acetylation in supercritical CO₂ during the temperature increase process

The supercritical CO₂ treatment apparatus used in this study takes 35–40 min to reach the target temperature. The first experiment was thus focused on the phase behavior of the supercritical CO₂–acetic anhydride mixture during the temperature increase process, because the phase behavior of the mixture should affect the diffusion of acetic anhydride in wood as well as the extent of acetylation.

Figure 3 shows the changes in appearance of the inside of the reaction container during the temperature increase process. The photographs were taken through the sapphire window of the container. From room temperature to 70°C, the mixture was colorless and transparent, as is normal supercritical CO₂. A fine mist appeared from about 70° to 90°C. At temperatures above 90°C, the mist disappeared and the inside of the container became transparent again. The state of transparency was maintained even after the target temperatures were reached (120° and 130°C).

These results suggest that acetic anhydride started to diffuse as a fine mist in supercritical CO₂ at about 70°C, and that the fluid mixture finally turned into a single phase at temperatures higher than 90°C. Byun et al.²³ reported the phase behavior of a supercritical CO₂–acetic acid mixture. The mixture was compressed to a single phase, and the pressure was decreased until a second phase appeared.

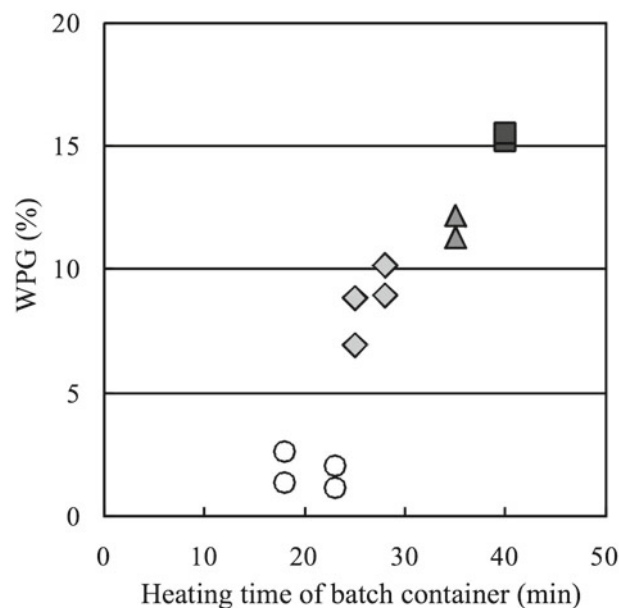


Fig. 4. Relationship between weight percent gain (WPG) and heating time of batch container from room temperature. Circles, 90°C; diamonds, 110°C; triangles, 120°C; squares, 130°C

They observed the appearance of a fine mist as an indicator of the dew point. The dew points were observed in conditions such that the pressure and the mole fraction of acetic acid were 10.37 MPa/0.047, 11.86 MPa/0.061, and 12.57 MPa/0.076, respectively. In our study, the mole fraction of acetic anhydride was about 0.060 at 70°C and about 0.074 at 90°C. These values are similar to those at which Byun et al. observed the dew point (as a mist), which supports our explanation of the phase behavior of the supercritical CO₂–acetic anhydride mixture in the temperature increase process.

Figure 4 illustrates the WPG of the specimens in the temperature increase process. Each specimen was taken out of the reaction container to stop the reaction when the temperature reached 90°C, 110°C, or the target value (120° or 130°C). The WPG of the specimens increased greatly at

110°C, whereas increase of WPG was slight at 90°C. It was concluded that the acetylation progressed rapidly in a very short time because the increase of the temperature from 90° to 110°C took only several minutes. WPG increased with increasing temperature and reached about 15% at 130°C (about 40 min after the heating was begun).

It was shown that the acetylation of wood was possible in supercritical CO₂. Moreover, it was recognized that the acetylation progressed rapidly after the temperature in the container reached 90°C. Based on the aforementioned results, it is suggested that the acetic anhydride reached the reaction sites in the wood quickly because supercritical CO₂ and acetic anhydride formed a single phase at temperatures greater than 90°C. In addition, Goldstein et al.⁷ reported the best acetylation condition to be uncatalyzed acetic anhydride in xylene at 100°–130°C. This temperature range is almost the same as the one in which supercritical CO₂ and acetic anhydride form a single phase. Therefore, it is reasonable that WPG increased greatly within the few minutes in which the temperature rose from 90°C to 110°C.

Features of acetylated wood treated in supercritical CO₂

The relationship between WPG and acetylation time in supercritical CO₂ was investigated. Acetylation time was defined as zero when the internal temperature of the container reached the target value, i.e., 120° or 130°C (Fig. 5). The results of liquid-phase and vapor-phase acetylation with uncatalyzed acetic anhydride performed in this study are included in Fig. 5. For the specimens acetylated in supercritical CO₂, the WPG was 12%–16% when the acetylation time was zero. WPG increased with increasing acetylation time to around 20% at 3–4 h and 24%–28% at 24 h.

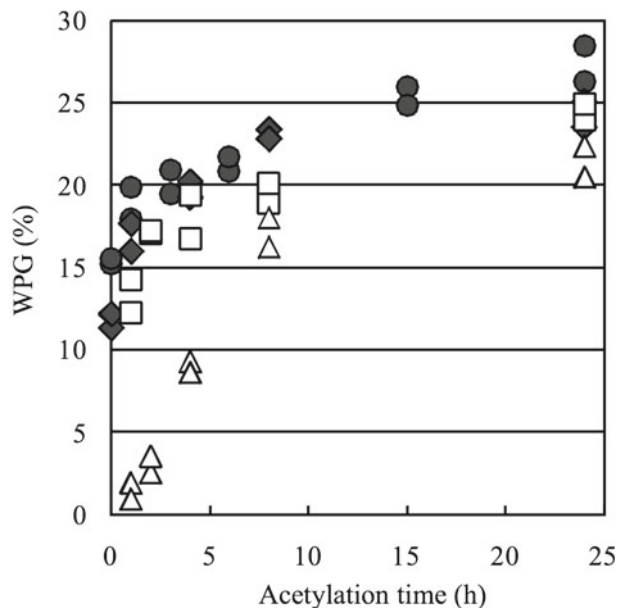


Fig. 5. Relationship between WPG and acetylation time. *Filled diamonds*, supercritical CO₂ (120°C); *filled circles*, supercritical CO₂ (130°C); *open squares*, liquid phase; *open triangles*, vapor phase

Acetylation in supercritical CO₂ at 130°C showed a higher WPG overall than that at 120°C.

Figure 6 shows the relationship between ASE and acetylation time. For the specimens acetylated in supercritical CO₂, ASE was 50%–70% when the temperature reached the target values. Furthermore, ASE increased up to 60%–76% after 1 h. It was shown that high dimensional stability was obtained in a short acetylation time using supercritical CO₂. Three or four hours later, the ASE was maintained at high values of around 75%–80%. It is known that the ASE of acetylated wood increases linearly up to around 15%–20% of WPG and then levels off.²⁴ In the case of acetylation in supercritical CO₂, it is considered that the increase of ASE leveled off after 3–4 h acetylation because WPG reached about 20% after 3–4 h acetylation.

According to the calculation based on the assumption of Nishino,²² the number of hydroxyl groups that can be acetylated in x g of oven-dried softwood is $9.46 \times 10^{-3} x$ mol. The mean value of the oven-dried weight of the specimen used in this study was 0.597 g. Therefore, the number of hydroxyl groups that can be acetylated in our specimens is assumed to be 5.64×10^{-3} mol on average. Based on this value, the molar ratio of the acetic anhydride to hydroxyl groups used here was calculated to be 2.83 for supercritical CO₂, 4.70 for vapor phase, and 188 for liquid phase. The ratio for supercritical CO₂ may even be smaller because acetic anhydride could partly be exhausted with CO₂ from the back-pressure regulator during the temperature increase process: about 30% of acetic anhydride was possibly lost from 70°C (at which acetic anhydride started to diffuse into CO₂) to 120°C, based on the exhaustion rate of CO₂ in the same temperature range. Therefore, it was clarified that acetylated wood which had a high dimensional stability of around 80% ASE could be produced by acetylation in supercritical CO₂ in a

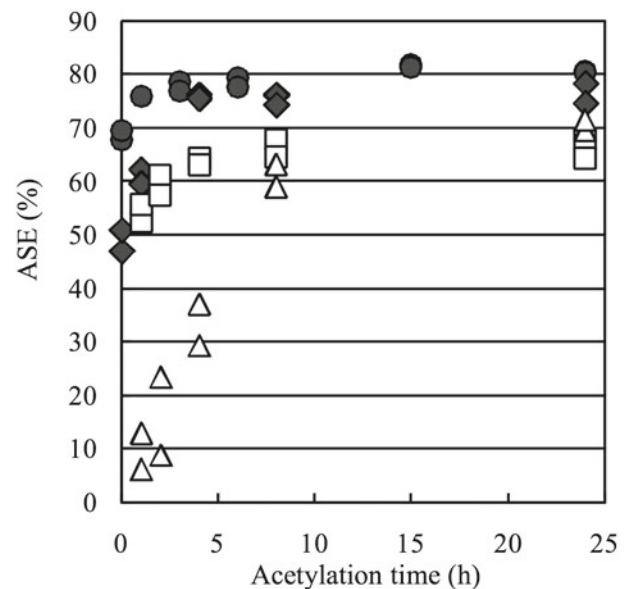


Fig. 6. Relationship between antiswelling efficiency (ASE) and acetylation time. *Filled diamonds*, supercritical CO₂ (120°C); *filled circles*, supercritical CO₂ (130°C); *open squares*, liquid phase; *open triangles*, vapor phase

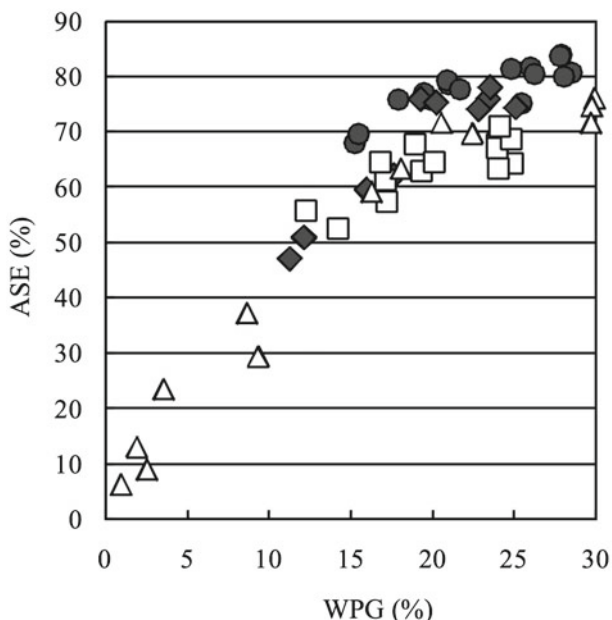


Fig. 7. Relationship between ASE and WPG. *Filled diamonds*, supercritical CO₂ (120°C); *filled circles*, supercritical CO₂ (130°C); *open squares*, liquid phase; *open triangles*, vapor phase

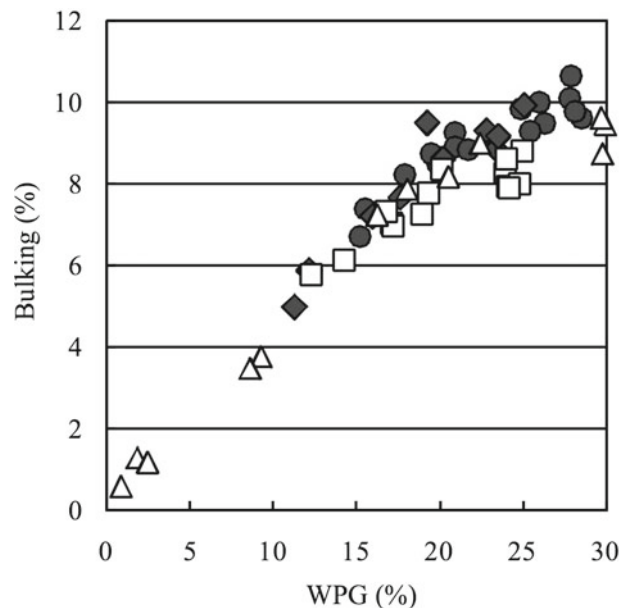


Fig. 8. Relationship between bulking and WPG. *Filled diamonds*, supercritical CO₂ (120°C); *filled circles*, supercritical CO₂ (130°C); *open squares*, liquid phase; *open triangles*, vapor phase

short treatment time with little acetic anhydride consumption at the same level as in the vapor phase.

Figure 7 shows the relationship between ASE and WPG. Above 15% WPG, ASE of the acetylation in supercritical CO₂ was higher than that of the liquid-phase and vapor-phase acetylation with uncatalyzed acetic anhydride. Analysis of variance was then performed for the plot of WPG greater than 15%. As a result, differences in ASE of acetylation in supercritical CO₂ (120° or 130°C) and conventional acetylation (liquid phase or vapor phase) were statistically significant (maximum value, $P = 0.030$).

It was reported that the bulking effect was a major factor in the dimensional stabilization by acetylation.^{5,6} It was also reported that the ASE of the wood improves as the bulking effect of the acetylation is enhanced.²⁵ Thus, the relationship between bulking and WPG was investigated for each acetylation in this study (Fig. 8). Above 15% WPG, acetylation in supercritical CO₂ caused a higher bulking effect than other conventional acetylation processes. The results of analysis of variance for the plot of WPG greater than 15% showed that the differences in bulking of acetylation in supercritical CO₂ (120° or 130°C) and conventional acetylation were statistically significant (maximum value, $P = 0.048$).

From these results, we can conclude that acetylation in supercritical CO₂ has a higher bulking effect and leads to higher ASE compared with other conventional acetylation processes when WPG is above 15%. The detailed reasons for the finding that acetylation in supercritical CO₂ causes a higher bulking effect are under investigation. As one possibility, it is thought that supercritical CO₂ treatment with high pressure has some influence on the swelling of the cell wall. It has been proved that the initial swelling results in

faster reaction and greater bulking.²⁶ In our previous paper¹⁸ about improvement of the water permeability of sugi heartwood by pretreatment with supercritical CO₂, a slight increase in the dimensions of the specimens was observed after the treatment (L direction, <0.07%; R and T directions, <0.32%). It is also possible to assume that acetylation in supercritical CO₂ might enhance the reactivity of cellulose and hemicelluloses. Although these polysaccharides are responsible for the moisture sorption and swelling of wood, they are much less reactive than lignin in conventional acetylation.^{27,28} Therefore, if supercritical CO₂ enables easier penetration of acetic anhydride into the polysaccharides, it should effectively enhance the dimensional stability of wood. The effect of acetylation in supercritical CO₂ on the swelling state of the cell wall and the reactivity of polysaccharides should be investigated in detail in future work.

Conclusions

Sugi heartwood was acetylated with acetic anhydride in supercritical CO₂ (120° or 130°C, 10–12 MPa). The acetylation promptly progressed with little acetic anhydride consumption at the same level as vapor-phase acetylation, and acetylated wood that had 75%–80% ASE could be produced in 3–4 h. It is supposed that the acetylation in supercritical CO₂ caused a higher bulking effect, because acetylation in supercritical CO₂ had higher bulking than the liquid-phase and vapor-phase acetylation performed in this study at WPG of more than 15%. It is indicated that supercritical CO₂ and acetic anhydride started to form a single

phase at around 90°C and therefore the acetic anhydride reached the reaction sites in the wood quickly.

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