ORIGINAL ARTICLE

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Potassium acetate-catalyzed acetylation of wood at low temperatures II: vapor phase acetylation at room temperature

Abstract Ezomatsu wood blocks were impregnated with potassium acetate (KAc) and then exposed to acetic anhydride vapor at 25°C and 120°C. The KAc-impregnated wood was rapidly acetylated at 120°C, and only 6 min was needed to achieve 20% weight percent gain (WPG). The WPG increased with increasing catalyst loading (CL), but it turned to decrease above 20% CL probably because the diffusion of acetic anhydride vapor was hindered by excess KAc depositing in the cell lumina. Thus, careful control of CL is necessary in the vapor-phase acetylation. KAc was also effective in catalyzing the vapor-phase acetylation at 25°C: the KAc-impregnated wood attained 20% WPG within 7 days, whereas the WPG did not exceed 10% even after 1 month in the uncatalyzed system. Irrespective of treatment methods, the hygroscopicity of wood was reduced and its dimensional stability was improved with an increase of WPG. These results confirm that the use of KAc simplifies the acetylation process at room temperature with minimal loss of acetic anhydride.

Key words Acetylation · Potassium acetate · Catalyst · Dimensional stability

Introduction

Acetylation is an effective method to improve the practical performances of wood. Wood acetylation is usually performed in liquid acetic anhydride at high temperatures to assure uniform modification in shorter reaction time. This liquid-phase treatment, however, requires the take-up of a large excess of reactant solution during the treatment and removal afterward, and, as a result, vapor-phase acetylation has been attempted by several researchers. According to Stamm and Tarkow,[1] 20%–25% weight gain (weight percent gain; WPG) is achieved within 6–12 h at 90°C using 20% pyridine/acetic anhydride as a vapor-generating solution. Baird[2] showed that the reaction time could be shortened by elevating the temperature, and that the WPG exceeded 20% in 1–2 h at 130°C. More recently, Rowell et al.[3] found that the vapor-phase acetylation was much slower than the liquid-phase treatment at 120°C, while both treatments gave the same WPG after 24 h. All these results suggest the possibility of vapor-phase acetylation, but high reaction temperature is required in such cases.

We recently found that potassium acetate (KAc) enables sufficient acetylation of solid wood at low temperatures (20°–40°C).[4,5] For example, 20% WPG is attained within 24 h at 40°C when the wood is previously impregnated with KAc. If KAc is also effective in vapor-phase treatment, the reaction system could be simplified and the loss of chemical could be minimized. In this article, we describe the catalytic effects of KAc in vapor-phase acetylation at room temperature (25°C). In addition, the reduced hygroscopicity and improved dimensional stability achieved by low-temperature acetylation are compared with those resulting from conventional treatment at high temperature (120°C).
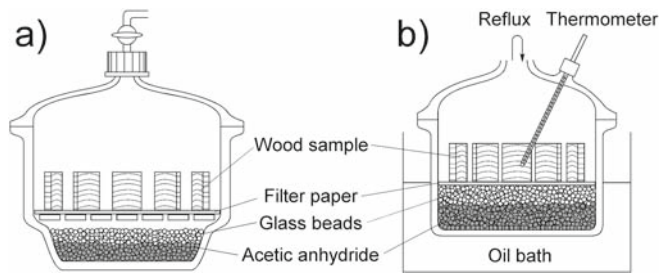
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Materials and methods

Wood samples

Cross sections of ezomatsu (*Picea jezoensis* Carr.) measuring 25 (radial) × 25 (tangential) × 5 mm (longitudinal) were used. Some of the irregular specimens were excluded on the basis of their density and volumetric swelling in water. The density of the selected specimen was 0.37 ± 0.01 g/cm^3 in a completely dry condition, and its volumetric swelling in water was $13.2\% \pm 0.7\%$.

Fig. 1a, b. Apparatus for vapor-phase acetylation at **a** 25°C and **b** 120°C

Fig. 2. Volumetric swelling due to catalyst impregnation (ΔV_{cat}) as a function of catalyst loading (*CL*). *Straight line* depicts the calculated value

Catalyst impregnation

The wood specimens were soaked in 2.5%, 5%, 10%, 20%, and 40% aqueous solutions of KAc under reduced pressure overnight. The specimens were air-dried at room temperature for at least 2 days, and then oven-dried at 105°C for 12 h.

KAc-catalyzed acetylation in vapor phase

Figure 1 illustrates the apparatus for vapor-phase acetylation. For room temperature treatment, six wood specimens (ca. 5 g) were put in a desiccator (inner volume: ca. 2500 cm^3) in which 100 ml of acetic anhydride (AA) was placed, and the pressure in the desiccator was reduced by using an aspirator to induce sufficient vaporization of AA. To prevent rippling of the AA liquid, glass beads were placed in the bottom of the desiccator. The desiccator was then kept at 25° ± 1°C for 1, 2, 4, 7, 12, 20, and 30 days. Similar settings were used for treatment at 120°C, while an oil bath and a reflux condenser were attached to a flask (inner volume: ca. 1000 cm^3) for the heating and recovery of AA. The reaction times were 0.5, 1, 2, 3, 6, 12, and 30 min for the KAc-catalyzed acetylation, and 6, 12, 30, 45, 60, and 120 min for the uncatalyzed acetylation.

After the prescribed reaction time, the specimens were picked up and immediately soaked in ice–water to stop the reaction. The specimens were then leached in running water for at least 3 days to remove the remaining acetic anhydride, acetic acid, and KAc. The leached specimens were air-dried for 2 days and then oven-dried at 105°C for 12 h before the oven-dry weights and dimensions were measured.

Moisture sorption and dimensional stability tests

The unmodified and acetylated wood specimens were conditioned at 20°C and 57% relative humidity (RH) for 1 month and then the equilibrium moisture contents (*M*) were determined. The specimens were then soaked in water at room temperature for 24 h under reduced pressure and were subsequently boiled at 95°–100°C for 15 min. The boiled specimens were cooled to room temperature and the water-swollen volumes were measured.
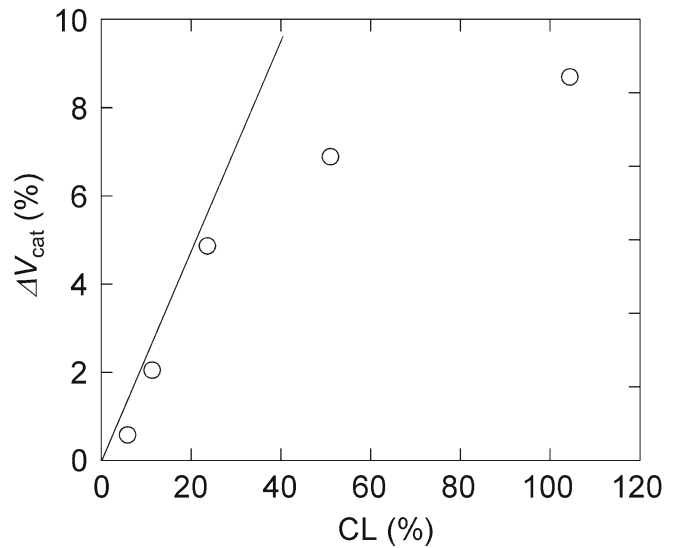
Results and discussion

Effect of catalyst loading

The WPG due to the introduction of KAc, namely, the catalyst loading (CL), was in proportion to the KAc concentration (*x*) of the aqueous solution used for the impregnation treatment:

$$\mathrm{CL} = 2.59x \quad (R^2 = 1.00) \tag{1}$$

Figure 2 shows the volumetric swelling due to the KAc impregnation (ΔV_{cat}) as a function of CL. Significant swelling due to the KAc impregnation indicated the introduction of KAc into the wood cell wall. When we assume that the density of KAc in the wood cell wall is identical to its bulk density ($\rho_{cat} = 1.57$ g/cm^3) and that the lumina volume remains unchanged through the treatment, ΔV_{cat} can be calculated from CL, ρ_{cat}, and the oven-dry density of wood (ρ_0) according to the following equation:

$$\Delta V_{cat}(\%) = \mathrm{CL} \times \frac{\rho_0}{\rho_{cat}} \tag{2}$$

The calculated values are shown in Fig. 2 as a straight line. The experimental value of ΔV_{cat} deviated from the calculated value above 20% CL, probably because some excess KAc deposited in the cell lumina. Thus 20% is a critical CL value reflecting the introduction of KAc into the wood cell wall.

Figure 3 shows the effects of CL on the WPG due to the KAc-catalyzed acetylation at 120°C. It should be mentioned that WPG does not include the amount of catalyst because it is calculated on the basis of wood weight after the removal of KAc by sufficient leaching in water. WPG increased with increasing CL, but then tended to decrease above 20% CL. Presumably, the diffusion of AA vapor was hindered by the
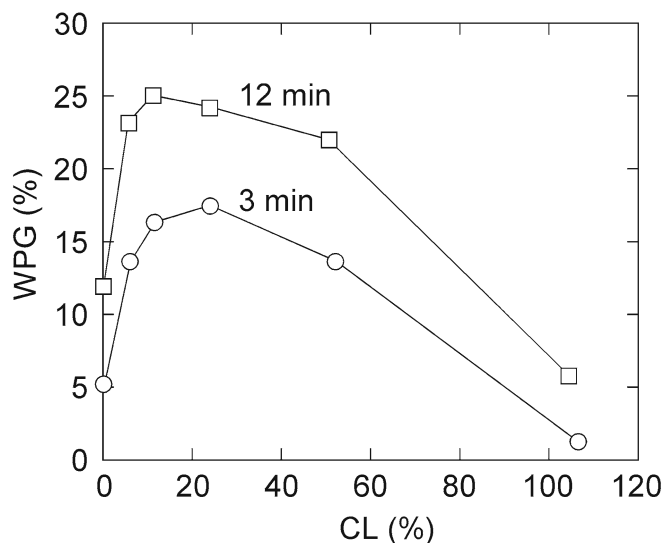
Fig. 3. Effects of CL on the weight percent gain (*WPG*) due to acetylation at 120°C. *Circles*, 3-min reaction time; *squares*, 12-min reaction time
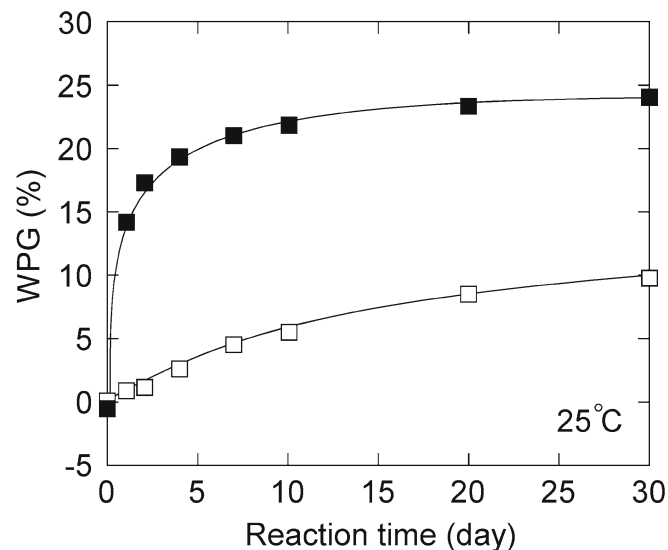
Fig. 5. Reaction profile at 25°C. *Open squares*, uncatalyzed; *filled squares*, KAc-catalyzed
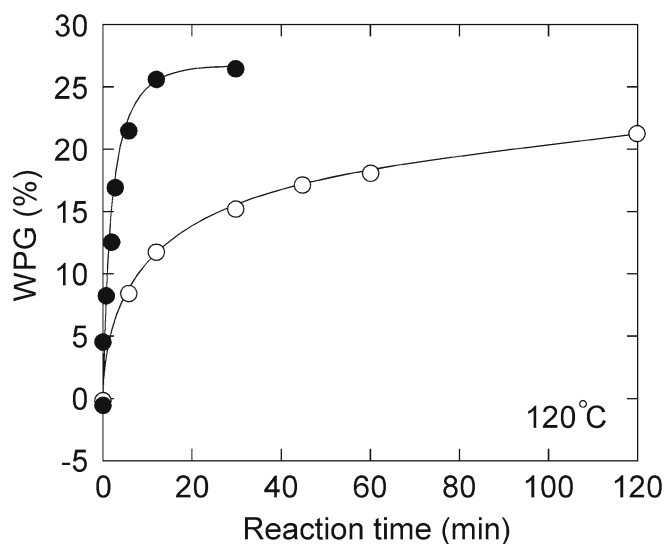
Fig. 4. WPG due to acetylation at 120°C as a function of reaction time. *Open circles*, uncatalyzed; *filled circles*, KAc-catalyzed

deposition of excess KAc in the cell lumina. Such an adverse effect has been observed in the KAc-catalyzed acetylation of rayon,[6] but not in the liquid-phase acetylation of wood.[7] These results suggest that CL should be carefully controlled in vapor-phase acetylation. Hereafter, we describe the KAc-catalyzed acetylation at 23% CL where the catalytic effect of KAc is maximized.

Reaction profile of vapor-phase acetylation

Figure 4 shows the WPG due to the vapor-phase acetylation at 120°C as a function of reaction time. The acetylation reaction was extraordinarily accelerated in the presence of KAc as in the liquid-phase acetylation, and only 6 min

was needed to attain a 20% WPG. This reaction time was much shorter than that in the uncatalyzed system and comparable with that in the liquid-phase KAc-catalyzed acetylation.[5]

It should be noted that the reaction in the uncatalyzed system (20% WPG at 120 min) was slightly faster than that in the liquid-phase acetylation of ezomatsu wood[5] and Sitka spruce wood.[7,8] This fact seemed contradictory to previous studies that suggested slower reaction in vapor-phase modification.[3,9] It was considered that the actual temperature within the wood specimen may have been higher than the prescribed temperature because the reaction heat could not be immediately diffused in gaseous media having lower thermal conductivity.

Figure 5 shows the reaction profile at 25°C. Although the WPG in the uncatalyzed system did not exceed 10% even after 1 month, the KAc-catalyzed acetylation attained 20% WPG within 7 days. One week is too long as an industrial process, but it is realistic for property enhancement of valuable wooden parts such as musical instruments. For such small-scale treatment in workshops or studios, low reaction temperature and the vapor-phase process are quite advantageous because it can be completed with simple equipment and the least loss of chemicals.

Hygroscopicity and dimensional stability

Figure 6 exhibits the equilibrium moisture content (*M*) of acetylated wood as a function of WPG. The *M* value linearly decreased with increasing WPG, and no significant difference was recognized among the treatment methods and temperatures.

To evaluate the dimensional stability of acetylated wood, we calculated the antiswelling efficiency (ASE) from the volumetric swelling in water for unmodified (S_u) and modified (S_t) wood according to the following equation:
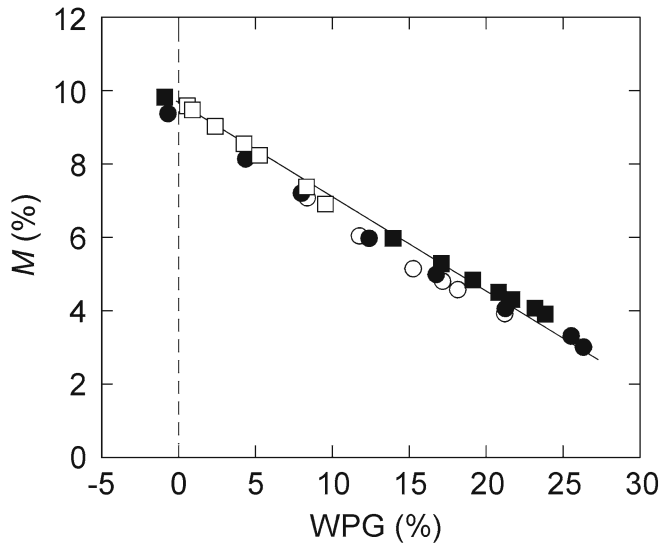
Fig. 6. Equilibrium moisture content (*M*) at 57% relative humidity as a function of WPG. *Open symbols*, uncatalyzed; *filled symbols*, KAc-catalyzed; *circles*, 120°C; *squares*, 25°
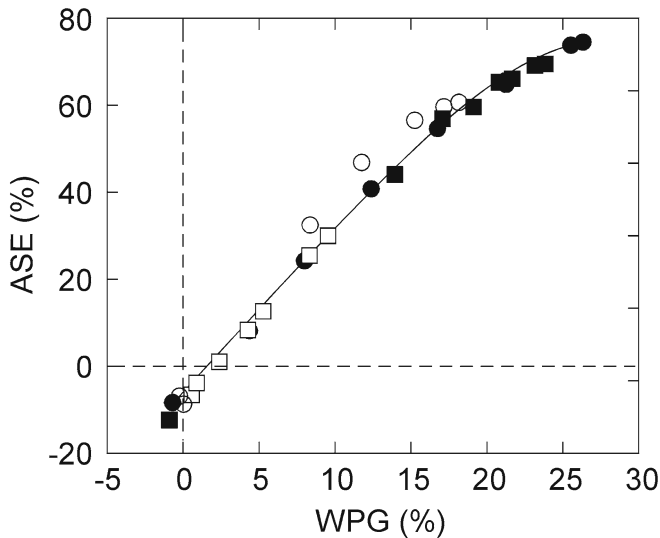
Fig. 7. Plots of WPG against antiswelling efficiency (*ASE*). *Open symbols*, uncatalyzed; *filled symbols*, KAc-catalyzed; *circles*, 120°C; *squares*, 25°

$$ASE\,(\%) = 100 \times \frac{S_u - S_t}{S_u} \qquad (3)$$

The ASE is plotted against WPG in Fig. 7. At small WPGs, the acetylated wood showed ASE values less than 0. Such

degradation was explained in terms of the slight shrinkage caused by loss of extractives during the leaching process. However, the ASE increased with increasing WPG as a whole, irrespective of treatment methods. From these results, it was proved that KAc had no adverse effects on the reduced hygroscopicity and improved dimensional stability of acetylated wood.

Conclusions

KAc-impregnated wood was exposed to acetic anhydride vapor at 25°C and 120°C. Irrespective of temperature, the acetylation reaction was effectively accelerated in the presence of KAc. At 25°C, a 20% WPG was achieved within 7 days after prior impregnation of KAc, whereas the WPG in the uncatalyzed system did not exceed 10% even after 1 month. The hygroscopicity and dimensional stability of the acetylated wood depended on the WPG regardless of treatment methods. These results suggest that the KAc-catalyzed vapor-phase acetylation is a useful method that allows simplified treatment at room temperature with minimum loss of reagents.

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