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ORIGINAL ARTICLE

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Potassium acetate-catalyzed acetylation of wood at low temperatures I: simplified method using a mixed reagent

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Abstract Ezomatsu wood blocks were acetylated in a mixture of acetic anhydride and acetic acid containing excess potassium acetate (KAc). The mixture method enabled rapid acetylation at 120°C: a 20% weight gain (weight percent gain; WPG) was achieved within 30 min while the WPG did not exceed 18% after 120 min of conventional uncatalyzed acetylation. At 40°C, however, a satisfactory WPG was not achieved with the mixture method because both the wood swelling and KAc concentration in the reagent solution were limited at that temperature. In addition, the antiswelling efficiency attained by the mixture method was irregularly low, probably because of nonuniform reaction involving shrinkage of the cell lumina. These results suggest that the mixture method is not advantageous for low-temperature acetylation, whereas it enables simple and rapid acetylation at high temperature.

Key words Acetylation · Potassium acetate · Catalyst · Dimensional stability

Introduction

Acetylation is a promising method for improvement of dimensional stability and durability of wood. For effective acetylation of wood, various catalysts have so far been proposed. Among them, potassium acetate (KAc) is an excellent catalyst allowing extraordinarily rapid acetylation of wood: only 2 min is required to achieve a 20% weight gain (WPG) by KAc-catalyzed acetylation at 120°C, whereas the uncatalyzed acetylation needs several hours of heating.[1] The catalytic effect of KAc has been suggested by earlier investigations[2–4] and a practical method of KAc-catalyzed acetylation has already been patented.[5] In such cases, the reaction temperature is relatively high (≥100°C) for uniform and adequate modification for a short reaction time.

We recently found that KAc also enables sufficient acetylation (WPG > 20%) at low temperatures (≤40°C), whereas the WPG is limited (<10%) in uncatalyzed and pyridine-catalyzed systems.[6] Such a low reaction temperature is fascinating for small-scale acetylation of valuable wooden parts, such as musical instruments, because it requires no complicated equipment for heating and recovery of chemicals. The water-soluble nature and safety of KAc are also advantageous for that purpose.

A problem in KAc-catalyzed acetylation is a time-consuming impregnation process. In our previous study,[6] wood specimens were acetylated by two steps: (1) soaking of wood in aqueous solution of KAc followed by drying, and (2) soaking of the KAc-impregnated wood in acetic acid at a prescribed reaction temperature. The first step allows effective introduction of KAc into the wood cell wall, although it requires considerable time for soaking of the wood and dehydration afterward. If sufficient WPG is given by using the mixture of acetic anhydride and KAc, the time-consuming impregnation process can be avoided to shorten the total treatment time. Such a "mixture method" has been proposed for the acetylation of rayon[7] and wood[4] at high temperatures, but detailed information is not available for low reaction temperatures. In this article, we describe the reaction profile of wood acetylation in a mixed reagent at 40°C and 120°C to clarify the advantages and disadvantages of the mixture method.

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Materials and methods

Wood samples

Cross sections of ezomatsu (*Picea jezoensis* Carr.) measuring as 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 0.38 ± 0.01 g/cm^3 in a completely dry condition, and its volumetric swelling in water was 13.0% ± 0.3%.

Catalyst impregnation and acetylation

Figure 1 shows the methods of acetylation. For the uncatalyzed acetylation (method I), oven-dried wood specimens were soaked in acetic anhydride (AA) at room temperature under reduced pressure for 12 h, and then heated at 40°C or 120°C.

Method II is a conventional KAc-catalyzed acetylation. The wood specimens were soaked in 10% aqueous solution of KAc under reduced pressure for 24 h, air-dried at room temperature for at least 2 days, and then oven-dried at 105°C for 12 h. The KAc impregnation resulted in 22.5% weight gain and 6.5% swelling in volume. The specimens were then acetylated in AA as in method I.

In method III, we used a mixture of AA, acetic acid (AC), and KAc (4:1:2, w/w/w). Part of the excess KAc precipitated in the mixed reagent. The oven-dried wood specimens were soaked in the mixed reagent at room temperature under reduced pressure for 12 h, and then heated at 40°C or 120°C, as in method I.

For acetylation at 40°C, the wood specimens and the reagent solutions were put in glass bottles that were put in a temperature-controlled chamber. For high-temperature acetylation, the wood specimens and the reagent solutions were heated in a flask equipped with a reflux condenser. Five specimens were used for each treatment condition, and the amount of reagent solution (500 g) was in sufficient excess of the weight of wood specimens (4–6 g). After the prescribed reaction time, the specimens were immediately placed in ice–water to stop the reaction and were subsequently leached in running water for at least 3 days to remove the remaining AA, AC, and KAc. It was confirmed that the KAc was almost completely removed by leaching because the oven-dry weight of specimens did not change by prolonged leaching for 3 to 7 days, irrespective of the initial KAc content. The leached specimens were air-dried for 2 days and then oven-dried at 105°C for 12 h to measure their oven-dry weights and dimensions.

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 content (*M*) was 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 their water-swollen volume was measured.

Results and discussion

Reaction profiles

Figure 2 shows the WPG due to the acetylation at 120°C plotted against the reaction time. As suggested by earlier studies,[1,6] the acetylation reaction was extraordinarily accelerated in the presence of KAc: method II achieved 23% WPG within 3 min, whereas the WPG for method I did not exceed 20% within 120 min. Method III was also effective in accelerating the acetylation reaction, and a 20% WPG was attained within 30 min. These results suggest that the mixture method is effective at high temperature for the acceleration of wood acetylation without a time-consuming KAc impregnation process.

Figure 3 shows the reaction profile at 40°C. As in the high-temperature acetylation, method II was effective in

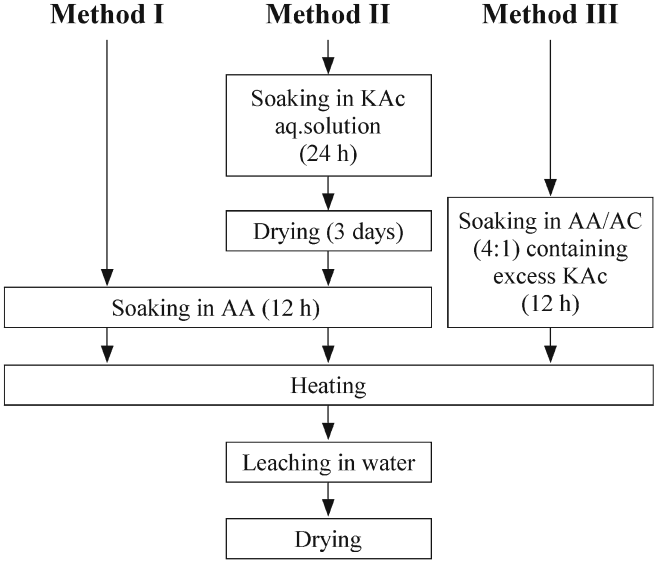

Fig. 1. Methods of acetylation. *AA*, Acetic anhydride; *AC*, acetic acid; *KAc*, potassium acetate

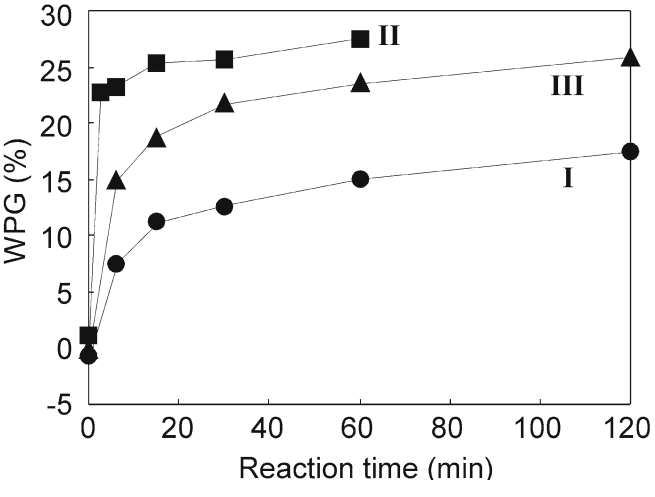

Fig. 2. Weight percent gain (*WPG*) due to acetylation at 120°C as a function of reaction time. *Circles*, uncatalyzed (method I); *squares*, KAc-impregnated acetylation (method II); *triangles*, mixture method (method III)

accelerating the acetylation reaction: 21% WPG was achieved within 8 h by method II, whereas method I gave no significant WPG. The very slow reaction in method I is explained by the insufficient penetration of AA into the wood cell wall. As suggested by Hill et al.,[8] the acetylation reaction can hardly occur when the penetration of AA is hindered by tight intermolecular hydrogen bonds formed between the amorphous wood polymers. In contrast, a large amount of KAc was previously introduced into the wood cell wall in method II, and it possibly allowed easier penetration of AA and subsequent KAc-catalyzed reaction.

Method III was not effective at 40°C: the WPG leveled off after 2 days and it did not exceed 20% within 8 days. Such a slow reaction was considered to be due to insufficient swelling of wood and low KAc concentration in the mixed reagent. The initial swelling of wood in the reagent solution (ΔV_s) is listed in Table 1. At 120°C, the wood was significantly swollen in the solutions. However, the wood swelling was negligible (0.4%, method I) or slight (3.4%, method III) at 40°C, while the initial swelling in method II was greater (6.5%) because of previous introduction of KAc. Hence, the insufficient initial swelling is a possible reason for the relatively slow reaction in method III. On the other hand, it should be remembered that the reaction rate of KAc-catalyzed acetylation depends on the catalyst loading.[1] When we assume that the lumina volume remains unchanged through the treatments, the actual catalyst loading into the wood cell wall (CL′) can be estimated from ΔV_s and the KAc concentration in the reagent solutions (x) according to the following equation:

$$\mathrm{CL}'\,(\%) = \frac{\rho_i}{\rho_0} \times \Delta V_S \times \frac{x}{100}, \quad (1)$$

where ρ_0 (ca. 0.38 g/cm^3) is the oven-dry density of wood, and ρ_i is that of KAc (1.6 g/cm^3) or reagent solutions (1.1 g/cm^3). The x values were experimentally determined to be 6.4% and 31.8% at 40°C and 120°C, respectively. The calculated CL′ values are listed in Table 1. The large CL′ value in method II (18.5%) was reasonably close to the total catalyst loading (22.5%), and their difference (4.0%) was attributable to the deposited KAc in the cell lumina. However, the CL′ value in method III was only 0.6% at 40°C, in contrast with the large CL′ value (14.0%) at 120°C. This fact indicates that sufficient KAc is not supplied from the mixed reagent at 40°C, and therefore the reaction becomes slower.

These results suggest that the mixture method is not advantageous for low-temperature acetylation whereas at high temperature, it enables rapid acetylation with single soaking step. For satisfactory results at low temperature, method II using previous KAc impregnation is advisable.

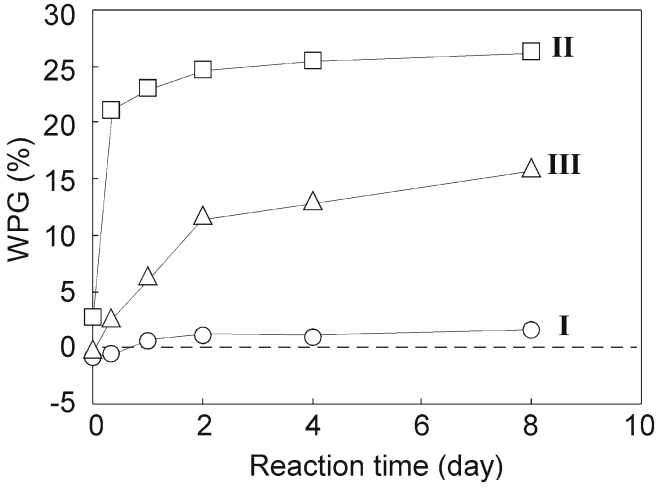

Fig. 3. Reaction profile at 40°C. *Circles*, uncatalyzed (method I); *squares*, KAc-impregnated acetylation (method II); *triangles*, mixture method (method III)

Hygroscopicity and dimensional stability

Figure 4 shows 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.

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:

$$\mathrm{ASE}\,(\%) = 100 \times \frac{S_u - S_t}{S_u} \quad (2)$$

The ASE values are plotted against WPG in Fig. 5. The ASE increased with increasing the WPG as a whole, but

Table 1. Volumetric swelling of wood (ΔV_s) in reagent solutions and actual catalyst loading in the wood cell wall (CL′)

Reaction system	40°C		120°C	
	ΔV_s (%)[a]	CL′ (%)[b]	ΔV_s (%)[c]	CL′ (%)[b]
AA (method I)	0.4	0	9.3	0
AA (method II)	6.5[d]	18.5	20.0	–
AA/AC (4:1 w/w) (method III)	3.4	0.6	15.4	14.0

AA, Acetic anhydride; AC, acetic acid
[a] Determined after soaking for 1 h in the reagent
[b] Calculated from ΔV_s and the concentration of potassium acetate (KAc) in the reagent solutions
[c] Determined after soaking for 5 min in the reagent
[d] Including the volumetric swelling due to the previous KAc impregnation

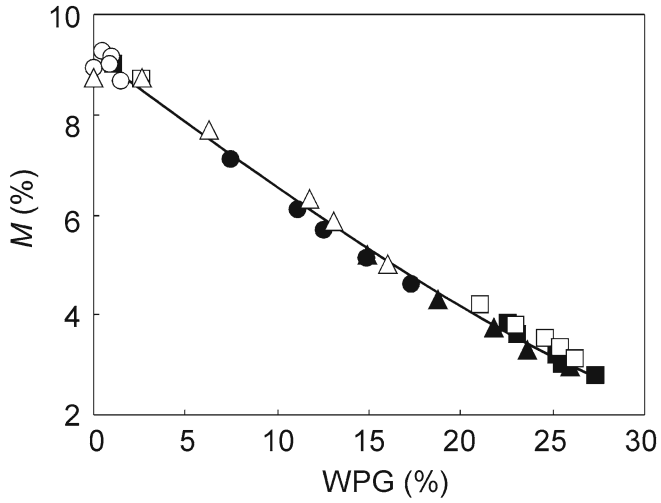

Fig. 4. Equilibrium moisture content (*M*) of acetylated wood at 20°C and 57% RH relative humidity plotted against the WPG. *Filled symbols*, acetylation at 120°C; *open symbols*, reaction at 40°C; *circles*, uncatalyzed (method I); *squares*, KAc-impregnated acetylation (method II); *triangles*, mixture method (method III)

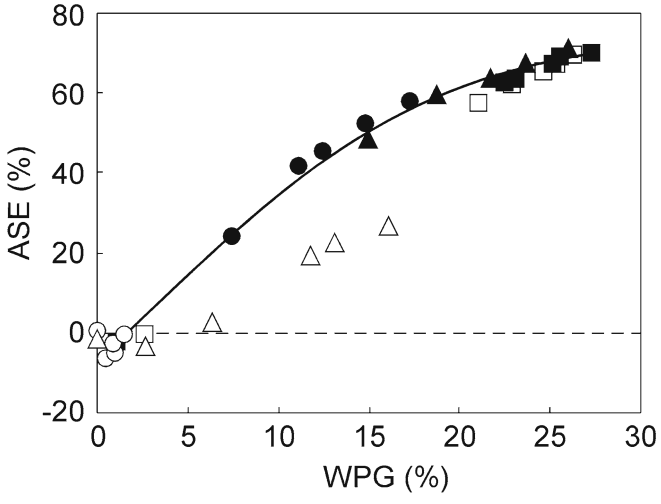

Fig. 5. Antiswelling efficiency (ASE) plotted against WPG. *Filled symbols*, acetylation at 120°C; *open symbols*, reaction at 40°C; *circles*, uncatalyzed (method I); *squares*, KAc-impregnated acetylation (method II); *triangles*, mixture method (method III)

method III at 40°C gave irregularly low ASE values. Because the wet volume of wood was almost constant irrespective of treatment method, the irregular ASE from method III was attributed to the less pronounced bulking effect. Figure 6 shows the bulking effect, that is, the volumetric swelling due to acetylation (ΔV) as a function of WPG. The wood bulking due to method III at 40°C was significantly smaller than those due to the other methods at the same WPG. This may be due to nonuniform acetylation of wood at low temperatures. As discussed above, wood is not sufficiently swollen in the reagent solutions at 40°C. Thus, the extent of the acetylation reaction is limited to areas that both the AA and KAc can easily access (e.g., to the inner surface of the cell wall). Such a partial acetylation might result in the

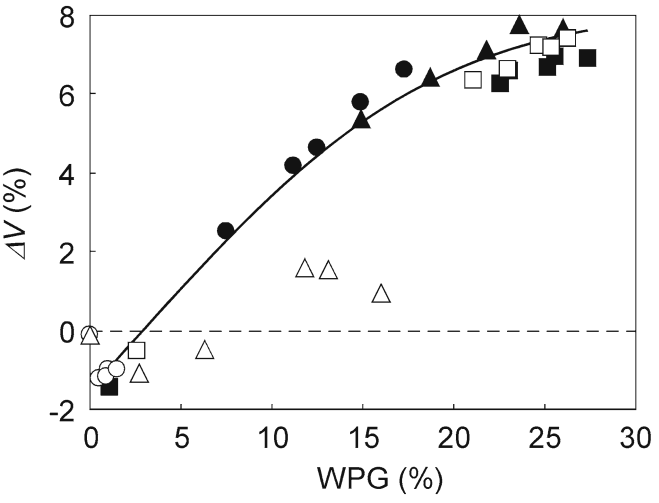

Fig. 6. Bulking effect (ΔV) as a function of WPG. *Filled symbols*, acetylation at 120°C; *open symbols*, reaction at 40°C; *circles*, uncatalyzed (method I); *squares*, KAc-impregnated acetylation (method II); *triangles*, mixture method (method III)

shrinkage of cell lumina instead of external swelling, and therefore give irregularly small ΔV and ASE values. Although such speculation needs to be proved by detailed microscopic observation or precise measurement of lumina volume, the mixture method is not effective at low temperature as a method of dimensional stabilization.

Conclusions

Ezomatsu wood blocks were acetylated in a mixture of acetic anhydride and acetic acid containing excess potassium acetate (KAc). The mixture method was not effective in accelerating the acetylation reaction at 40°C, and the treated wood showed irregularly low dimensional stability. The relatively slow reaction in the mixed reagent was explained by insufficient catalyst loading in the wood cell wall. In addition, the low dimensional stability was interpreted by the shrinkage of cell lumina resulting from nonuniform acetylation. These results suggest that the mixture method is not advantageous for low-temperature acetylation, while it enables simple and rapid acetylation at high temperatures.

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