

Non-uniform reaction of solid wood in vapor-phase acetylation

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Abstract To clarify the non-uniform reaction of wood during vapor-phase acetylation, spruce wood blocks were exposed to acetic anhydride vapor at 120°C. Weight percent gain (WPG) due to the acetylation was estimated from the equilibrium moisture content at 25°C and 60% relative humidity. The diffusion of reagent vapor was much faster along the longitudinal direction than along the tangential direction. When the end surface was exposed to the reagent vapor for 48 h, 20% WPG, which was known to have sufficient stability and durability, was achieved to a depth of 42.5 mm. However, this depth was only 6.5 mm when the straight-grain surface was exposed. The reaction profiles were successfully approximated using reaction time (t), reaction rate (k'), delay time (t_d'), and a parameter n reflecting the diffusion-controlled reaction. The t_d' value increased almost linearly as the depth increased from the surface. The k' value ranged from 0.02 to 0.03 h⁻¹, regardless of the depth and direction of diffusion. The n value decreased with an increase in the depth and approached 1–2. These values enabled the prediction of the degree of acetylation at any reaction time and positions of wood during vapor-phase acetylation.

Keywords Vapor-phase acetylation · Hygroscopicity · Non-uniform reaction · Reaction rate

Introduction

Acetylation is a method of chemical modification to improve the dimensional stability [1], anti-weathering

properties [2] and resistance to biodegradation [3] of wood. The acetylated wood is already used for window frames and bridges in European countries because of its prolonged lifetime especially in exterior uses [4].

Wood acetylation is usually carried out in liquid acetic anhydride. However, this liquid-phase treatment requires the uptake of a large excess of reactant solution during treatment and subsequent removal. As a result, vapor-phase acetylation has been attempted by several researchers. Stamm and Tarkow [1] found that thicker wood requires a longer reaction time because the diffusion of vapor varies as the square of the thickness. Consequently, the maximum dimensions of wood veneer and wood blocks that can be treated using the vapor-phase method within a practically feasible period are only 1/8 of an inch thick or less and only a few inches long. Rowell et al. [5] showed that the vapor-phase acetylation was much slower than the liquid-phase treatment at 120°C, but that both treatments gave the same WPG after 24 h of acetylation of wood chips. These results suggest that vapor-phase acetylation is influenced by the diffusion of reagent vapor and that large-dimension wood is always non-uniformly acetylated, even by prolonged treatment. However, few attempts have been made on the non-uniform reaction of solid wood in vapor-phase acetylation.

If sufficient performance is achieved by non-uniform acetylation, uniform modification that consumes a large amount of reagent is not needed. For example, surface acetylation might effectively improve the mechanical stability of wooden boards and beams because their bending properties are dominated by their surfaces. To make such an intelligent gradient, the non-uniform reaction of wood during vapor-phase acetylation should be clarified.

In this study, we investigated the non-uniform acetylation of spruce wood blocks in a vapor-phase system and

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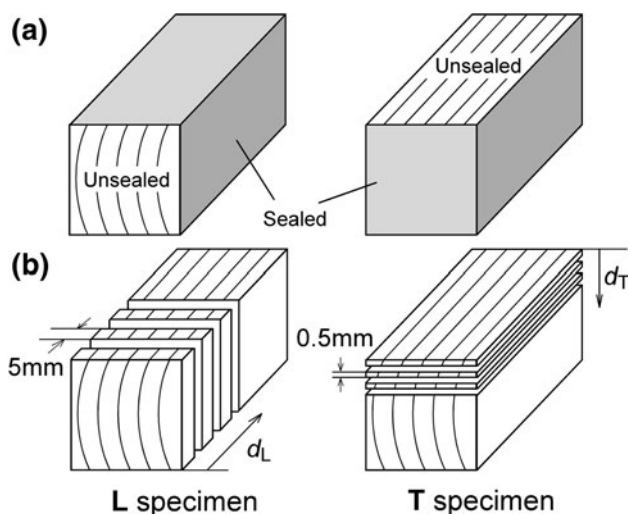


Fig. 1 Appearance of wood samples. **a** Sealed with silicon rubber and PTFE sheet prior to acetylation; **b** cut and sliced after acetylation

analyzed the results using a modified rate equation in which the diffusion of reagents are considered.

Materials and methods

Wood samples

Sapwood of Sitka spruce (*Picea sitchensis* Carr.) was cut into blocks with dimensions of 30 mm (tangential, T) \times 30 mm (radial, R) \times 100 mm (longitudinal, L). Figure 1a shows the appearance of the wood specimens. To limit the diffusion of reagent vapor along the L or T directions, all surfaces except the RT or LR surfaces were sealed with silicon rubber and a polytetrafluoroethylene (PTFE) sheet. Hereafter, the former is referred to as the L specimen and the latter as the T specimen.

Acetylation

Figure 2 illustrates the apparatus used for vapor-phase acetylation. Acetic anhydride (AA, 125 ml) was placed in the bottom of a glass flask (inner volume: ca. 1000 cm³) equipped with a reflux condenser. To prevent the reagent from rippling and wetting the wood specimens, glass beads and PTFE mesh were added. The wood specimens were then placed in glass flasks with their unsealed surface facing downward, and the flasks were heated at 120°C for 1–48 h using an oil bath. After the treatment, the wood specimens were removed from the flasks and soaked in cold water to stop the reaction. Finally, the cooled specimens were dried roughly and the sealing rubber was scraped off using a hand plane.

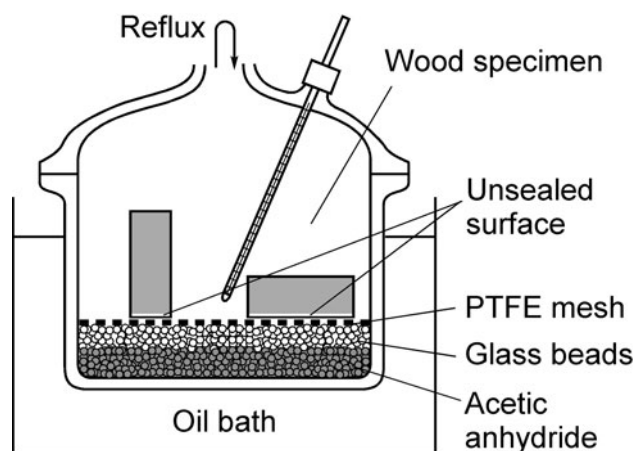


Fig. 2 Apparatus for vapor-phase acetylation

Figure 1b explains the separation of wood specimens. The L specimens were cut along the longitudinal direction about 5 mm from the RT surface, which had been exposed to the AA vapor. The T specimens were sliced along the tangential direction at about 0.5 mm from the LR surface. The cut blocks and sliced flakes were then leached in running water for at least 48 h, after which they were air-dried overnight. When the T specimens were treated for 24 h or longer, the edges of some flake samples showed a lighter color. This color change indicated that a small amount of AA vapor passed through the sealing and reacted with the LT surface of the T specimen. Therefore, the edges (5–8 mm from the edge) of all flake samples were removed prior to the following experiments.

The air-dried blocks and flakes were subsequently completely dried in an oven at 105°C for more than 24 h and weighed. Those samples were finally conditioned at 25°C and 60% relative humidity (RH) for at least 2 weeks to determine their equilibrium moisture contents (M).

Results and discussion

The degree of acetylation is usually evaluated by the WPG based on the weight of unmodified wood. However, in the present study, the WPG of the local portion inside a specimen could not be determined because its unmodified weight was not previously available. In such a case, chemical analysis [6] and spectroscopic methods [7–9] are usually used to evaluate the degree of acetylation. However, those methods always need complicated procedures and analytical instruments. On the other hand, it should be noted that the equilibrium moisture content of acetylated wood (M_t) decreases monotonously with increasing WPG, regardless of the reaction temperature and type of catalyst [10–15]. The M_t is also a good indication of dimensional

stability because the hygroscopicity of wood is closely related to its dimensional stability. Thus, we evaluated the WPG of acetylated wood based on its hygroscopicity in this study. Figure 3 shows the relative equilibrium moisture content (M_t/M_u) plotted against the WPG of acetylated wood. In this case, wood specimens were thin (5 mm) enough to ensure a uniform reaction. The M_t/M_u value decreased monotonously with increasing the WPG, and the plots of the present results overlapped with those of previous results passing through the origin (WPG = 0%, $M_t/M_u = 1$) [14, 15]. This fact suggests that the negative correlation shown in Fig. 3 is a general trend in wood acetylation. Therefore, the plots of the present results (filled circles) including that of the unmodified wood (WPG = 0%, $M_t/M_u = 1$) were approximated by the following equation:

$$\text{WPG (\%)} = 10.59(M_t/M_u)^2 - 50.88(M_t/M_u) + 40.23. \quad (1)$$

Using Eq. 1, the WPG of wood can be evaluated even when its unmodified weight is unknown. Figure 4 shows the variations in WPG due to acetylation for 48 h as a function of the depth (d_L , d_T), i.e., the distance from the unsealed surface exposed to the AA vapor. The L specimen showed greater WPG than the T specimen at the same depth. In L specimen, 20% WPG was achieved to a depth of 42.5 mm, whereas this depth was only 6.5 mm in T specimen. That difference was reasonable when we consider the diffusion coefficient of non-swelling gases through spruce wood. According to Petty [16], the diffusion coefficient of air along the L direction of spruce wood

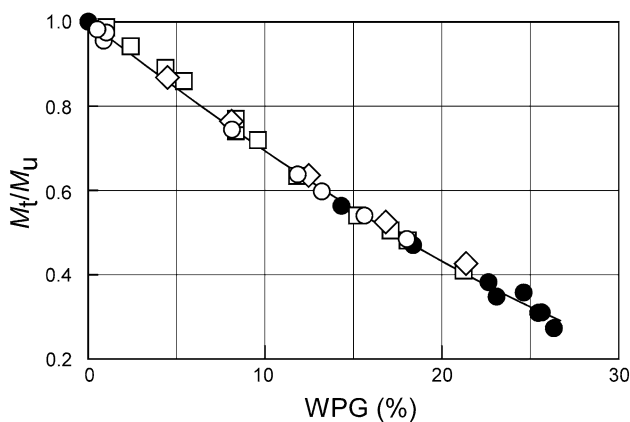


Fig. 3 Relationship between the relative equilibrium moisture content (M_t/M_u) of acetylated wood at 25°C and 60% RH and weight percent gain (WPG) owing to acetylation. M_t and M_u are the equilibrium moisture contents of acetylated and unmodified wood, respectively. *Filled circles* vapor-phase acetylation at 120°C, *open circles* liquid-phase acetylation at 40°C and 120°C [14], *open squares* vapor-phase acetylation at 25°C and 120°C [15], *open diamonds* vapor-phase acetylation at 120°C in the presence of potassium acetate [15], *solid curve* regression curve for the present results expressed by Eq. 1

is about 100 times greater than that in the T direction. That is, the depth allowing certain concentration of gas within a constant diffusion time is about 10 times greater in the L direction than that in the T direction.

The WPG is plotted against the reaction time in Fig. 5. The reaction started slower and the reaction rate became

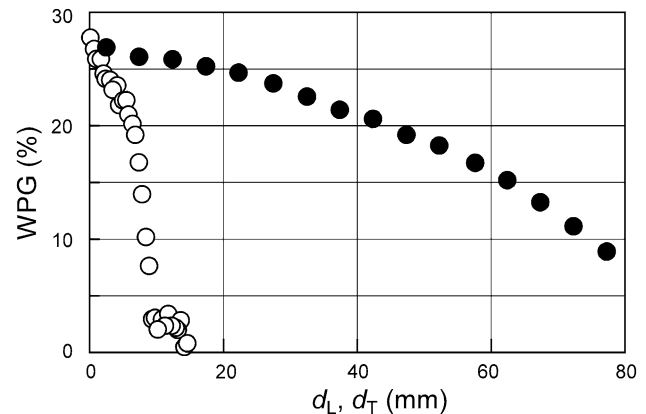


Fig. 4 Variations in WPG owing to acetylation for 48 h as a function of depth (d_L and d_T) i.e., distance from the unsealed surface. *Filled circles* L specimen, *open circles* T specimen

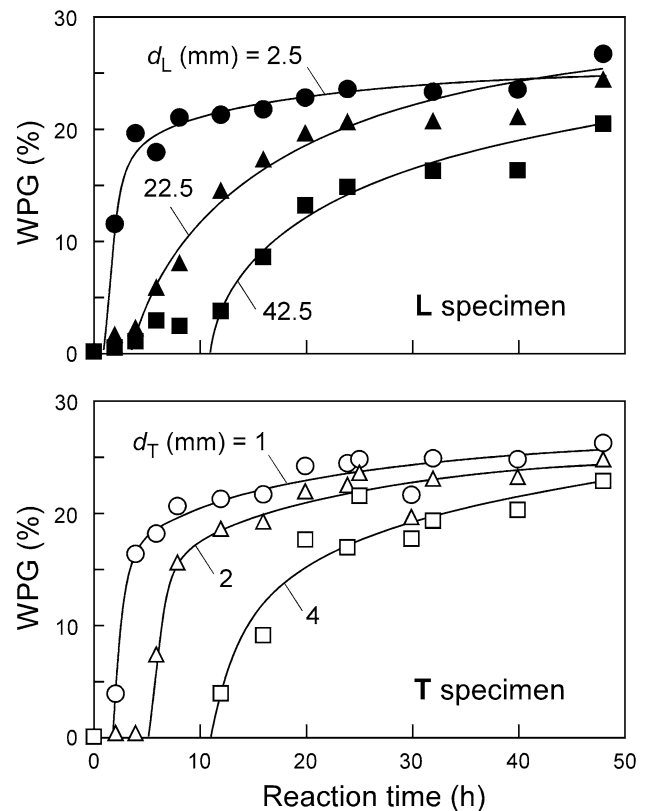


Fig. 5 Reaction profiles of vapor-phase acetylation at the indicated depth (d_L and d_T). *Filled plots* L specimen, *open plots* T specimen, *solid lines* approximation determined using the modified rate equation (Eq. 4)

smaller as the depth increased. This delay indicates that AA diffused from the unsealed surface, and the smaller reaction rate in deeper parts may have been due to the lower concentration of AA inside the wood block.

Next, we attempted to formulate the experimental results. To express the delay of reaction, a delay time (t_d) was introduced into a first-order reaction equation:

$$\text{WPG}(t) = a(1 - e^{-k(t-t_d)}), \tag{2}$$

where $t(h)$ is the reaction time, $t_d(h)$ is the delay time, a (%) is the ultimate WPG, and $k(h^{-1})$ is the rate constant. The a value was fixed at 27.5% based on the experimental values of uniform acetylation for 48 h. The results of approximation conducted using Eq. 2 and least square method are shown in Fig. 6 as broken lines. The approximation was fairly good for the deeper parts, but not good for areas near the surface.

Figure 7 shows the reaction parameters in Eq. 2 as a function of depth. The t_d value increased and the k value decreased as depth increased. The decrease in k values seemed reasonable because the concentration of reagent at deeper parts is thought to be lower than that near the surface. However, it should be remembered that the k value does not indicate the actual rate of acetylation, but rather the apparent rate influenced by diffusion of the reagent. In addition, Eq. 2 did not fit the experimental values well, as exhibited in Fig. 6. To provide more accurate results, we used the modified version of rate equation proposed by Minato [17].

$$\text{WPG}(t) = a(1 - e^{-k't})^{\frac{1}{n}}, \tag{3}$$

where $k'(h^{-1})$ is the rate constant and n is a measure of hindrance of the diffusion of the reagent to the reaction site. It has been suggested that Eq. 3 fits experimental results well, irrespective of reaction temperatures and types

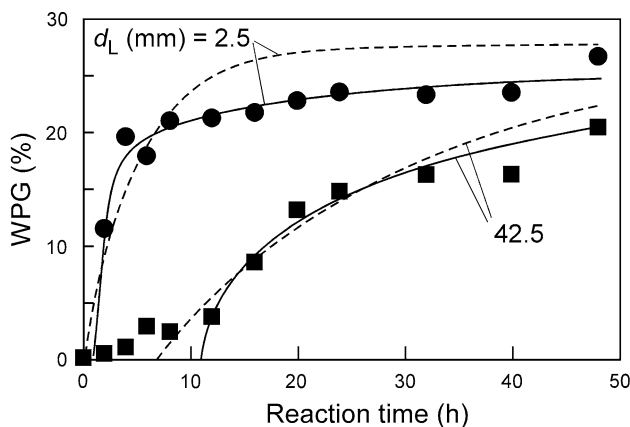


Fig. 6 Application of first-order reaction equation (Eq. 2, broken lines) and modified rate equation (Eq. 4, solid lines) to the experimental results of L specimens at different positions

of catalyst [12–15, 17, 18]. By introducing delay time (t_d'), Eq. 3 can be expanded to include a delayed reaction:

$$\text{WPG}(t) = a(1 - e^{-k'(t-t_d')})^{\frac{1}{n}}. \tag{4}$$

The results of approximation using Eq. 4 are shown in Figs. 5 and 6 as solid lines. The calculated values agreed well with the experimental results, regardless of the distance from the surface. The reaction parameters in Eq. 4 are plotted against depth in Fig. 8. The t_d' values increased almost linearly with increasing depth, and the t_d' value of the T specimen was 12 times greater than that of the L specimen at the same depth. These findings suggest that the diffusion of the reagent was much slower along the T direction than the L direction. In contrast to the k values shown in Fig. 7, the k' values did not vary greatly. Specifically, the average value of k' was $0.029 h^{-1}$ for the L specimen and $0.024 h^{-1}$ for the T specimen. Therefore, the real reaction rate of acetylation is thought to be almost constant when the effects of diffusion are excluded.

The n values were greater than 8 near the surface, but decreased to 1–2 with increasing depth. At the exposed surface, the rate of the actual reaction between the reagent and hydroxyl groups of wood components was extremely fast because the reaction temperature and the concentration of reagent were sufficient. Therefore, the diffusion

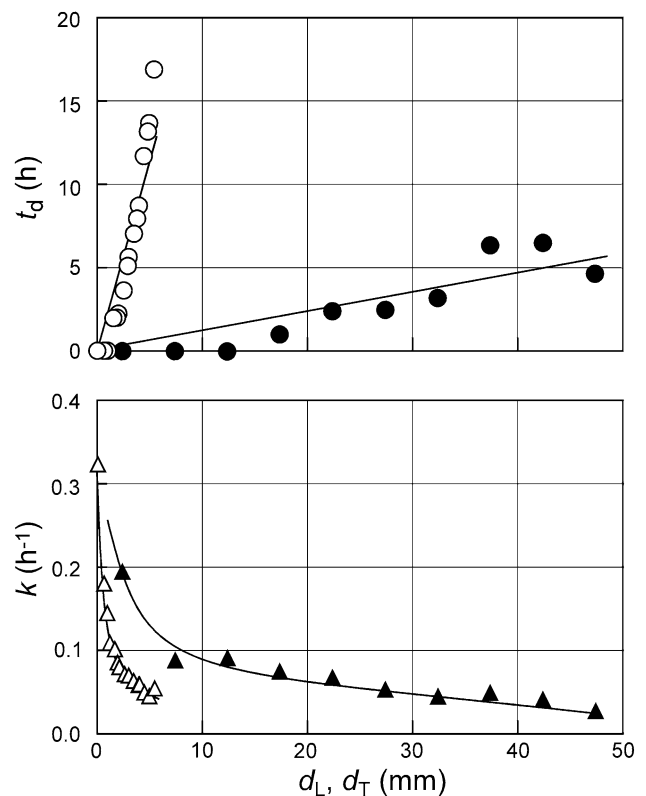


Fig. 7 Effects of depth (d_L and d_T) on the reaction parameters of the first-order reaction equation (Eq. 2). Filled plots L specimen, open plots T specimen

becomes rate-determining step of the acetylation and consequently the n value becomes far from unity near the surface [17, 18]. Conversely, the actual reaction becomes the rate-determining step at deeper parts because of the lower concentration of AA. Consequently, the first-order reaction equation satisfies the reaction profiles at the deeper part, and the n value becomes closer to 1.

Although reaction kinetics of liquid-phase acetylation has been well investigated, few attempts have been made on the non-uniform reaction of solid wood in vapor-phase acetylation. Using Eq. 4 and the reaction parameters exhibited in Fig. 8, we can estimate the degree of acetylation of any parts in a solid wood from the reaction time

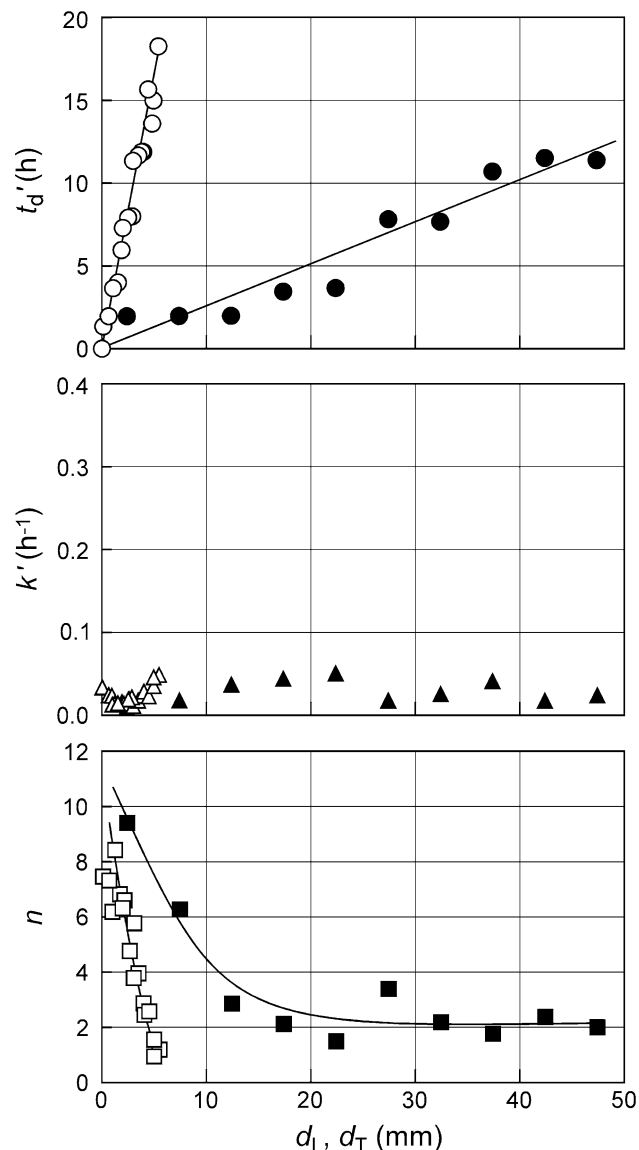


Fig. 8 Reaction parameters of modified rate equation (Eq. 4) plotted against depth (d_L and d_T). Filled plots L specimen, open plots T specimen

and the depth. It allows to predict sufficient reaction time in vapor-phase system, and also, it enables selective surface modification with the minimum consumption of reagent.

Conclusions

Spruce wood blocks were acetylated at 120°C in a vapor-phase system, and variations in WPG were evaluated based on their hygroscopicity. AA vapor diffused much more easily along the longitudinal direction than along the tangential direction. When the RT surface was exposed to the AA vapor for 48 h, 20% WPG was achieved to a depth of 42.5 mm, whereas this depth was only 6.5 mm when the LR surface was exposed. The experimental results were successfully approximated by a modified rate equation in which the delay of reaction was considered. This equation enabled the prediction of the degree of acetylation at any reaction time and the position of wood during vapor-phase acetylation.

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