ORIGINAL ARTICLE

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Dependence of reaction kinetics and physical and mechanical properties on the reaction systems of acetylation I: reaction kinetic aspects

Abstract The dependence of the reaction parameters of acetylation on the reaction mixture was compared among uncatalyzed, acetic anhydride-xylene mixed, and acetic anhydride-pyridine mixed solutions. Wood meal and blocks were used to examine the effect of sample size. A first-order rate equation was applied to the data, and a rate constant and leveling off value of weight gain (WG) were estimated. The rate-determining step was examined from the viewpoint of activation energy. The results were as follows: (1) Regarding the magnitude of the rate constant, the order was pyridine system > uncatalyzed system > xylene system. (2) The ultimate value of WG was lower in the uncatalyzed and xylene systems than the pyridine system, probably because of the swelling ability of pyridine. (3) The activation energies of acetylation estimated for wood meal were 120, 135, and 110 kJ/mol for the uncatalyzed, xylene, and pyridine systems, respectively. (4) The characteristics of the diffusion-controlled reaction became marked when the acetylation was carried out in the pyridine system, at elevated temperature, and for wood blocks. Under these conditions, the supply of reagent to the reaction site might not be sufficient to fuel the reaction.

Key words Acetylation · Reaction kinetics · Activation energy · Rate-determining step · Weight gain

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Introduction

Acetylation is one of the most promising methods for dimensional stabilization of wood because of the high performance attained, and low loading to the surroundings, and low manufacturing cost, among other reasons. Recently, many publications have discussed the durability to weathering,[1] reaction kinetics,[2,3] and physical properties[4] of acetylated wood.

Norimoto[5] reviewed investigations performed before 1990 and presented many reaction systems, methods of controlling reaction conditions, and physical, mechanical, and additional properties. However, few investigations have dealt with reaction kinetics or discussed the properties attained by different reaction phases (e.g., vapor phase or liquid phase) or the different reaction mixtures (e.g., in pyridine or xylene).

In this study, we investigated the acetylation of wood with respect to reaction kinetics. For the optimization of reaction conditions and property enhancement of the product, it is important to analyze such kinetic parameters as the rate constant and activation energy.

Hill and coworkers[2] reported the activation energy of acetylation to be about 20–50 kJ/mol depending on the solution or data-analyzing method. This value seems too low to be the activation energy for a common organic reaction. Therefore, the reaction might be controlled by some other step, such as penetration or diffusion of the reagent. By excluding such a rate-determining step and increasing the accessibility of the reagent to the reaction site, we tried to estimate the real activation energy of acetylation. Furthermore, the reaction parameters were compared for three typical acetylation systems.

Experiments

Materials and reagents

Sitka spruce (*Picea sitchensis* Carr.) was used as meal (150–355μm) and as a block [25mm (T) × 30mm (R) × 5mm (L)] chiefly for determining the reaction rate and dimensional change, respectively. In the case of block samples, specimens cut from consecutive parts were assigned to a series of reaction conditions. Before acetylation, extraction with alcohol-benzene (v/v 1:2) was carried out using Soxhlet's extractor for both wood meal (8h) and blocks (24h). Reagent-grade acetic anhydride, pyridine, and xylene were used.

Acetylation

The acetylation of wood meal was carried out in a glass vessel 27mm in inner diameter (i.d.) and 200mm deep under a reflux condenser. We chose the reaction solutions: acetic anhydride only, an acetic anhydride-xylene mixture (v/v 1:1 and 3:1), and an acetic anhydride-pyridine mixture (v/v 4:1). Hereafter we refer to these solutions as the uncatalyzed system, xylene system, and pyridine system, respectively. The reaction was started by adding about 1.5g of oven-dried wood meal to 35ml of the reaction solution, which was previously heated at a prescribed temperature. The reaction was stopped by pouring the reaction mixture into methanol. The wood meal was filtered using a G3 glass filter under aspiration, and thoroughly rinsed with water. The reaction was conducted at 60°–140°C for up to 72h. The weight gain (WG) was calculated on the basis of the oven-dried weight before and after the reaction.

In the case of the block samples, a glass vessel of 37mm i.d. and 120mm depth was used. Prior to the reaction, the reaction solution was impregnated under reduced pressure at room temperature for 4–6h until all bubbling ceased. The samples (three pieces for each reaction condition) were then placed into about 60ml of preheated reaction solution. After the reaction, the samples were dropped into methanol and rinsed with running water for more than 24h. The dimensions of the samples were then determined in water-swollen and oven-dried states. For acetylation of block samples, the uncatalyzed system, xylene system (xylene/acetic anhydride 1:1), and pyridine system (pyridine/acetic anhydride 1:4) were tested.

Results and discussion

Estimation of reaction parameters for acetylation of wood meal

Figure 1 shows the relation between WG and reaction duration for the uncatalyzed system. The acetylation can be represented as

$$R — OH + (CH_3CO)_2O \rightarrow R — OCOCH_3 + CH_3COOH$$
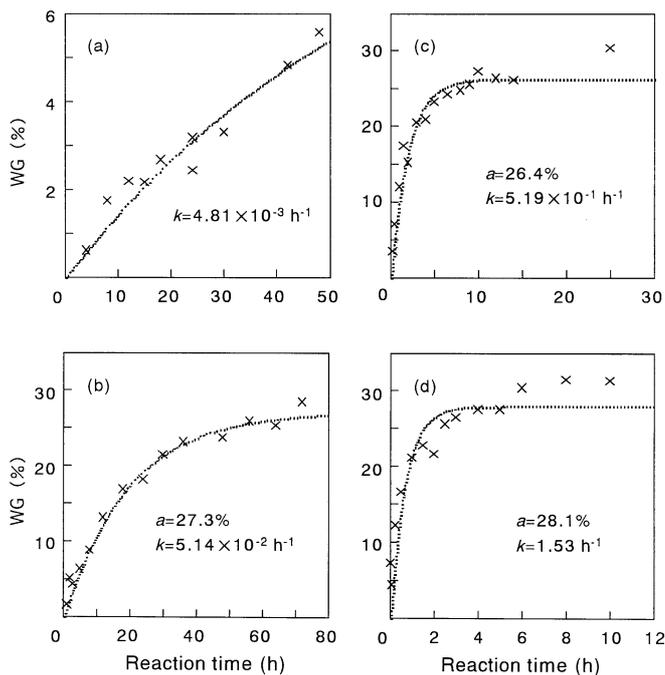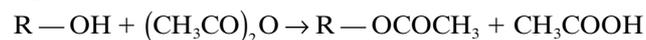
Fig. 1. Profiles of the reaction of wood meal in the uncatalyzed system at 80°C (**a**), 100°C (**b**), 120°C (**c**), and 140°C (**d**). *Dashed lines* were obtained by the regression of the first-order rate equation. *WG*, weight gain

where R-OH is the hydroxyl group in wood components. Although the rate of acetylation is proportional to the number of hydroxyl groups available for the reaction and the concentration of acetic anhydride, when too much acetic anhydride is supplied to the available hydroxyl groups the rate is proportional only to the number of remaining hydroxyl groups. Therefore, the reaction can be represented as:

$$\text{Rate} = -d[R — OH]/dt = k_2[R — OH][(CH_3CO)_2O]$$
$$\doteqdot k_1[R — OH]$$

where k_2 and k_1 are second-order and pseudo first-order rate constants, respectively. The broken lines in Fig. 1 shows the regression curves when the first-order reaction equation

$$y = a(1 - e^{-kt}) \qquad (1)$$

was applied to the observed data. In Eq. (1), y is WG (%), t is the reaction time (h), k is the rate constant (h^{-1}), and a is the leveling-off (or ultimate) value of WG (%).

A commercial computer program for nonlinear regression was used to estimate k and a. The optimum values of k and a were obtainable in the temperature range 100°–140°C, although the optimum a for 80°C could not be obtained because of a lack of data for later reaction stages. Therefore, the k value of 80°C was estimated using the mean value of a for 100°, 120°, and 140°C.

The regression curve fitted to the observed values lower than to those at 120°C but less successfully than to those at 140°C. The rate of acetylation apparently may be controlled
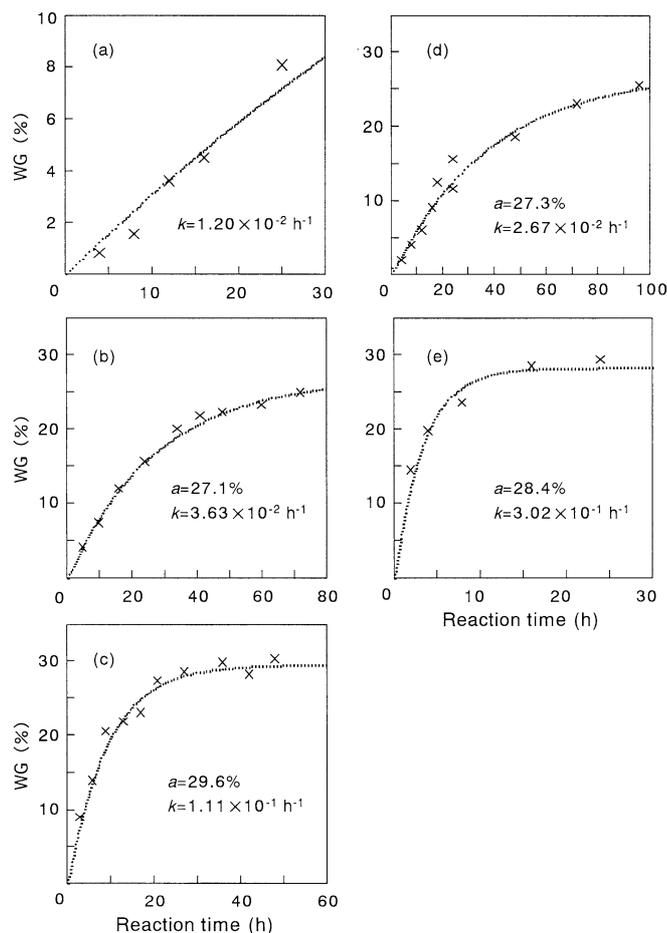
Fig. 2. Profiles of the reaction of wood meal in an acetic anhydride/xylene (1:1) mixture at 100°C (**a**), 100°C (**b**), and 120°C (**c**), and of a 3:1 mixture at 100°C (**d**) and 120°C (**e**)

Fig. 3. Dependence of the rate constant on the volume fraction of acetic anhydride in the xylene system

by either of two processes: (1) access of reagent to the reaction site by diffusion or penetration, or (2) real reaction between reagent and hydroxyl groups. The particle size of the wood meal used was not small enough to have completely broken cell wall layers. Therefore, some other barrier that limits access to the inside of the particles remains. At an elevated temperature, the former process becomes the rate-determining step because of the rapid nature of the reaction. In such cases, the reaction does not fulfill the first-order rate equation, and the observed values deviate downward from the regression curve.

The k and a values were attached in Fig. 1. The estimated leveling-off value of WG (a) was 26%–28% at 100°–140°C, although the observed values were higher, especially with a longer reaction time and more elevated temperature. This suggests that under severe reaction conditions the cell layer structure was partly broken up by the hydrolytic action of acetic acid (by-product of acetylation), and reaction sites emerge anew.

Figure 2 shows the results for the xylene system along with the a and k values obtained in the same manner as for the uncatalyzed system. When the acetic anhydride/xylene mix was 1:1 (v/v), the k value for 100°C was calculated

using the mean value of a at 110° and 120°C. The reaction was much slower than in the uncatalyzed system. When a 3:1 (v/v) mixture of acetic anhydride/xylene was used, the reaction was markedly accelerated. Figure 3 shows the dependence of the rate constant on the ratio of acetic anhydride in the reaction mixture. The reaction rate monotonously decreased depending on the dilution with xylene, independent of the reaction temperature.

The leveling-off value for WG in the xylene system was the same as in the uncatalyzed system. Xylene is commonly used to remove by-products of the reaction (which causes degradation of the wood) and to prevent cracks during the drying process.[5] However, in terms of the reaction rate, dilution with xylene did not offer any advantage.

The results for the pyridine system are shown in Fig. 4. Also in this case, the k value at 60°C was estimated by fixing the leveling-off value to the mean value of a obtained at 80°, 100°, and 120°C. The observed values at temperatures above 120°C did not successfully adjust to the first-order rate equation, probably for the same reason as for the uncatalyzed reaction at elevated temperatures. The estimated k values were far greater than those found in the uncatalyzed and xylene systems. Pyridine can swell wood greatly and create a new region accessible to the reaction solution, which might accelerate the reaction. The calculated leveling-off value for WG was also somewhat higher than that in the uncatalyzed and xylene systems. On the other hand, the observed value reached about 40%, which was comparable to the theoretical value (38.5%) estimated by Norimoto.[5]

Activation energy was obtained for each reaction system by the so-called Arrhenius plot shown in Fig. 5. Here, the
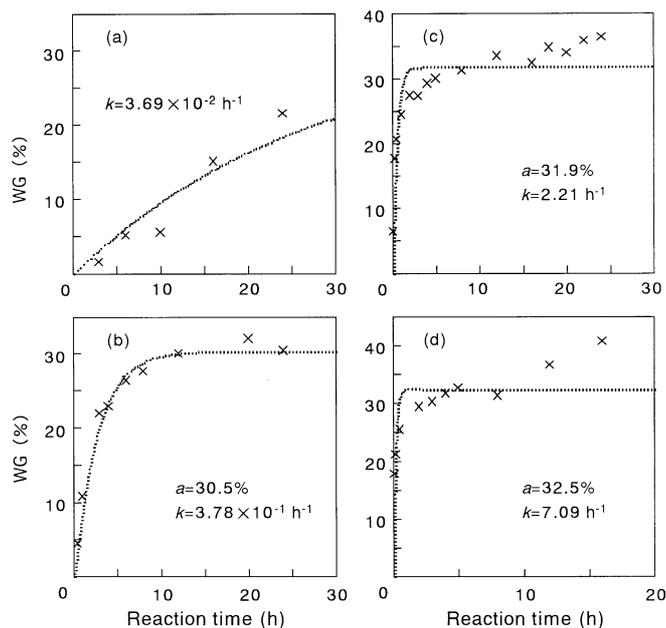
Fig. 4. Profiles of the reaction of wood meal in the acetic anhydride/pyridine mixture at 60°C (**a**), 80°C (**b**), 100°C (**c**), and 120°C (**d**)
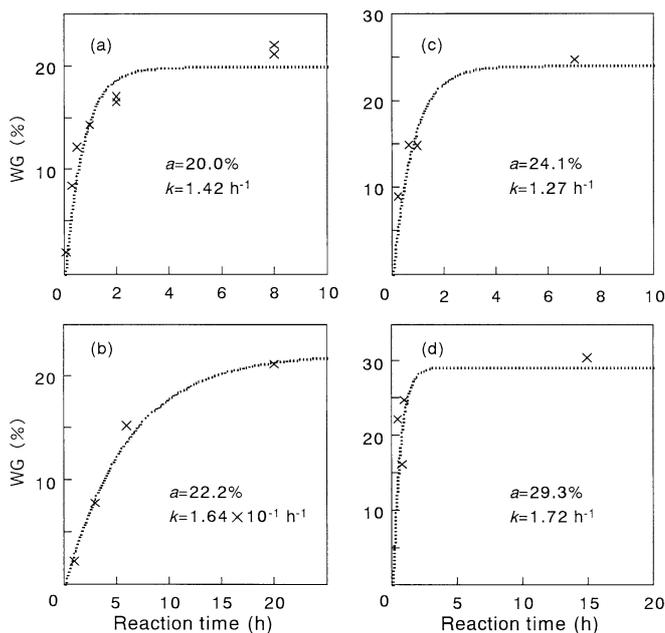
Fig. 6. Profiles of the reaction of wood blocks in the uncatalyzed system at 120°C (**a**), acetic anhydride/xylene (1:1) mixture at 120°C (**b**), and acetic anhydride/pyridine (4:1) mixture at 80°C (**c**) and 120°C (**d**)
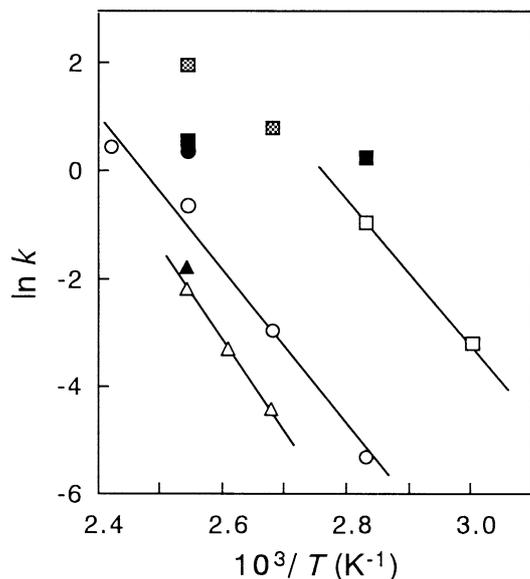
Fig. 5. Arrhenius plot. *Open symbols*, wood meal; *solid symbols*, wood block; *circles*, uncatalyzed system; *triangles*, xylene system; *squares*, pyridine system (*Gray squares* were not used for linear regression)

linear regression for the pyridine system was conducted for only two plots under 100°C because the first-order rate equation did not successfully adjust to the data above 120°C. The activation energies estimated from the slopes of the regression lines were 120, 135, and 110 kJ/mol for the uncatalyzed, xylene, and pyridine systems, respectively. The order of activation energy among reaction systems was the reverse that of the reaction rate. This is probably due to the fact that the shortage of reagent supplied to the reaction site became conspicuous with the acceleration of the reaction, and it took on a diffusion-controlled reaction whose activation energy is generally low. Therefore, the real activation energy of acetylation would be the 135 kJ/mol estimated for the system with the lowest reaction rate, the xylene system, or greater.

Estimation of reaction parameters for the acetylation of wood block

The wood blocks were mainly subjected to a determination of dimensional stability, which will be discussed in a later report. Nevertheless the WG data were analyzed and are discussed here from a kinetic perspective.

Figure 6 shows the relation between WG and reaction time when the block-type samples were used. Equation (1) was again applied, and a and k were calculated. The calculated leveling-off values for block samples were significantly lower than those for wood meal treated under similar conditions. In the case of block samples, neighboring fibers would mutually restrict the swelling of the cell wall; accordingly, the extension of the reaction site might be limited especially in the uncatalyzed and xylene systems, which would result in lowering the leveling-off value of WG.

The rate constants estimated for block samples were larger than those for wood meal except for the pyridine system at 120°C. This seems to be related with the lower leveled-off WG; it is feasible that the lower leveling-off value for WG shortens the time required. The smaller rate constant observed at 120°C in the pyridine system might indicate that the reaction is controlled by access of the reagent to the reaction site. This resulted in an extremely

low activation energy (8.7 kJ/mol) when roughly estimated between 80° and 120°C.

Hill and coworkers[2] reported the activation energy for the acetylation of softwood blocks 20 mm (T) × 20 mm (R) × 5 mm (L) in uncatalyzed and pyridine systems. They estimated the rate constant by two methods: (1) from the reaction rate at the initial stage of the reaction, and (2) from the rate constant of diffusion based on Fick's law. In the former case, the activation energies were 50.9 and 41.6 kJ/mol and in the latter case 34.2 and 20.5 kJ/mol for the uncatalyzed and pyridine systems, respectively. These values are fairly low compared to those obtained for wood meal in the present study. Therefore, an activation energy of this level is normal when access of a reagent to the reaction site becomes a rate-determining step. Also in their results, the activation energy was always lower for the pyridine system than for the uncatalyzed system, suggesting that access of the reagent to the reaction site is far behind that of the real reaction, especially in the pyridine system.

In an acetic anhydride/xylene (v/v 1:1) solution, Ramsden and Blake[3] obtained an activation energy of 80–107 kJ/mol for wood blocks of many species. That the activation energy was high irrespective of the block sample is attributable to the xylene system. That is, in the xylene system the reaction rate is not so great as the supply of reagent to the reaction site cannot follow the reaction. Nevertheless, the activation energy estimated by Ramsden and Blake was still less than our result obtained for wood meal in the reagent mixture of the same composition.

Because of impregnation prior to acetylation, the cell lumen should be filled with the reagent even in block samples. Moreover, in the case of wood meal, it is unlikely that the cell layer was completely crushed. Therefore, it is strange that the activation energy differed markedly between wood meal and block samples. As stated above, the individual fibers in block samples might restrain the swelling, which limits access of the reagent to the reaction site. This resulted in a diffusion-controlled reaction and lowering of activation energy, whereas with wood meal the particles could swell freely, and the reagent could easily reach the reaction site. As a result, the reaction was not controlled by the supply of the reagent to the reaction site.

Conclusions

The reaction rate and apparent activation energy differ depending on the shape of the sample (wood meal or block) and the reaction system. As the rate-determining step of the reaction, two factors–access of the reagent to the reaction site and the real chemical reaction–can be assumed. The apparent activation energy varies widely depending on which is dominant. When the reaction rate is so great that the supply of reagent cannot keep up with the reaction, the activation energy became low (as in block samples) in the pyridine system and at high temperatures. When the reagent supply is sufficient, however, the activation energy is high, close to the real activation energy of acetylation. The latter situation is found with wood meal, the xylene and uncatalyzed systems, and at low temperatures. These interpretations were similar to the results found in the literature.

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