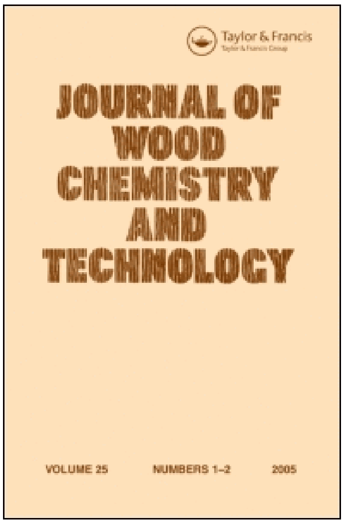

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Jian-Zhang Li[a]; Takeshi Furuno[b]; Wen-Rui Zhou[a]; Qian Ren[a]; Xiu-Zhi Han[c]; Jin-Ping Zhao[c]
[a] College of Material Science and Technology, Beijing Forestry University, Beijing, China [b] Faculty of Science and Engineering, Shimane University, Matsue, Shimane, Japan [c] Beijing New Building Material Group Companies, Beijing, China

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Properties of Acetylated Wood Prepared at Low Temperature in the Presence of Catalysts

Jian-Zhang Li,[1] Takeshi Furuno,[2] Wen-Rui Zhou,[1] Qian Ren,[1] Xiu-Zhi Han,[3] and Jin-Ping Zhao[3]
[1]College of Material Science and Technology, Beijing Forestry University, Beijing, China
[2]Faculty of Science and Engineering, Shimane University, Matsue, Shimane, Japan
[3]Beijing New Building Material Group Companies, Beijing, China

Abstract: In the presence of catalysts such as sodium acetate, zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate, acetylation of wood at 75°C was investigated. The results showed that it was possible to endow wood with high dimensional stability at low temperature by a catalyzed acetylation method. In particular, the magnesium chloride–catalyzed acetylation of wood showed very little or no effect on the color change or mechanical property of wood, as contrasted to those of the zinc chloride or magnesium perchlorate–catalyzed treatment, which showed a great effect. In addition, the concentrations of catalysts proved to have an effect on weight percent gain.

Keywords: Catalyst, color change, mechanical property, wood acetylation

INTRODUCTION

Chemical modification of wood improves its dimensional stability and durability. Acetylation with acetic anhydride is promising in this context.[1−4] The resistance of acetylated wood against micro-organisms and its other properties are remarkable.[1−2,5−7] Acetic anhydride used for acetylation is environmental friendly compared with other chemicals used for wood protection. Acetylation can be performed with or without catalysts and co-solvents, respectively. Usually, liquid phase reactions are favored but gas phase reactions have also been studied.[8] Fiber board and flakeboard acetylation were studied by Rowell

Address correspondence to Jian-Zhang Li, College of Material Science and Technology, Beijing Forestry University, Beijing, China. E-mail: lijianzhang@126.com

et al.[9] and Simonson and Rowell.[4] Acetylation in semi-industrial scale and in industrial scale has been described by Becker and Militz[3] and Simonson and Rowell.[4]

For shortening the reaction time and protecting wood from degradation and color change during acetylation catalysts were looked for. Potassium acetate and sodium acetate,[10−12] dimethylformamide,[13] and trifluoroacetic acid[14] have been studied. Strong mineral acid or acid salt as catalysts always cause hydrolysis of the polysaccharide moiety of wood, resulting in decreased physical properties. Pyridine and dimethylformamide as catalysts cause odor problems. Moreover, their separation from the excess acetic anhydride and acetic acid at the end of the process is difficult. The utilization of salt catalysts needs a two step process: (1) Impregnating the wood with catalysts and drying and (2) The acetylation.

In this study, the solid state catalysis approach was followed. We used sodium acetate, zinc chloride, magnesium perchlorate, and magnesium chloride. For evaluating the catalytic efficiency the weight percent gain (WPG) and the antiswelling efficiency (ASE) of modified wood were calculated. The effects of the catalysts on the strength properties and color change of wood were also observed.

MATERIALS AND METHODS

Wood Specimens

Sapwood specimens of sugi (*Cryptomeria japonica* D. Don) were used. The specimens used for dimensional stability and color change experiments having a size of 30(R) × 30(T) × 5(L) mm were initially extracted with a mixed solution of ethanol and benzene (vol/vol = 1/2) for 12 h, and with acetone for another 12 h using a Soxhlet extractor. The specimens used for strength properties measurement with a size of 20(R) × 20(T) × 320(L) mm were initially immerged in a mixed solution of ethanol and benzene (vol/vol = 1/2) for 7 days and in boiling water for another 12 h. All of the extracted specimens were then dried at 105°C for 24–48 h. Subsequently, their oven-dried weights and sizes were measured. Five specimens were used for each reaction condition.

Chemical Agents

Acetic anhydride [$(CH_3CO)_2O$], sodium acetate (CH_3COONa), zinc chloride ($ZnCl_2$), magnesium perchlorate [$Mg(OCl_4)_2$], magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and all the other chemical agents used were of chemical grade from Wako Pure Chemical Industries, Ltd., Japan.

Preparation of Catalyzed Acetylated Wood

Dissolving Catalysts in Acetic Anhydride

The catalysts were dissolved in acetic anhydride separately with stirring and heating to prepare catalytic acetic anhydride solutions with several different concentrations (0.1–1.0%).

Preparation of Catalyzed Acetylated Wood

The specimens were immersed in catalytic acetic anhydride solutions at reduced pressure for 30 min and at atmospheric pressure for 24 h. Then the specimens were wrapped with polyvinylidene chloride film and aluminum foil and heated at 75°C for different periods (2–8 h).

After this treatment, the specimens used for dimensional stability and color change experiments were immersed in water at reduced pressure for 30 min and leached in flowing water for 24 h, and then they were extracted with acetone for 12 h. Afterward the specimens were oven-dried at 105°C for 24 h, and their sizes and weights were measured. The weight percent gain (WPG) of acetylated specimens was calculated on the oven-dried weight basis.

After being acetylated, the specimens used for measuring strength properties were immersed in water at reduced pressure for 30 min and leached in flowing water for 7 days. Then they were oven-dried at 105°C for 48 h and their WPG was also calculated.

EVALUATION OF CATALYZED ACETYLATED WOOD

Dimensional Stability Measurement

The specimens for dimensional stability measurement were immersed in distilled water, then they were put in a vacuum oven, and the pressure was reduced to about 0.01 MPa. After 30 min at this reduced pressure, the interior of the oven was allowed to return to atmospheric pressure for 24 h at room temperature. After this operation, the sizes of the water-absorbed specimens were measured. From the changes in volumetric dimensions the antiswelling efficiency (ASE) during water absorption was calculated.

Modulus of Dynamic Elasticity, Static Modulus of Elasticity, and Bending Strength Tests

The resonance frequency of the tap sound for specimens by a FFT analyzer (Ono Sokki CF-360) using the flexural-vibration method of free-free beams was measured. The modulus of dynamic elasticity was calculated by the following formula (1):

$$E_d = 4\, f^2 l^2 \rho \tag{1}$$

where E_d is the modulus of dynamic elasticity (Pa), f is the resonance frequency (Hz), l is the length of the beam (m), and ρ is the density ($kg \cdot m^{-3}$).

The modulus of dynamic elasticity, static modulus of elasticity, and bending strength of specimens were obtained from the static bending tests by means of an autograph (Shimadzu AG-5000A) using a 280 mm span and a 10 mm/min head speed.

Measurement for the Color Changes of Catalyzed Acetylated Specimens

The color on the cross-section of specimen before and after treatment was measured by spectrophotometer (MINOLTA CM-3700d) according to the CIE 1976 L*a*b* color system. Five specimens were used for each treatment and three areas (5 × 5 mm) were measured for each specimen. The color difference of specimens was calculated by the following formula (2):[15]

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{2}$$

where Δ E* is the color difference, Δ L* is the lightness difference, and Δ a* and Δ b* are the chroma differences.

RESULTS AND DISCUSSION

Acetylation at Low Temperature in the Presence of Catalysts

Figure 1 shows the effects of catalysts on the acetylation of wood at 75°C. For comparison, the results from the same reaction condition at 75°C and 120°C without a catalyst are also shown in Figure 1.

At 75°C without a catalyst, even in 8 h reaction, the acetylated wood gained about 10% WPG and 30% ASE, showing not a high dimensional stability. This means that the acetic anhydride can hardly smoothly react to wood at low temperature without a catalyst.

In the presence of sodium acetate dissolved into acetic anhydride, the acetylation of wood at 75°C was accelerated. The values of WPG and ASE of catalyzed acetylated wood were higher than those of uncatalyzed ones at the same reaction condition. However, the sodium acetate dissolved into acetic anhydride did not show so remarkable a catalytic effect in comparison with its pre-loading on wood.[12]

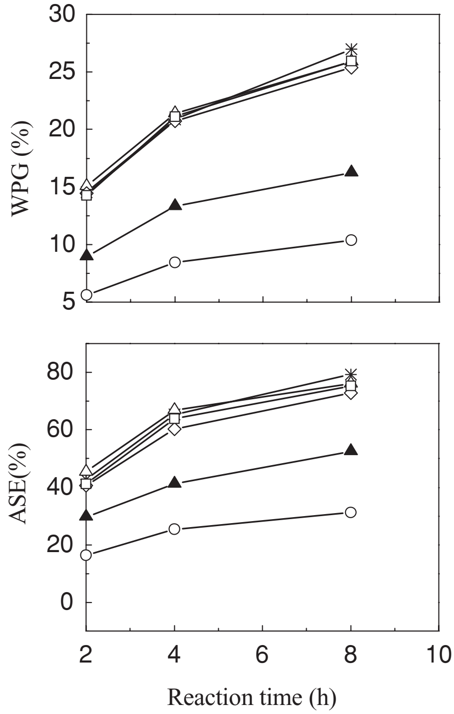

Figure 1. Acetylation of wood with or without catalysts. Symbols: ○ = 75°C without catalyst, ◇ = 120°C without catalyst, ▲ = 75°C with sodium acetate as a catalyst, □ = 75°C with zinc chloride as a catalyst,✳ = 75°C with magnesium perchlorate as a catalyst, △ = 75°C with magnesium chloride hexahydrate as a catalyst. Note: All the concentrations of catalytic acetic anhydride solution are about 0.8%.

The acetylation of wood at 75°C was markedly accelerated in the presence of zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate dissolved in acetic anhydride. The catalyzed acetylated wood showed much higher values of WPG and ASE than the uncatalyzed one at the same reaction condition. And the catalyzed acetylation at 75°C corresponded approximately to that at 120°C without a catalyst. In 8-h reaction, the catalyzed acetylation could give wood WPG value of about 25% and ASE value of more than 75%.

From the aforementioned experiments, it is found that zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate as catalysts dissolved in acetic anhydride could yield a very effective catalytic effect on the acetylation of wood, and the catalyzed acetylated wood gained much higher values of WPG and ASE than the uncatalyzed one at the same reaction condition. Even at 75°C, a rather low reaction temperature, the catalyzed acetylation could endow wood with a great dimensional stability, while the uncatalyzed one could

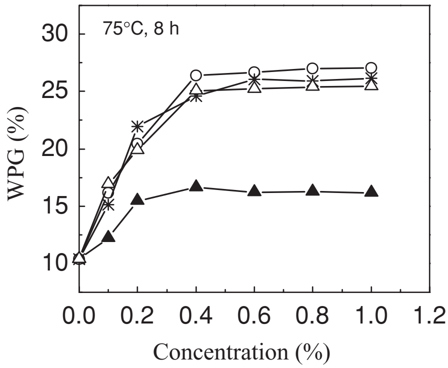

Figure 2. Effects of concentrations of catalysts on the weight percent gain (WPG) of wood. Symbols: ▲ = sodium acetate as a catalyst, ○ = zinc chloride as a catalyst, ✳ = magnesium perchlorate as a catalyst, Δ = magnesium chloride hexahydrate as a catalyst.

only give a low or not high dimensional stability. This means that wood can be acetylated easily at low temperature in the presence of zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate as catalysts dissolved in acetic anhydride.

Effect of Concentrations of Catalytic Acetic Anhydride Solution on Acetylation of Wood

Figure 2 shows the relationship between concentrations of catalytic acetic anhydride solution and WPG of acetylated wood. The catalysis of sodium acetate, zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate for acetylation was testified by the fact that the WPG increased with the concentration increasing.

The acetylated wood made a remarkable increase in WPG at the initial increment of the concentrations of zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate as catalysts. At higher concentrations, this increase slowed down and the WPG showed a constant value when the concentrations of catalyst exceeded 0.4–0.6%. In contrast, sodium acetate dissolved in acetic anhydride could not accelerate the acetylation of wood notably as compared with the three other catalysts mentioned earlier or sodium acetate itself used for pre-loading on wood.[12]

Mechanical Properties

Figure 3 shows the modulus of dynamic elasticity, static modulus of elasticity, and bending strength of treated and untreated wood specimens.

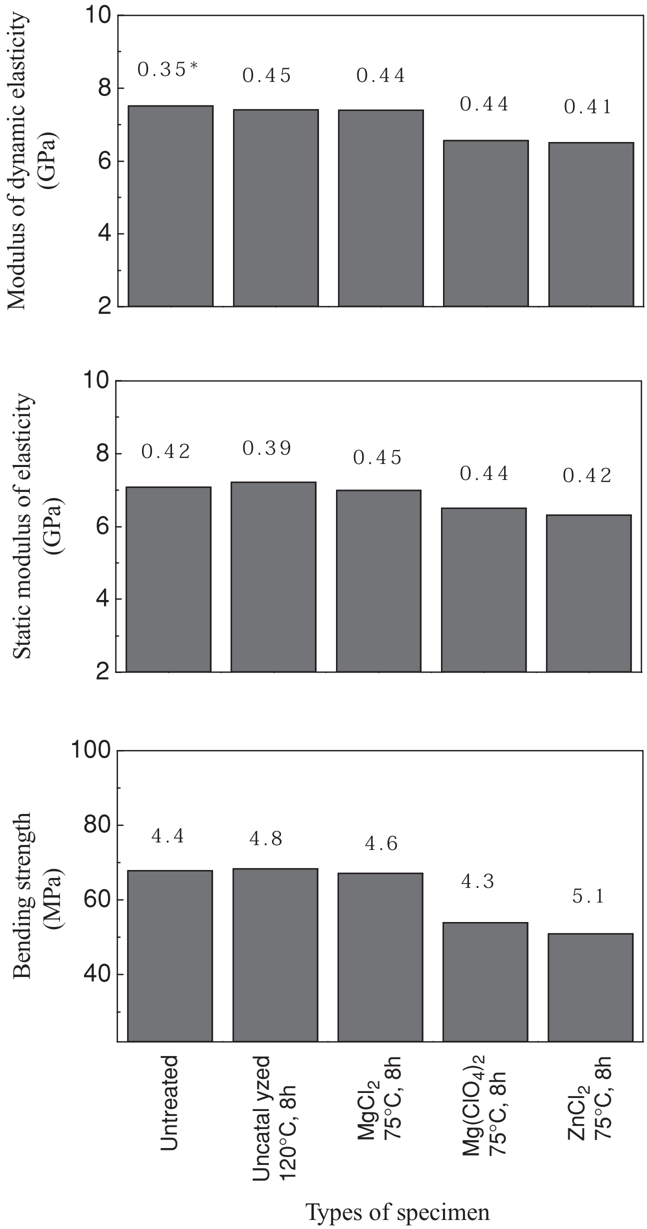

Figure 3. Mechanical properties of untreated and treated specimens. Note: *Standard deviation**:** $S = \sqrt{\frac{\sum_{i=1}^{n}(Xi-\overline{X})^2}{n-1}}$**, n = 5.**

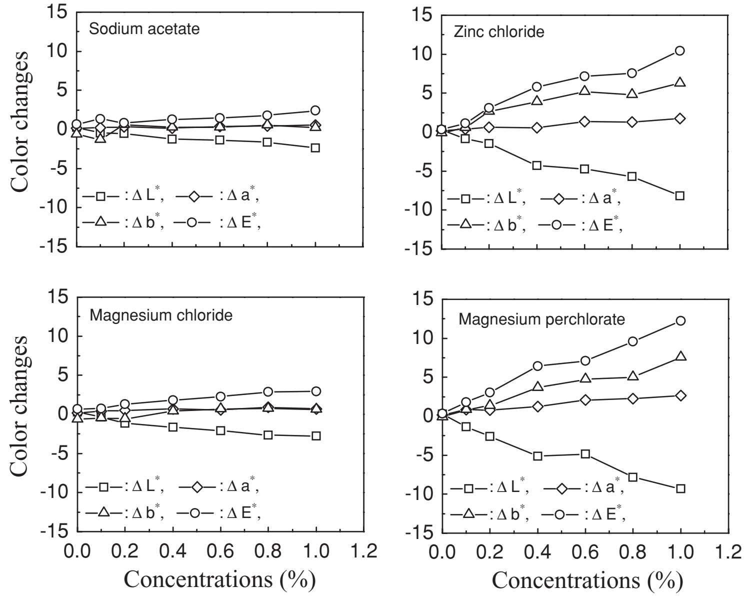

Figure 4. Effects of concentrations on color changes of specimens. Symbols: Δ L* = change in brightness difference, Δ a* and Δ b* = changes in chroma difference, Δ E* = change in color difference.

In an 8-h reaction at 75°C, the magnesium chloride–catalyzed acetylated wood showed no or little marked change in modulus of dynamic elasticity, static modulus of elasticity, or bending strength, and the uncatalyzed acetylated wood also showed no significant change in mechanical properties in correspondence with the conclusion attained by the former researcher.[2] On the other hand, in an 8-h reaction at 75°C, the zinc chloride and magnesium perchlorate–catalyzed acetylated wood showed a considerable decrease in mechanical properties, especially in bending strength. This may be due to the fact that zinc chloride is a strong Lewis acid, yielding a rather strong acidic reaction condition; and magnesium perchlorate is an oxidizer, which leads to wood disintegrating, resulting in decrease of mechanical properties of catalyzed acetylated wood.

Effect of Catalysts on the Color Change of Wood

Figure 4 shows the effects of concentrations of catalysts on the color changes of catalyzed acetylated wood. The 0 value of the concentration of catalysts refers to the value of color changes of the uncatalyzed acetylation.

From Figure 4 we can find that the sodium acetate and magnesium chloride-catalyzed acetylation hardly caused wood to change the color at 75°C even for 8 h at lower concentration values. With the increase of the concentration of catalysts, the lightness of treated wood decreased gradually and the color difference increased slightly, while the Δ a* and Δ b* values showed little or no change.

On the other hand, the zinc chloride and magnesium perchlorate-catalyzed acetylation for 8 h reduced very greatly the lightness of treated wood and the treated wood became dark-colored, especially at higher concentration values. The Δ a* of the two catalyzed acetylated wood changed slightly, but the Δ b* increased greatly, leading the treated wood to get a yellow color. For this reason, the color difference of wood increased remarkably. This is similar to the decrease of strength properties of catalyzed acetylated wood. In other words, the acidic reaction condition or the oxidation caused the degradation of wood, resulting in the color change of wood.

CONCLUSIONS

From Figure 4 we can find that the sodium acetate– and magnesium chloride–catalyzed acetylation hardly caused wood to change the color at 75°C even for 8 h at lower concentration values. With the increase of the concentration of catalysts, the lightness of treated wood decreased gradually and the color difference increased slightly, while the Δ a* and Δ b* values showed little or no change.

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CONCLUSIONS

The catalyzed acetylation of wood with acetic anhydride using sodium acetate, zinc chloride, magnesium perchlorate, and magnesium chloride hexahydrate as catalysts dissolved in acetic anhydride was investigated in this study. The results verified that the catalyzed acetylation, especially magnesium chloride–catalyzed acetylation at low temperature, could confer to wood high-dimensional stability along with little or no reduction of mechanical properties and little or no color change.

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