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Chemical modification of wood by anhydrides without solvents or catalysts

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Abstract Acetylated, propionylated, butyrylated, isobutyrylated, and hexanoylated woods were prepared at several temperatures. The reaction rate, dimensional stability, and changes in the ratios of specific gravity and dimensions in the tangential and radial directions were estimated. The reaction rate of propionylation was slow at temperatures under 90°C but increased with the temperature. The butyrylated, isobutyrylated, and hexanoylated woods showed little or no weight percent gain (WPG) and little or no antishrinkage efficiency (ASE) below 110°C even for 24h, but they achieved significant WPG and ASE values at 140°C with a longer reaction time. The acetylated, propionylated, and butyrylated woods showed almost the same values for dimensional stabilization efficiency based on WPG (DSE). The specific gravity and dimensions ratios for acetylated, propionylated, and butyrylated woods compared to those of untreated wood increased with an increase in WPG.

Key words Wood · Acetylation · Propionylation · Butyrylation · Dimensional stabilization efficiency

Introduction

Many studies have been done to overcome the disadvantages of wood. Of all the chemical modifications for wood, most studies have been done with acetylation,^{1–7} which can endow wood with high dimensional stability and resistance to biodegradation. Acetylated wood has been used in the building industry; it has performed well and offers broad utility. On the other hand, the general acetylation method with acetic anhydride gives a by-product that introduces an

acidic condition to the wood, which includes an acetic acid smell and acid hydrolysis of cellulose, resulting in strength loss and acidic corrosion of the metal fasteners used in the acetylated wood.

Studies of other anhydrides reacting with wood have been done in limited conditions. For example, propionic anhydride and butyric anhydride dissolved in xylene have been used to react with wood without catalysts. It was pointed out that the reaction of propionic anhydride and butyric anhydride with wood were much slower than that of acetic anhydride.¹ Much more study is needed for a better understanding of the reaction of wood with anhydrides.

Propionic, butyric, isobutyric, and hexanoic acids show weaker acidity than acetic acid. In this case, propionic, butyric, isobutyric, and hexanoic anhydrides can be expected to be less harmful to wood when used as modifiers (propionic, butyric, isobutyric, and hexanoic acids are produced as by-products). Consequently, it may be essential and significant to study the modification of wood with propionic, butyric, isobutyric, and hexanoic anhydrides.

Most of the procedures to modify wood developed over the years have complicated reaction schemes using either a catalyst or an organic co-solvent. The use of strong mineral acid or acid salt catalysts causes hydrolysis of the carbohydrate polymers, resulting in damage to the wood structure. When pyridine or dimethylformamide is used as a catalyst in wood acetylation, two problems result: first, the smell of these two compounds is never completely removed from the wood because they are strongly sorbed by wood; second, for both chemicals it is difficult to separate them from the excess acetic anhydride and acetic acid by-product after acetylation.

Use of a solvent, which reduces the reaction rate because of dilution of modifiers, would require complicated separation procedures to recover the chemicals after the reaction. Organic solvents are often harmful to humans and the environment. Therefore, it is the best to eliminate both catalysts and organic solvents in the reaction system. In this paper, we describe the use of propionic, butyric, isobutyric,

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and hexanoic anhydrides reacting with hinoki specimens without solvents or catalysts, and we characterize these reactions.

Materials and methods

Wood specimens

The specimens, 30(R) × 30(T) × 5(L) mm and obtained from the sapwood portion of hinoki (*Chamaecyparis obtusa* Endl.), were extracted with a mixed solution of ethanol and benzene (v/v, 1:2) for 12 h and with acetone for another 12 h in a Soxhlet apparatus. After extraction, the specimens were dried at 105°C for 24 h. The oven-dried weights and the sizes of the specimens were then measured. Three specimens were used for each reaction condition.

Chemicals agents

Acetic anhydride [(CH₃CO)₂O], propionic anhydride [(CH₃CH₂CO)₂O], butyric anhydride [(CH₃CH₂CH₂CO)₂O], isobutyric anhydride {[(CH₃)₂CHCO]₂O}, hexanoic anhydride {[CH₃(CH₂)₄CO]₂O}, and all the other chemical agents used in this experiment were of chemical grade from Wako Pure Chemical Industries.

Reaction of wood with anhydrides

Impregnation

To compare the reaction rate and the dimensional stability of the various anhydride-treated woods, acetylated wood was also prepared. A reduced-atmospheric pressure method was employed to impregnate the anhydrides into specimens as follows: the specimens were immersed in acetic, propionic, butyric, isobutyric, or hexanoic anhydride, respectively. After being exhausted by a vacuum pump for 30 min (10–50 mmHg), the specimens were exposed to atmospheric pressure overnight at room temperature.

Modification of wood

The impregnated specimens with 180%–200% anhydride were wrapped with polyvinylidene chloride film and aluminum foil and were then heated at several temperatures and different fixed reaction times (2, 4, 8, 12, and 24 h, respectively). After extraction with acetone for 12 h in a Soxhlet apparatus, the specimens were oven-dried at 105°C for 24 h. Subsequently they were weighed and their sizes were measured.

Evaluation of modified woods

Weight percent gain, bulking coefficient, rate of reaction

The weight percent gains (WPGs) of the treated woods were calculated on an oven-dried weight basis by measuring

the extractive-free untreated specimens and the treated specimens. The bulking coefficients (Bs) were also determined for all prepared specimens.

The rate of reaction was calculated using the following formula.

$$R = \text{WPG}/t$$

where R is the rate of reaction (% · h⁻¹); WPG is the weight percent gain (%); and t is the reaction time (h).

Dimensional stability measurements and water-leaching test

The treated and untreated specimens were immersed in distilled water and were then placed in a desiccator. After being exhausted by a vacuum pump for 30 min (10–50 mmHg), the specimens were exposed to atmospheric pressure for 1 day at room temperature. The sizes and weights of the specimens were then measured. The antishrink efficiencies (ASE-w) during water absorption of treated specimens were calculated based on the volumetric change. The specimens were oven-dried again at 105°C for 24 h. The antishrink efficiencies (ASE-d) and WPGs of treated specimens were calculated based on the changes in weights and dimensions after oven-drying. This operation was repeated three more times to test the water-leaching resistance of treated specimens.

Dimensional stabilization efficiency

The dimensional stabilization efficiency (DSE) was calculated using the following formula.

$$\text{DSE} = \text{ASE-w}/\text{WPG}$$

where DSE is the dimensional stabilization efficiency; ASE-w is the antishrink efficiency; and WPG is the weight percent gain.

Results and discussion

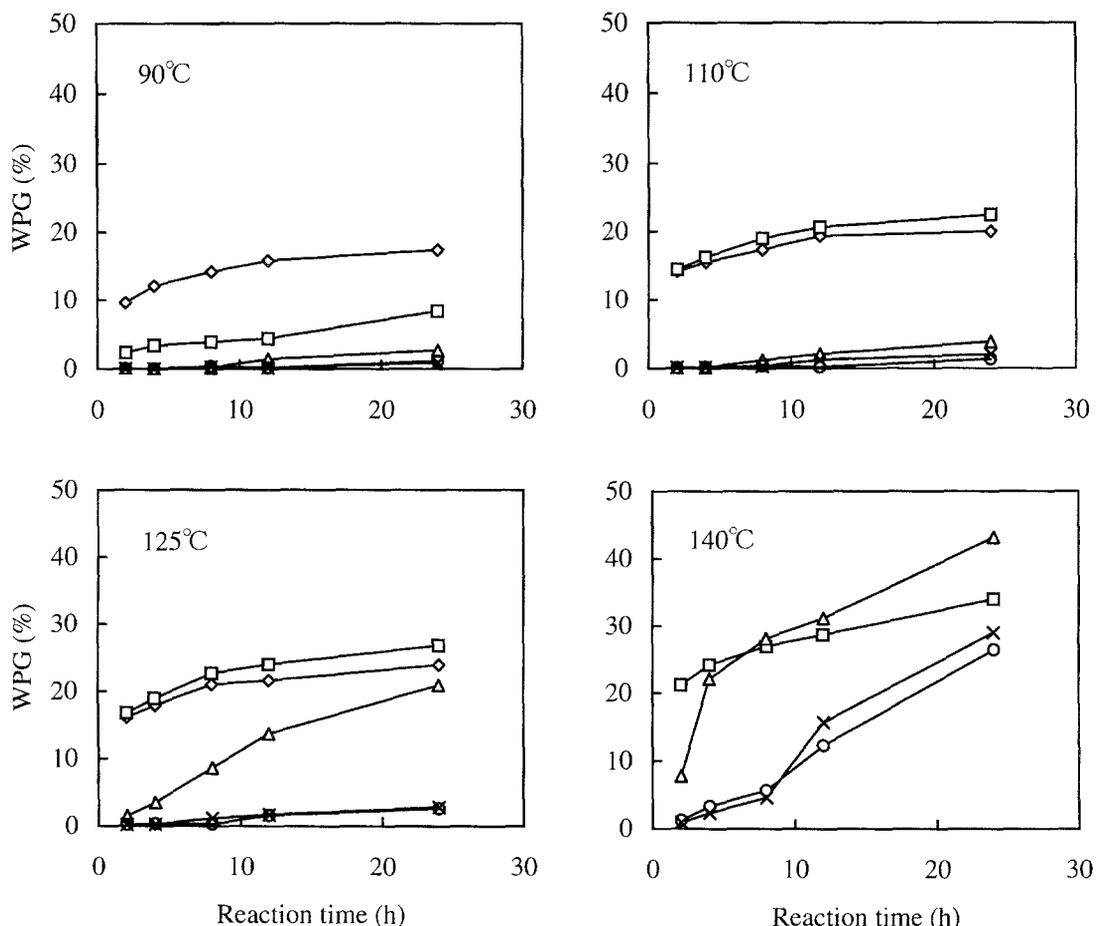
Effects of reaction temperature and reaction time on WPG

Figure 1 shows the effects of the reaction temperature and reaction time on the WPG of treated specimens. The WPG increased with the increment of reaction temperature and reaction time.

At 90°C, the specimens treated with butyric anhydride, isobutyric anhydride, and hexanoic anhydride gained hardly any weight (WPG < 3%) at 24 h. The acetylated wood measured 9.6% WPG at 2 h and 17.4% WPG at 24 h. The propionylated wood showed a small weight gain at 24 h of reaction, but it was far less than that seen with the acetylated wood.

At 110°C, the butyrylated, isobutyrylated, and hexanoylated woods had weight gains of less than 4% at 24 h. Otherwise, the WPGs of the propionylated wood increased rapidly with the increment of reaction time, and

Fig. 1. Effects of reaction temperature and reaction time on weight percent gain (WPG). *Diamonds*, acetylated wood; *squares*, propionylated wood; *triangles*, butyrylated wood; *circles*, isobutyrylated wood; *crosses*, hexanoylated wood



the WPGs were higher than those of acetylated wood at the same reaction time.

At 125°C, the WPGs of propionylated wood increased quickly at the beginning of the reaction. Although the acetylated wood also showed high WPGs, the WPG values were lower than those of propionylated wood at the same reaction time. The WPGs of the butyrylated wood began to increase markedly with the increased reaction time: the WPG was 8.6% at 8 h and 20.9% at 24 h. The isobutyrylated and hexanoylated specimens showed little weight gain: the WPGs were less than 5% at 24 h.

At 140°C, the WPGs of the propionylated wood increased quickly with the increment of reaction time: the WPG was 21.2% at 2 h and 34.0% at 24 h. The WPG of propionylated wood reacting at 140°C for 4 h was roughly equal to the WPG reacting at 125°C for 12 h or at 110°C for 24 h. The WPG of butyrylated wood increased quickly with the reaction time, and it became higher than that of propionylated wood after 8 h. The isobutyrylated and hexanoylated specimens achieved rather high WPGs at more than 12 h: the WPGs were 12.2% and 15.7% at 12 h, and 26.4% and 28.4% at 24 h, respectively. The acetylation experiment did not take place at 140°C because the boiling point of acetic anhydride is below 140°C.

From the above experiments, it was found that the reaction temperature and reaction time had significant effects

on the WPGs of anhydride-treated woods, especially the specimens treated with anhydrides with more than three carbon atoms, such as butyric anhydride, isobutyric anhydride, and hexanoic anhydride. The results can be explained by the steric effect theory⁸: because the anhydrides with more carbon atoms have a larger molar volume, more thermal energy is needed to overcome the steric hindrance when they react with wood.

Effects of reaction time and reaction temperature on the rate of reaction

The effects of the reaction time and reaction temperature on the rate of reaction between wood and anhydrides without solvents or catalysts are shown in Fig. 2. The rates of isobutyrylation and hexanoylation are not illustrated in Fig. 2 because few active data were obtained during the experiment.

The specimens were impregnated with excessive anhydrides and hermetically wrapped with polyvinylidene chloride film and aluminum foil to avoid the effects of a concentration change on the reaction rate. Although the acids (yielded as by-products during the reaction procedure) reduce the concentration, they may bulk the wood and accelerate the reaction, which is good for practical

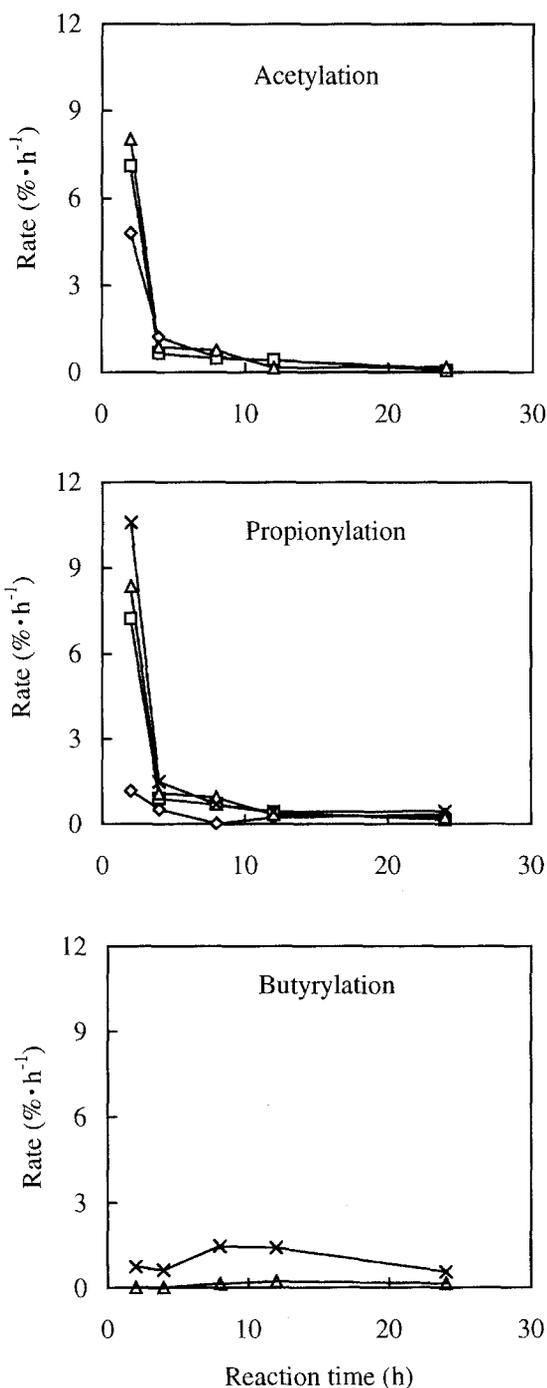


Fig. 2. Effects of reaction time on reaction rate. *Diamonds*, 90°C; *squares*, 110°C; *triangles*, 125°C; *crosses*, 140°C

use. On the other hand, it makes the result difficult to analyze.

It was found that the acetylation and propionylation rates decreased with an increase in reaction time. It stands to reason that the hydroxyl groups, as points in the cell walls of wood that react with anhydrides to convert them to ester groups, decrease with increasing reaction time.

The acetylation process had a rather high reaction rate at 90°C during the initial 2h. The reaction rate increased with the increment of reaction temperature and decreased rapidly along with the reaction time.

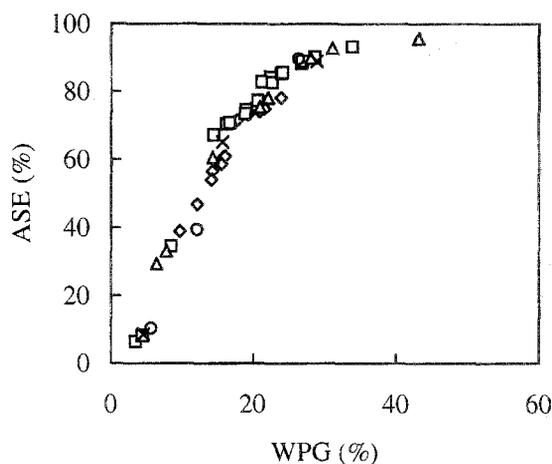


Fig. 3. Effects of weight percent gain (WPG) on antiswelling efficiency (ASE) of treated woods. Symbols are the same as in Fig. 1

Although the reaction rate of propionylation was low at 90°C, it increased gradually with the increment of reaction temperature and became higher than that of acetylation when the temperature exceeded 110°C. Propionylation showed a high reaction rate during the initial 2h at 140°C.

When the reaction temperature was lower than 110°C, the butyrylation process showed little or no reaction rate. The reaction rate of butyrylation increased slightly with an increase in reaction time at 140°C and started to decrease when the reaction time was longer than 12h.

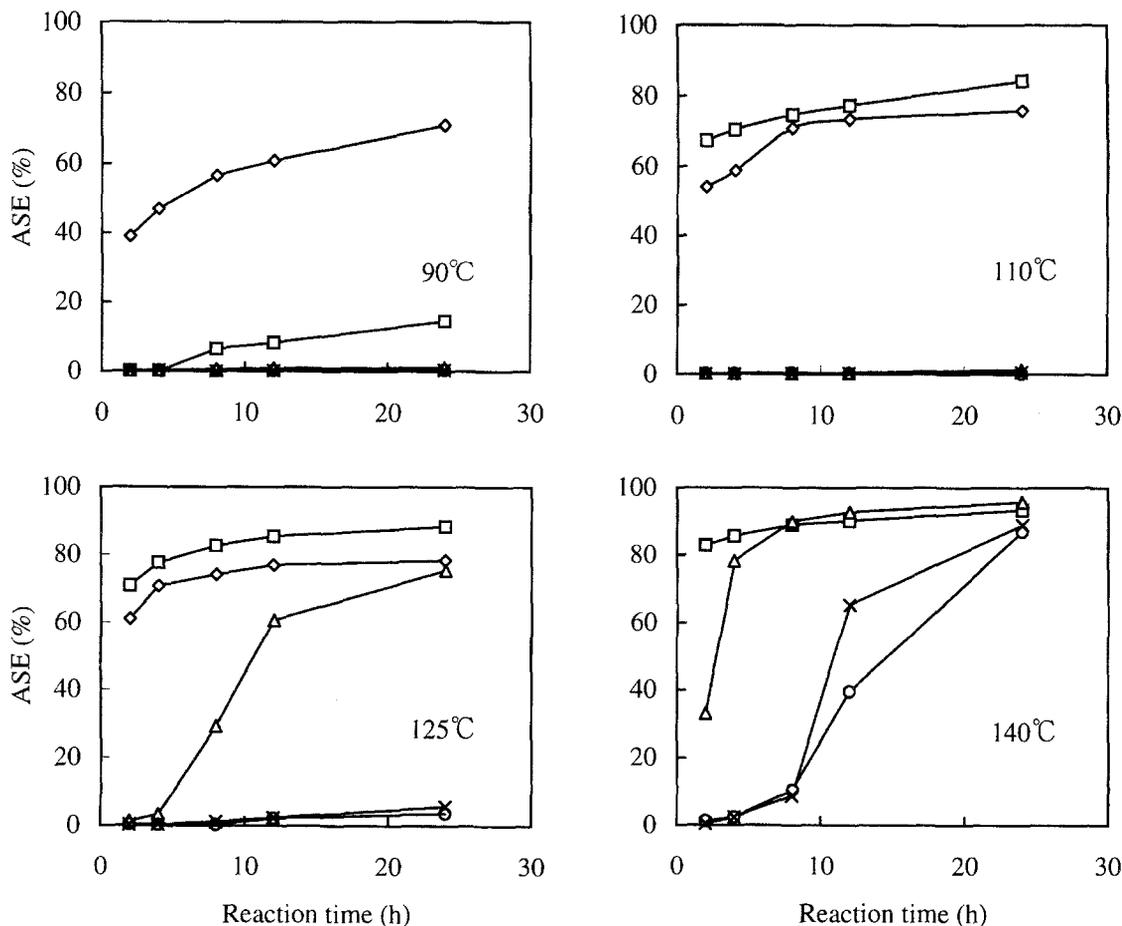
The above experimental results were different from the conclusions of Goldstein et al.¹ They pointed out that the propionic and butyric anhydrides reacted far more slowly with wood than did acetic anhydride. In their study, after a 10-h reaction time (in xylene at 125°C with ponderosa pine) acetylation produced a weight gain of 17%, compared with a weight gain of less than 4% for propionylation and no weight gain for butyrylation. After a 30-h reaction time, propionic anhydride produced a weight gain of 10%, and the reaction with butyric anhydride produced little or no weight gain. The disparities between our experimental results and Goldstein's experimental results remain unexplained, but probably they are due to the differences in wood specimens or the solvents used in the experiments.

Effects of WPG and reaction time on ASE-w of specimens

The relations between the ASE-w and the WPG of specimens treated with anhydrides are shown in Fig. 3. The acetylated, propionylated, butyrylated, isobutyrylated, and hexanoylated woods showed almost the same tendency. Their ASE-w values increased linearly with the initial increment of WPGs, but the increasing tendency started to decline when the WPGs exceeded 30%.

Anhydrides can react chemically with cell wall components of wood, and they consequently bulk the cell wall

Fig. 4. Effects of reaction time on antismwelling efficiency (ASE) of treated woods. Symbols are the same as in Fig. 1



of wood. Research involving cell wall bulking treatments⁹ reported that the increase in wood volume was directly proportional to the WPG. When this bulked wood comes into contact with water, it is difficult to cause additional swelling compared to untreated wood: the higher the WPG, the less the additional swelling. This is why the treated specimens are effective in terms of dimensional stability. However, the increase in the ASE-w values started to slow when the WPGs were more than about 30%. It was suggested that the decrement in the ASE-w values might be due to the fact that the volume of added chemicals was enough to rupture the cell wall,¹⁰ which could make the bulking volume of wood after water absorption larger than that of untreated wood.

The relations between the ASE-w and the reaction time of acetylation, propionylation, butyrylation, isobutyrylation, and hexanoylation are shown in Fig. 4. Their ASE-w values increased with the increment of reaction time.

At 90°C, the ASE-w of acetylated wood attained 70%. The other anhydride-treated specimens showed little or no ASE-w increase except propionylated wood, which showed a slight ASE-w increase.

At 110°C, the acetylated wood achieved 60% ASE-w in about 4h and 70% ASE-w in about 8h. The ASE-w of the propionylated wood reached 60%–80%. The other anhydride-treated woods showed little or no ASE-w.

At 125°C, the ASE-w of the acetylated wood rose to 80%, and the ASE-w of the propionylated wood was 90%. The ASE-w of the butyrylated wood increased abruptly with the reaction time and reached 80%. The isobutyrylated and hexanoylated woods still showed little or no ASE-w.

At 140°C, the propionylated wood was 80% ASE-w within 2h and reached 90% ASE-w. The ASE-w of the butyrylated wood increased abruptly with the increment of reaction time and approached 90%. The ASE-w values of isobutyrylated and hexanoylated woods increased after a delay and attained 90% ASE-w in 24h.

Relation between bulking coefficient and WPG of the treated woods

The relations between the bulking coefficient (B) and the WPG of acetylated, propionylated, butyrylated, isobutyrylated, and hexanoylated woods are shown in Fig. 5. The B evidently increased with the increments of WPG. There were little differences in the B and WPG among acetylated, propionylated, and butyrylated woods. In this case, all the treated woods with higher WPGs demonstrated higher bulking effects, so they could be expected to show higher ASE-w and ASE-d values.

Dimensional stabilization efficiency of treated woods

Figure 6 shows the relations between the DSE and the WPG of acetylated, propionylated, and butyrylated woods. The acetylation, propionylation, and butyrylation treatments produced almost the same DSE values at the same WPG, and the DSE decreased with an increase in WPG. The DSEs of isobutyrylated and hexanoylated woods are not shown in Fig. 6 because only a few active data were obtained in this experiment.

WPG and ASE-d changes with wet-dry cycles

Changes of WPG and ASE-d with the wet-dry cycles in the leaching test are shown in Fig. 7. The acetylated, propionylated, butyrylated, isobutyrylated, and hexanoylated woods showed little or no change in WPG and ASE-d after four wet-dry cycles. This finding indicates that all of the modified woods had high resistance to water

leaching because of the covalent bonds (ester groups) being formed between wood and the anhydrides.

Changes in the ratios of specific gravity and dimensions of treated woods

Figure 8 shows changes in the ratios of specific gravity (ρ_t/ρ_0 , where ρ_t is the specific gravity of treated wood and ρ_0 is that of untreated wood) and dimensions in the tangential direction (T_t/T_0 , where T_t is the dimension in the tangential direction of treated wood and T_0 is that of untreated wood) and radial direction (R_t/R_0 , where R_t is the dimension in the radial direction of treated wood and R_0 is that of untreated wood) of acetylated, propionylated, and butyrylated woods to those of untreated wood with WPG. Those of isobutyrylated and hexanoylated woods are not shown in Fig. 8 because few active data were obtained for them in the experiment.

The ρ_t/ρ_0 , T_t/T_0 , and R_t/R_0 ratios for all the treated woods increased with the increment of WPG. The slopes of the ρ_t/ρ_0 , T_t/T_0 , and R_t/R_0 ratios were almost the same for the acetylated, propionylated, and butyrylated woods.

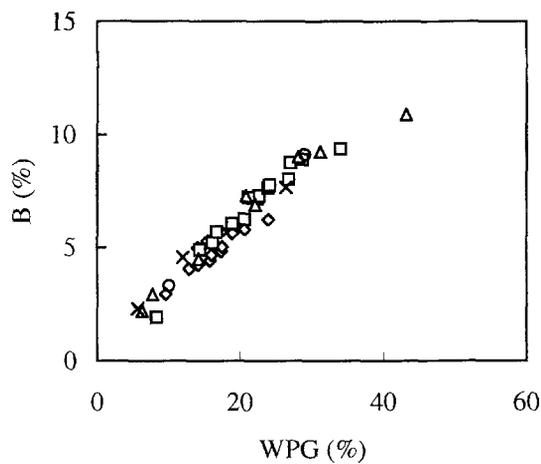


Fig. 5. Effects of weight percent gain (WPG) on bulking coefficient (B) of treated woods. Symbols are the same as in Fig. 1

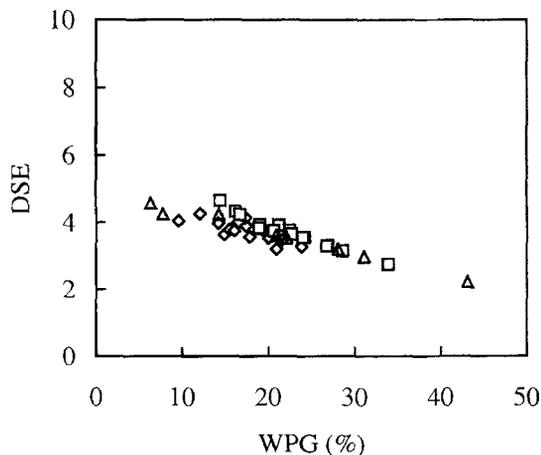


Fig. 6. Effects of weight percent gain (WPG) on dimensional stabilization efficiency (DSE) of treated woods. *Diamonds*, acetylated wood; *squares*, propionylated wood; *triangles*, butyrylated wood

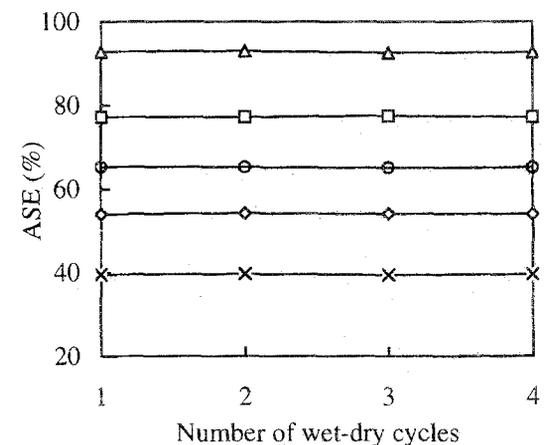
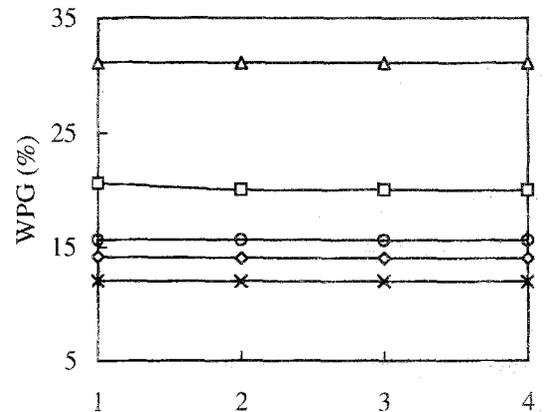


Fig. 7. Changes of antishrink efficiency (ASE) and weight percent gain (WPG) after four wet-dry cycles. Symbols are the same as in Fig. 1

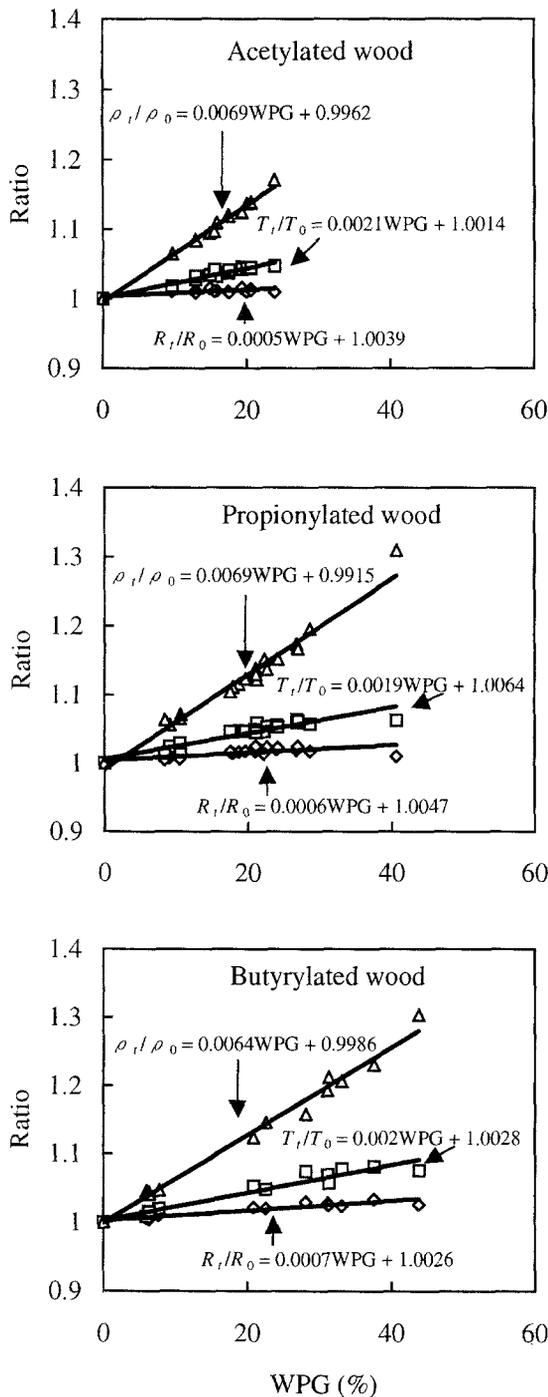


Fig. 8. Changes in the ratios of specific gravity (ρ_t/ρ_0) and dimensions in the tangential direction (T_t/T_0) and radial direction (R_t/R_0) of treated woods to those of untreated wood with weight percent gain (WPG)

Conclusions

The reaction rates for wood plus propionic anhydride and wood plus butyric anhydride increased with the reaction temperature. When the temperature exceeded 110°C , the propionylated wood had higher WPG and ASE-w values than acetylated wood with the same reaction time. The butyrylation began to show a fairly good reaction rate at 125°C . The isobutyrylated and hexanoylated woods attained high WPG and ASE-w values only at 140°C . Because isobutyric anhydride and hexanoic anhydride have a strong smell and react slowly with wood, they are not as apposite as acetic anhydride or propionic anhydride for use as wood modifiers.

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