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ORIGINAL ARTICLE

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Dimensional stability of wood acetylated with acetic anhydride solution of glucose pentaacetate

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Abstract Five wood species were acetylated with acetic anhydride (AA) solution of glucose pentaacetate (GPA) at 120°C for 8h, and the effect of GPA on the dimensional stability of the acetylated wood was investigated. Some GPA was introduced into the wood cell wall during acetylation. The GPA remaining in the cell lumen penetrated the cell wall effectively after heating to more than 140°C for 10min. The bulking effects of GPA resulted in a 10%–30% increase in the anti-swelling efficiency of the acetylated wood with 20% GPA/AA solution in place of AA. Hydrophobic GPA did not deliquesce under highly humid conditions and it remained in the cell wall after boiling in water.

Key words Acetylation · Glucose pentaacetate · Bulking effect · Dimensional stability

Introduction

Acetylation is an excellent method for improving the dimensional stability of wood, which depends on the hydrophobic and bulky nature of the acetyl groups introduced into the amorphous region of the wood cell wall. Many attempts have been made to achieve more effective acetylation with various catalysts and solvents, but it is difficult to replace all active adsorption sites of wood constituents with acetyl groups. In addition, the acetyl groups introduced do not completely occupy the intermolecular space for moisture adsorption. Thus the dimensional stability of the acetylated wood is limited even though extreme treatment conditions are employed.[1]

On the other hand, the dimensional stability of wood can be improved by impregnation treatments. When the wood cell wall is swollen with polyethylene glycol (PEG), sugars, and salts, it swells only slightly with moisture adsorption. In most cases, however, the impregnating substances are deliquescent and water soluble. Therefore, such impregnation treatments are not applicable when wood is used under wet or highly humid conditions.[2]

If a hydrophobic substance is introduced into the wood cell wall during acetylation, the dimensional stability of the acetylated wood must be improved by the bulking effect of the impregnating substance without a complicated procedure and extreme treatment conditions. From this point of view, we attempted to introduce glucose pentaacetate (GPA) into the wood cell wall from its acetic anhydride (AA) solution. This paper deals with the bulking effects of GPA on the dimensional stability of acetylated wood.

Materials and methods

We used α,β-D-GPA and AA commercially available from Pfanstiehl Laboratory and Wako Pure Chemicals, respectively. Sitka spruce (*Picea sitchensis*) wood specimens of 30mm (R, radial direction) ×30mm (T, tangential direction) ×5mm (L, longitudinal direction) were soaked in 0%–30% GPA/AA solutions for 2 days and then heated in a flask at 120°C for 8h. These specimens were air-dried and then completely dried in vacuo at room temperature. The weight and dimensions of the specimens absolutely dried were measured before and after acetylation.

To examine the penetration of GPA into the wood cell wall, untreated and acetylated spruce wood specimens were soaked in molten GPA at 140°C for 1h. The weight and dimensions of the specimens were measured before and

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Table 1. Specific gravity of absolutely dried untreated wood specimens (γ_{u0})

Species	Symbol	γ_{u0}
Sitka spruce (*Picea sitchensis*)	S	0.40
Japanese cypress (*Chamaecyparis obtusa*)	C	0.45
Japanese oak (*Quercus crispula*)	JO	0.64
Japanese birch (*Betula Maximowicziana*)	B	0.66
Red oak (*Quercus rubra*)	R	0.70

after soaking. Some of the untreated and acetylated spruce wood specimens were heated at 100°, 120°, 140°, and 160°C for 10min in a drying oven.

Sitka spruce, Japanese cypress (*Chamaecyparis obtusa*), Japanese oak (*Quercus crispula*), Japanese birch (*Betula maximowicziana*), and red oak (*Quercus rubra*) specimens of 30mm (R) ×30mm (T) ×5mm (L) were acetylated with AA and 20% GPA/AA solution. Table 1 lists the specific gravity of the absolutely dried specimens in the untreated state (γ_{u0}). The specimens were soaked in the reagents for 2 days and then heated at 120°C for 8h. After being dried absolutely in vacuo at room temperature, the acetylated specimens were heated at 160°C for 10min in a drying oven. They were then equilibrated at 25°C and 33%, 57%, 75%, 92%, and 97% relative humidity (RH), and their weight and dimensions were measured. Then the specimens were soaked in water, boiled mildly at 95–98°C for 1h, and washed in flowing water for 1 week. The water-extracted specimens were then dried in vacuo at room temperature, and their weight and dimensions were measured. Finally, the specimens were boiled in acetone for 1h followed by washing in fresh acetone several times to remove the GPA. After removing the acetone in vacuo, their weight and dimensions were measured.

Results and discussion

Swelling of wood with introduction of GPA

Hereafter the acetylation with GPA/AA solution is described as "GPA acetylation," to distinguish it from "normal" acetylation using AA. To evaluate the bulking effects of the treatments, the specific swelling in volume, ΔV_0, is defined here by the following equation.

$$\Delta V_0(\%) = 100(V_{t0}/V_{u0} - 1)/\gamma_{u0} \qquad (1)$$

where V_{u0} and V_{t0} are the absolutely dry volumes of the untreated and acetylated specimens, respectively; and γ_{u0} is the specific gravity of the absolutely dried specimen in its untreated state. Figure 1 represents the relation between ΔV_0 and the weight percent gain (WPG) of the acetylated spruce wood specimens. Both the weight and volume increased with increasing WPG, and higher concentrations of GPA produced more swelling. This indicates that GPA penetrated the wood cell wall. However, the increase in ΔV_0 per increase in WPG due to GPA acetylation was less than that due to normal acetylation. Furthermore, white powdery GPA was deposited on the surface of the specimens when the concentration of GPA was 10% or higher. It suggested that some of the GPA was not effectively introduced into the wood cell wall or that it moved out of the wood cell wall during the evaporation of AA.

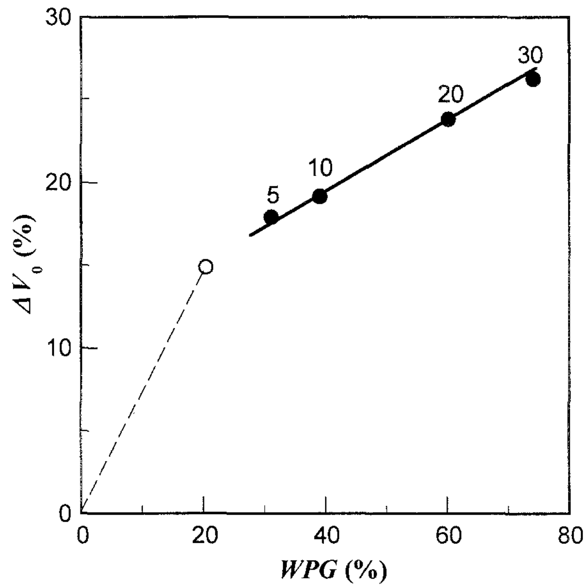

Fig. 1. Relation between specific increase in volume (ΔV_0) and weight percent gain (*WPG*) of spruce wood specimens due to acetylation at 120°C for 8h. *Open circle*, normally acetylated; *closed circles*, acetylated with acetic anhydride (AA) solutions of glucose pentaacetate (GPA); *5–30*, percent concentrations of GPA

Penetration of GPA into the wood cell wall with heating

Because the melting points of α- and β-GPA are about 110°C and 130°C, respectively, we expected that the powdery GPA on the surface of specimens would disappear with heating at 130°C or higher. Figure 2 shows the effects of heating on the weight and volume of the untreated and acetylated spruce wood specimens. As the heating duration was too short to induce marked degradation of wood constituents, the weight of the specimens remained unchanged. In addition, the powdery GPA on the surface of specimens disappeared after heating above 140°C. Interestingly, the GPA-acetylated specimens swelled markedly after heating. This swelling was interpreted as penetration of GPA into the wood cell wall. Table 2 lists the changes in weight and volume of spruce wood specimens by the soaking in molten GPA. After heating in air, the weight and volume of specimens decreased slightly with the pyrolysis of wood constituents. In contrast, the volume of the acetylated specimens increased after soaking in GPA, whereas that of unacetylated specimens increased only slightly. This indicates that GPA penetrated the wood cell wall after heating it to above its melting point, especially when the wood was previously acetylated. The amorphous region of the wood cell wall is swollen with acetyl groups by acetylation. Such expanded intermolecular distance may be responsible for the easier penetration of GPA into the wood cell wall. Alternatively, the affinity of wood constituents for GPA might be en-

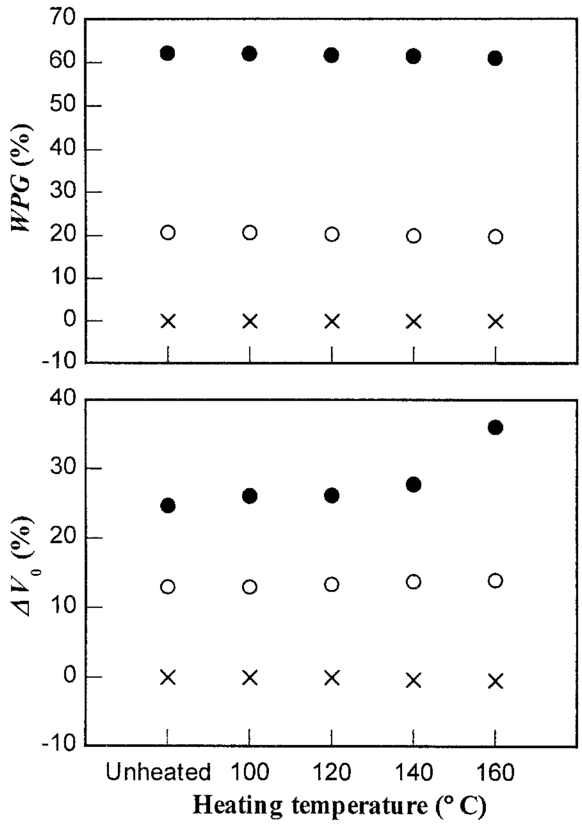

Fig. 2. Changes in weight (*WPG*) and volume (ΔV_0) of untreated and acetylated spruce wood specimens by heating for 10 min. *Crosses*, nonacetylated; *open circles*, normally acetylated; *closed circles*, acetylated with 20% GPA/AA solution

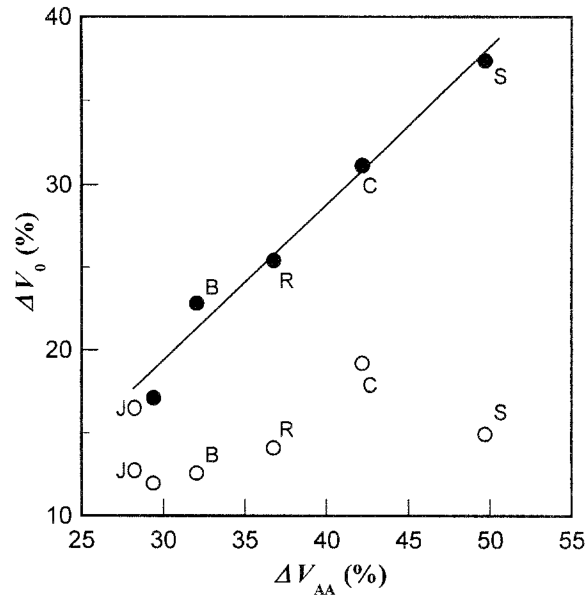

Fig. 3. Relations between the specific increased volume due to acetylation (ΔV_0) and that due to soaking in AA at 120°C (ΔV_{AA}). *Open circles*, normally acetylated; *closed circles*, acetylated with 20% GPA/AA solution and heated at 160°C for 10 min. For abbreviations see Table 1

Table 2. Changes in weight and volume of untreated and acetylated spruce wood specimens after soaking in molten GPA at 140°C for 1 h

Parameter	Nonacetylated		Acetylated	
	Heated in air	Soaked in molten GPA	Heated in air	Soaked in molten GPA
WPG (%)	−0.7	180.7	−0.1	173.2
Δv (%)	−0.2	0.1	−0.1	4.1

WPG, weight percent gain; Δv, swelling in volume; GPA, glucose pentaacetate

hanced by the introduction of hydrophobic acetyl groups. Based on these results, it is suggested that heating is an effective method for introducing GPA into the wood cell wall without degrading the wood constituents.

Figure 3 shows the specific increase in volume due to acetylation (ΔV_0) plotted against that due to soaking in AA at 120°C for 5 min (ΔV_{AA}). The ΔV_0 value of the normally acetylated wood was almost independent of ΔV_{AA}. This indicates that the ΔV_{AA} value reflects mainly the swelling of wood due to AA itself, rather than the effect of acetylation during the short soaking in AA. In contrast, the excellent linear relation between ΔV_0 and ΔV_{AA} for the GPA-acetylated specimens suggests that the greater swelling of wood in AA resulted in effective penetration of GPA into the wood cell wall.

Swelling of GPA-acetylated wood with moisture adsorption

To compare the swelling of the untreated and acetylated specimens, we defined the specific swelling in volume, ΔV_1, using the following equation.

$$\Delta V_1(\%) = 100(V/V_{u0} - 1)/\gamma_{u0} \quad (2)$$

where the V is the volume of specimens at various moisture contents (MC). The ΔV_1 values of the untreated and acetylated spruce wood specimens are plotted against the MC in Fig. 4. The volume of the untreated and normally acetylated specimens increased linearly with increasing MC and reached maximum levels at around 28% and 15% MC, respectively. In contrast, the GPA-acetylated specimens swelled only slightly with increasing MC, and their volume reached the maximum level at around 5% MC.

The increased volume of wood specimens, Δv, is expressed by the following equation.

$$\Delta v(\%) = 100(V/V_0 - 1) \quad (3)$$

where the V_0 is the volume of specimens absolutely dried. Figure 5 shows the Δv values of the untreated and treated spruce wood specimens plotted against RH. In the low RH range, the swelling of the GPA-acetylated wood was comparable to that of the normally acetylated wood. However, the GPA-acetylated wood swelled only slightly in the high RH range, whereas the normally acetylated wood began to swell rapidly above 80% RH. Such a trend was also recognized in the other wood species tested. These results suggested that GPA acetylation effectively suppressed the swelling of wood at high RH.

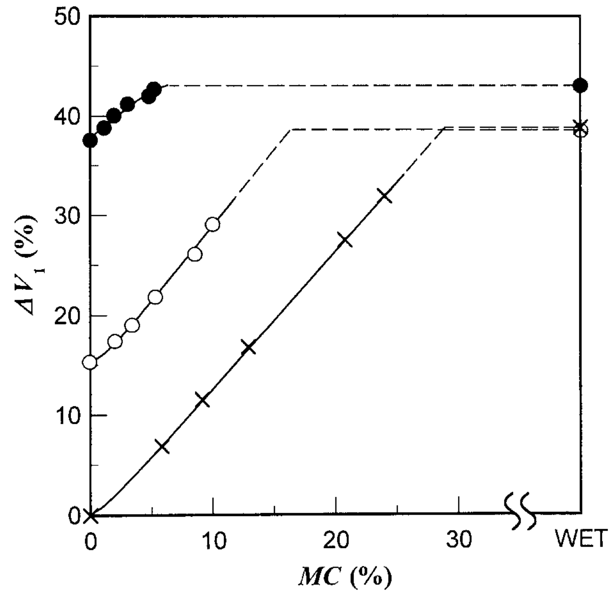

Fig. 4. Specific increased volume of spruce wood specimens (ΔV_1) plotted against the equilibrium moisture content (*MC*). *Crosses*, unacetylated; *open circles*, normally acetylated; *closed circles*, acetylated with 20% GPA/AA solution and heated at 160°C for 10 min

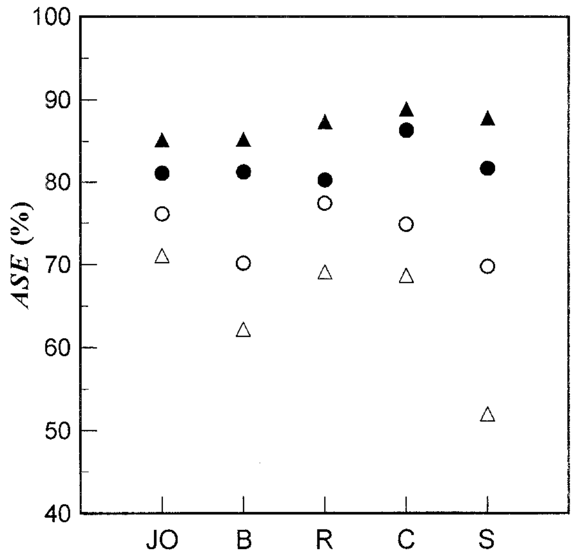

Fig. 6. Antiswelling efficiency (*ASE*) of acetylated wood. *Circles*, ASE values based on the volumetric swelling from 0% to 57% RH; *triangles*, ASE values based on the volumetric swelling from 0% RH to the wet condition; *open symbols*, normally acetylated; *filled symbols*, acetylated with 20% GPA/AA solution and heated at 160°C for 10 min. For abbreviations see Table 1

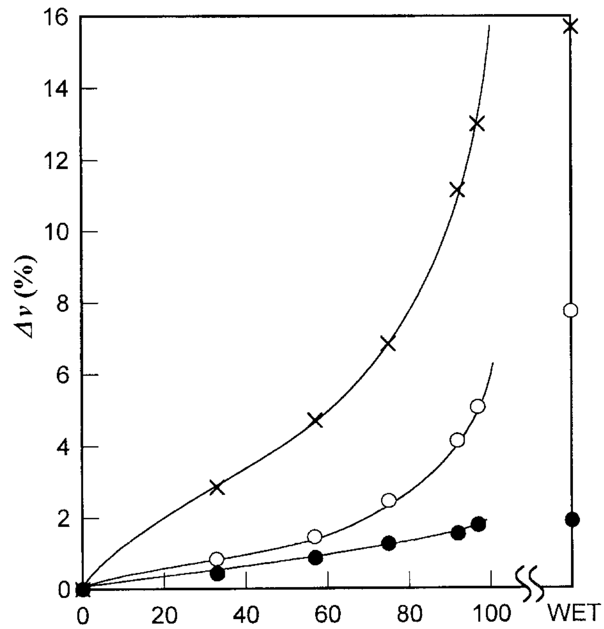

Fig. 5. Increase in volume of spruce wood specimens with moisture sorption (Δv) plotted against the relative humidity (*RH*). For *symbols* see Fig. 4

The dimensional stability of the acetylated wood was evaluated using antiswelling efficiency (ASE), defined by the following equation.

$$\mathrm{ASE}(\%) = 100[\Delta\nu(\text{untreated}) - \Delta\nu(\text{treated})]/\Delta\nu(\text{untreated}) \quad (4)$$

Figure 6 shows the ASE values of the acetylated wood specimens. Irrespective of wood species, the ASE values of the GPA-acetylated wood specimens were higher than those of the normally acetylated ones. It should be noted that the GPA-acetylated wood showed higher ASE values at higher RH, whereas the normally acetylated wood showed a reverse trend. Such characteristics of the GPA-acetylated wood were attributable to marked suppression of swelling at high RH, as shown in Fig. 5.

In general, the dimensional stability of acetylated wood depends on the hydrophobic nature and the bulking effect of the acetyl groups introduced. The hydrophobic nature of the acetyl groups is responsible for the lower MC and less swelling at low RH, with a reduction in active adsorption sites of wood constituents. However, the intermolecular space for moisture adsorption cannot be completely occupied by the acetyl groups, and therefore the acetylated wood swells rapidly at high RH. On the other hand, the GPA-acetylated wood is markedly swollen by GPA. Although the GPA might not affect the active adsorption sites of wood constituents, it physically occupies the intermolecular space to prevent further swelling of wood due to moisture adsorption. These are the reasons for the excellent antiswelling effects of GPA acetylation at high RH.

The swelling properties of the GPA-acetylated wood shown in Figs. 4 and 5 were qualitatively similar to those of PEG impregnated wood[3] because both are characterized by the bulking effect of the impregnating substances. However, hydrophobic GPA does not deliquesce even under highly humid conditions, whereas the deliquescence of PEG is sometimes problematic.

Figure 7 shows the changes in the volume of the acetylated specimens due to boiling in water and acetone. Because the GPA is insoluble in water, the volume of the GPA-acetylated wood remained almost unchanged after

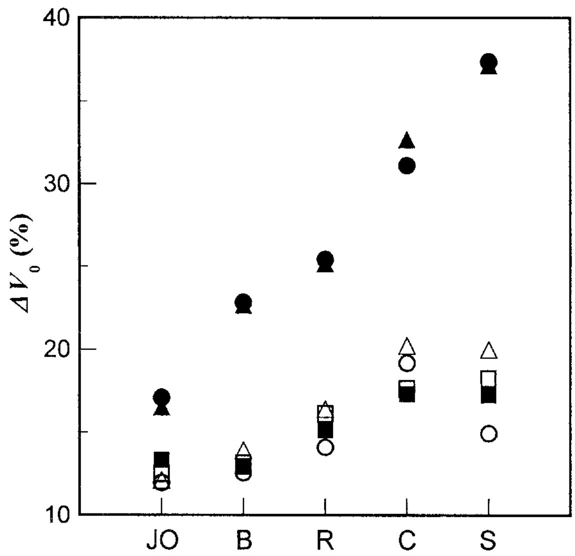

Fig. 7. Changes in specific volume of acetylated specimens (ΔV_0) after extraction in water and acetone. *Circles*, acetylated specimens; *triangles*, boiled in water for 1 h; *squares*, boiled in acetone for 1 h; *open symbols*, normally acetylated; *filled symbols*, acetylated with 20% GPA/AA solution and heated at 160°C for 10 min. For abbreviations see Table 1

boiling in water, and was near that of normally acetylated wood after washing in acetone. These results suggest an antiwater property of GPA-acetylated wood.

In this study, we employed GPA based on its availability and safety. However, it is thought that various hydrophobic substances other than GPA can also penetrate the wood cell wall in the same manner. Such a combined method might be effective for further property enhancement of wood by chemical modification. The mechanical properties of the GPA-acetylated wood will be reported in a future article.

Conclusions

Five wood species were acetylated with GPA/AA solution, and the bulking effect of GPA was investigated after introduction into the wood cell wall during acetylation. Some GPA remaining in the cell lumen was introduced into the cell wall by heating the specimen above the melting point of GPA. The bulking effect of GPA suppressed the swelling of wood, especially at high RH. Consequently, the ASE of acetylated wood specimens increased by 10%–30% using 20% GPA/AA solution in place of AA. GPA remained in the cell wall after boiling in water.

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