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ORIGINAL ARTICLE

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Swelling of acetylated wood I. Swelling in organic liquids

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Abstract To investigate the affinity of acetylated wood for organic liquids, acetylated yezo spruce wood specimens were soaked in various liquids, and their swellings were compared to those of untreated specimens. The acetylated wood was rapidly and remarkably swollen in liquids having low hydrogen bonding power such as benzene and toluene in which the untreated wood was swollen only slightly or very slowly. On the other hand, the swollen volume of wood in water, ethylene glycol, and alcohols remained unchanged or slightly decreased after the acetylation. The effect of acetylation was greater in liquids having smaller solubility parameters. The easier penetration of aprotic organic liquids into the acetylated wood was considered to be due to the reduction of polarity and the scission of hydrogen bonds in the amorphous wood constituents where the hydrophilic hydroxyl groups were substituted by hydrophobic acetyl groups.

Key words Wood · Acetylation · Swelling · Organic liquid · Solubility parameter

Introduction

Many researchers have dealt with the swelling of wood in various organic liquids for comprehensive understanding of wood–liquid interactions. Nayer and Hossfeld[1] found that the hydrogen bonding properties of organic liquids affected the swelling of wood. The important role of hydrogen bonding was also suggested by Horiike and Kato[2] who measured the heat of wetting of wood in various organic liquids. The investigations that followed by Ishimaru and Adachi[3] indicated that the wood swelling in liquids having only a proton acceptor was larger than that in liquids having both a proton acceptor and donor, and that a larger molar volume of liquid gave less swelling of wood when compared at the same proton-accepting power. Meanwhile Mantanis et al.[4,5] performed a precise measurement on the swelling rate of wood in various liquids and they concluded that the apparent activation energy in the swelling process corresponded well to that for the scission of internal hydrogen bonds among wood constituents. In recent thermodynamic approaches by Morisato et al.,[6–8] they discussed the cohesive interaction within the bulk liquids in the phased adsorption processes of wood. Although the correlations between wood swelling and liquid properties are not always clear, it is generally accepted that the swelling of wood involves competitive processes of the adsorption by hydrogen bonding and the scission of internal hydrogen bonds between the amorphous molecules of wood constituents, and therefore depends on the hydrogen bonding properties of liquids.

On the other hand, various chemical modifications have so far been proposed to improve the practical performances of wood. Among these, acetylation is a typical method involving the chemical reaction between the wood constituents and chemicals. By acetylation, the hydroxyl groups in the amorphous region of wood cell wall are substituted with acetyl groups. Consequently, the acetylated wood shows excellent dimensional stability with durability because of the bulky and hydrophobic nature of the introduced acetyl groups.[9]

It should be noted that acetylation is not only applied for wood modification but is also widely used to improve the compatibility of hydrophilic materials with hydrophobic substances. We recently found that a bulky hydrophobic glucose pentaacetate ($M_w = 390$) could be easily introduced into the acetylated wood cell wall, whereas it can hardly penetrate into the untreated wood cell wall.[10,11] This fact suggests that the acetylated wood can also be swollen in organic liquids inaccessible to the untreated wood. If so, various hydrophobic chemicals so far untested might be introduced into the wood cell wall by using an appropriate

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Table 1. Characteristics of liquids used

	Liquids	M_W	M_V (cm^3/mol)	SP [(cal/cm^3)$^{1/2}$]	ΔV (%)	
					Untreated	Acetylated[a]
Benzene (C_6H_6)	BE	78.1	89.4	9.2	2.0	23.1
Toluene ($C_6H_5CH_3$)	TO	92.1	106.4	8.9	4.9	21.5
Methyl acetate (CH_3COOCH_3)	AM	74.1	79.7	9.6	10.0	24.5
Ethyl acetate ($CH_3COOC_2H_5$)	AE	88.1	98.5	9.1	7.7	23.0
Acetone (CH_3COCH_3)	AC	58.1	74.0	9.9	11.8	24.1
1,4-Dioxane ($C_4H_8O_2$)	DI	88.1	85.7	10.0	8.9	25.4
Methanol (CH_3OH)	ME	32.0	40.7	14.5	16.4	21.3
Ethanol (C_2H_5OH)	ET	46.0	58.5	12.7	14.3	20.1
2-Propanol ($(CH_3)_2CHOH$)	PR	60.1	75.0	11.5	13.2	19.2
1-Butanol ($CH_3CH_2CH_2CH_2OH$)	BU	74.1	91.8	11.4	9.2	18.6
Ethylene glycol ($HOCH_2CH_2OH$)	EG	62.1	55.8	14.6	19.4	18.2
N,N-Dimethylformamide ($HCON(CH_3)_2$)	DF	73.1	77.0	12.1	20.7	26.3
Dimethylsulfoxide ($(CH_3)_2SO$)	DS	78.1	70.9	12.0	21.8	25.9
Water (H_2O)	WT	18.0	18.0	23.4	17.7	15.2

M_W, Molecular weight; M_V, molar volume; SP, solubility parameter; ΔV, swelling in volume after 240 days of soaking in liquids

[a] Includes the initial swelling due to acetylation as well as that due to the penetration of liquids

organic solvent, to expand the possibility of chemical modification of wood. However, little information is available for the swelling of acetylated wood in organic liquids. In this article, we compare the swelling of untreated and acetylated woods in various liquids to demonstrate the drastic changes in the affinity of wood due to acetylation.

Materials and methods

Two wood logs (I and II) of ezomatsu (*Picea yezoensis*) were sliced into two sets of specimens, each specimen with a size of 1 cm (L, longitudinal direction) × 3 cm (R, radial direction) × 3 cm (T, tangential direction). The specimens were previously extracted with water and acetone using a Soxhlet apparatus for 8 h to remove the natural extractives. The dimensions of wet specimens were measured just after the water extraction to evaluate their natural swelling ability. These specimens were then dried absolutely in vacuo at room temperature, and their weights and dimensions were measured.

Half of the dried specimens from log I were soaked in acetic anhydride overnight, and heated in a flask at 120°C for 8 h. The specimens were immediately cooled at room temperature and rinsed in running water for 1 week to remove the chemical reagents and acetic acid that remained. The specimens were then dried completely in vacuo at room temperature to determine their weights and dimensions. Next the specimens were soaked under vacuum in various liquids that are listed in Table 1. All liquids other than water (WT) and ethylene glycol (EG) were analytical grade for gas or liquid chromatography. The liquids and specimens were put into glass bottles that were then tightly closed with polytetrafluoroethylene sealing. The bottles were kept at 20°C over 240 days, and the dimensions of the specimens were measured intermittently. Six specimens were used for each testing condition.

Another set of specimens from log II was separated into four groups according to their densities. One group remained unacetylated and the other groups were acetylated at 120°C for 10 min, 1 h, or 8 h by the same method described above. The specimens were then washed in water and dried absolutely in vacuo. Those untreated and acetylated specimens were soaked in benzene (BE), toluene (TO), acetone (AC), methanol (ME), ethanol (ET), 2-propanol (PR), 1-butanol (BU), and WT at 20°C for 60 days and their dimensions were measured. Three specimens were used for each testing condition.

Results and discussion

Homogeneity of wood specimens

The basic characteristics of wood specimens are listed in Table 2. To evaluate the natural swelling ability of wood specimens, the water swelling of the untreated specimen ($\varDelta V_W$) was calculated from its wet volume (V_W) and absolutely dry volume (V_0) according to the following equation.

$$\varDelta V_W(\%) = 100(V_W - V_0)/V_0 \qquad (1)$$

As shown in Table 2, different logs gave different $\varDelta V_W$ values but the variation within the same log was small enough to assume the homogeneity of specimens in their natural swelling ability.

With acetylation, both the weight and volume of wood increased. The degree of acetylation was evaluated by weight percent gain (WPG) and swelling in dry volume ($\varDelta V_A$). The $\varDelta V_A$ was defined as follows:

$$\varDelta V_A(\%) = 100(V_A - V_0)/V_0 \qquad (2)$$

where the V_A is the absolutely dry volume of the acetylated wood specimen. The variations in WPG and $\varDelta V_A$ were very

Table 2. Characteristics of wood specimens

Log	Treatment	Treatment duration (h)	ΔV_{W} (%)	ρ_{U} (g/cm^3)	ρ_{A} (g/cm^3)	WPG (%)	ΔV_{A} (%)
I	Untreated	0	17.6 (0.3)	0.407 (0.006)	–	–	–
	Acetylated	8	17.6 (0.4)	0.404 (0.008)	0.471 (0.010)	26.5 (0.4)	8.1 (0.4)
II	Untreated	0	19.2 (0.3)	0.374 (0.008)	–	–	–
		0.17			0.385 (0.016)	5.9 (1.9)	0.6 (1.0)
	Acetylated	1	19.4 (0.2)	0.377 (0.008)	0.396 (0.017)	15.4 (0.9)	5.4 (0.2)
		8			0.411 (0.012)	26.4 (1.0)	7.6 (0.4)

Values in parentheses are standard deviations

ΔV_{W}, Water swelling of wood specimens in their untreated state; ρ_{U}, density of completely dry specimens before acetylation; ρ_{A}, density of completely dry specimens after acetylation; WPG, weight percent gain by acetylation; ΔV_{A}, swelling in volume of specimens due to acetylation

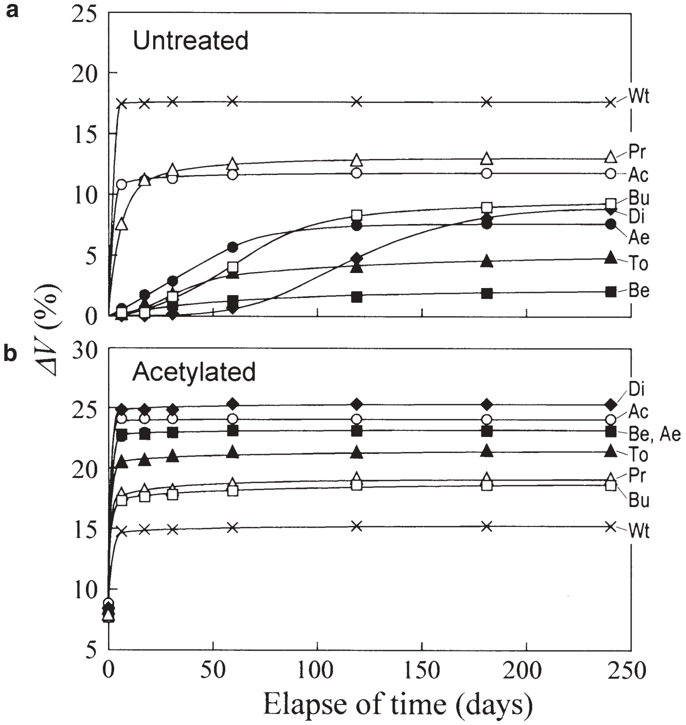

Fig. 1. Swelling in volume (ΔV) of **a** untreated and **b** acetylated wood specimens soaked in various liquids over time. For abbreviations, see Table 1. The ΔV of acetylated wood includes the initial swelling due to acetylation

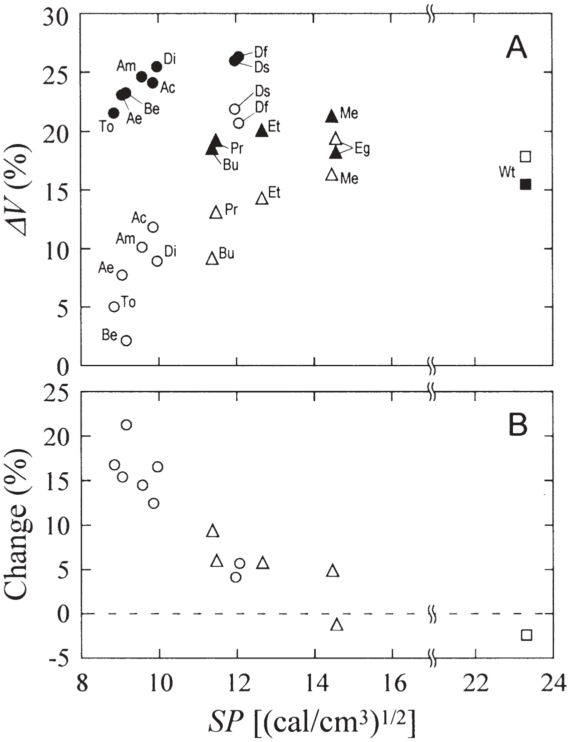

Fig. 2. Swelling in volume (ΔV) of wood specimens (**A**), and changes in ΔV due to acetylation (**B**) plotted against the solubility parameter of liquids (SP). *Circles*, aprotic organic liquids; *triangles*, protic organic liquids (alcohols and glycol); *squares*, water; *open plots*, untreated wood; *filled plots*, acetylated wood. For abbreviations, see Table 1

small except for those that received short (10min) treatment. It was thought that the small weight and volume gains due to the short treatment were compensated by the thermal degradation of wood components and the removal of extractives at the beginning of treatment, and resulted in wider variation in WPG and ΔV_{A}.

Swelling of acetylated wood in organic liquids

The volumetric swelling of wood in various liquids was calculated by the following equation,

$$\Delta V(\%) = 100(V_{\mathrm{S}} - V_0)/V_0 \tag{3}$$

where the V_{S} is the volume of wood specimen swollen in liquid. Figure 1 shows the swelling of untreated and acetylated wood specimens in various liquids over 240 days. The volume of untreated wood in WT reached its maximum within 1 day, while it swelled slightly and/or slowly in aprotic organic liquids such as BE, TO, ethyl acetate (AE), 1,4-dioxane (DI), and also in protic alcohols such as BU and PR having relatively large molar volumes. On the other hand, the acetylated woods swelled rapidly irrespective of the liquid. According to Mantanis et al.,[4,5] the swelling rate of wood is related to the activation energy required for the scission of hydrogen bonds previously formed between wood constituents. Because the acetyl groups introduced cannot form hydrogen bonds with each other, the rapid swelling of acetylated wood may reflect the reduction of cohesive forces between the wood constituents.

In Fig. 2, the maximum ΔV values are plotted against the solubility parameter (SP)[12] of liquids. According to

Ishimaru and Adachi[3] and Robertson,[13] organic liquids can be classified into two groups in respect of their effects on wood swelling and on the decreasing strength of paper: group I, liquids having only a proton acceptor; and group II, liquids having both a proton acceptor and donor. The former gives greater swelling than the latter at the same SP or proton-accepting power. As shown in Fig. 2A, the plots of untreated wood followed the trends seen in earlier reports, i.e., the ΔV in group I liquids were larger than those in group II liquids at the same SP, and a positive correlation between ΔV and SP was recognized for each group. On the other hand, the swollen volume of acetylated wood was clearly larger than that of untreated wood, except for that in EG and WT. The effect of acetylation was greater in liquids having smaller SP value as shown in Fig. 2B.

The drastic change in ΔV due to the acetylation can be interpreted by the following two factors: easier adsorption of nonpolar or low-polarity liquid molecules onto the wood where the low-polarity acetyl groups are introduced; and less energy required to break the internal hydrogen bonds among the wood constituents by the substitution of hydroxyl groups with acetyl groups. Both factors probably affect the swelling of acetylated wood, but further thermodynamic investigation is needed for more detailed discussion.

Anisotropic swelling of acetylated wood

The radial (ΔR) and tangential (ΔT) swelling of wood were calculated by using the radial (R) and tangential (T) dimensions of specimens according to the following equations:

$$\Delta R(\%) = 100(R_S - R_0)/R_0 \quad \text{and} \quad \Delta T(\%) = 100(T_S - T_0)/T_0 \tag{4}$$

where the subscript labels hold the same meanings as those in Eq. 3. Figure 3 shows the plots of ΔT versus ΔR for the untreated and acetylated wood specimens. The tangential swelling of untreated wood was almost proportional to its radial swelling up to a certain level, above which the radial swelling seemed to be restricted. That limiting point corresponded to the swelling of wood in water (ΔT = 12.0%, ΔR = 5.1%). Similar results have been obtained by Ishimaru and Maruta.[14] They speculated that the radial swelling of wood is restricted by the heterogeneous cell wall structure caused by factors such as the different orientation of cellulose microfibrils in radial and tangential cell walls. Another possible interpretation is the greater swelling of denser latewood involving the cellular deformation of earlywood to increase the anisotropy.

As indicated by the broken arrow in Fig. 3, the swelling of wood due to acetylation was more anisotropic (ΔT = 6.6%, ΔR = 1.5%) than that of untreated wood swollen in organic liquids. This difference was observed in various liquids, and the radial swelling of the acetylated wood seemed to be less restricted than that of the untreated wood at the higher swelling levels. Among major wood constituents, lignin and hemicelluloses are readily substituted at small WPGs, whereas the cellulose in wood is less reactive on acetylation.[15,16] Therefore, the location of the lignin-rich part such as the middle layer might affect the anisotropic swelling of acetylated wood.

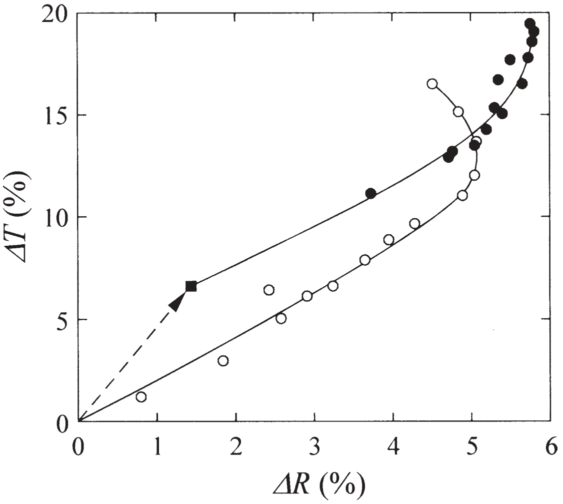

Fig. 3. Relationship between the tangential (ΔT) and radial (ΔR) swellings of wood specimens in various liquids. *Open circles*, untreated; *filled circles*, acetylated; *filled square*, absolutely dry acetylated wood; *broken arrow*, swelling due to acetylation

Effects of degree of acetylation

Figure 4 shows the effects of WPG on the ΔV of wood soaked in various liquids for 60 days. The 60-day soaking was not long enough to achieve maximum swelling, especially for the untreated wood in organic liquids, but enough to show drastic changes due to the acetylation. As shown in Fig. 4A, the volume of wood in aprotic liquids increased with increasing WPG, and it converged in a certain range (20%–25%) regardless of the liquid. That range suggests the limit of wood swelling restricted by the fiber-reinforced and/or multilayered structure of the wood cell wall. On the other hand, the effect of WPG on ΔV was less marked in protic liquids as shown in Fig. 4B. The ΔV in PR and BU leveled off at higher WPGs while that in ME and ET increased monotonously with increasing WPG. It was suggested that the molar volume of alcohol molecules influenced their penetration into the acetylated wood cell wall at high WPGs where the intermolecular space was limited by the introduction of bulky acetyl groups. The ΔV in EG and WT remained almost unchanged up to 15% WPG and then decreased slightly.

In general, the excellent dimensional stability of acetylated wood is attributed to the "bulking effect," that is, the wood cell wall is previously swollen by bulky acetyl groups while its maximum water-swelling remains unchanged. In organic liquids, however, the maximum swelling (ΔV) can change considerably after acetylation as shown in Fig. 4A. Therefore, the initial swelling of wood due to acetylation (ΔV_A) is not a direct indication of its dimensional stability. Thus, we calculated the swelling of wood due to the pen-

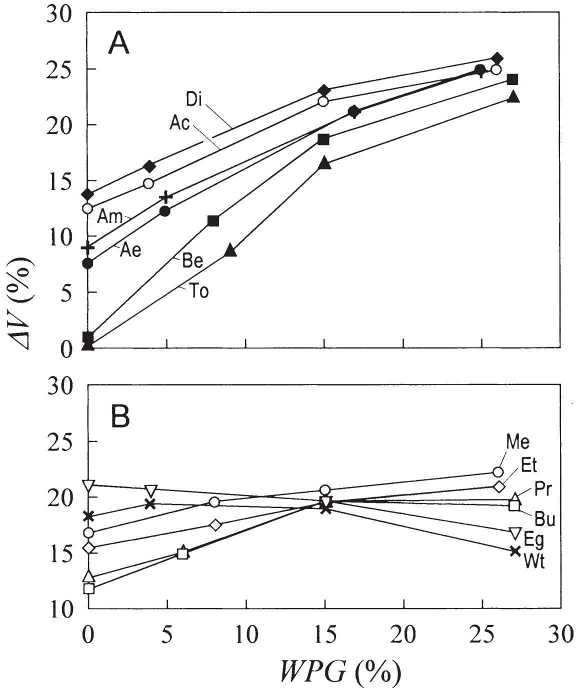

Fig. 4A,B. Effect of weight percent gain (*WPG*) on the swelling in volume of wood (ΔV) due to 60 days of soaking. **A** Aprotic liquids, **B** protic liquids. For abbreviations, see Table 1

etration of liquid itself (ΔV_S) according to the following equation:

$$\Delta V_S(\%) = \Delta V - \Delta V_A = 100(V_S - V_A)/V_0 \tag{5}$$

The reduction of ΔV_S is an indication of a dimensional stabilizing effect, i.e., the exclusion of liquids from the wood cell wall caused by acetylation. Figure 5 shows the plots of ΔV_S versus WPG. The remarkable reduction of ΔV_S in WT and EG showed the bulking effect of acetylation. In alcohols, the ΔV_S also decreased with increasing WPG but not remarkably. It was considered that the alcohols were certainly excluded by the bulking effect of the acetyl groups, but that effect was compensated with the improved affinity of acetylated wood for the hydrophobic part of the alcohol molecules. On the contrary, the ΔV_S increased almost linearly with increasing WPG when soaked in BE or TO. In these aprotic liquids, the acetyl groups must no longer be bulking "spacers" but a kind of compatibilizer. In DI, AC, methlacetate (AM), and AE, the ΔV_S remained unchanged or increased slightly as the WPG increased. This fact does not indicate that those liquids are less sensitive to the acetylation but that the swelling of the cell wall is limited by the cell wall structure at the extremely high swelling level in those liquids. From these results, it is suggested that the bulking effect of acetylation is valid only in hydrophilic liquids such as water and ethylene glycol.

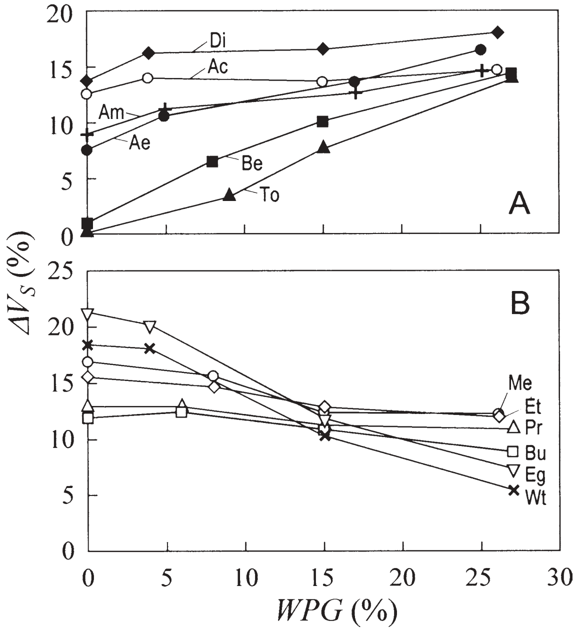

Fig. 5A,B. Volumetric swelling of wood due to the penetration of liquids (ΔV_S) as a function of WPG. **A** Aprotic liquids, **B** protic liquids. For abbreviations, see Table 1

Conclusions

Acetylated wood was swollen rapidly and remarkably in organic liquids in which untreated wood was swollen only slightly or slowly. The effect of acetylation on the maximum swelling of wood was greater in organic liquids having a smaller solubility parameter. The acetylation also resulted in greater anisotropy in transverse swelling than the normal swelling of untreated wood. The swelling of wood in aprotic liquids increased with the increasing degree of acetylation while that in protic liquids showed the reverse trend.

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