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Swelling of acetylated wood II: effects of delignification on solvent adsorption of acetylated wood

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Abstract To clarify the role of lignin in the affinities of acetylated wood for organic solvents, the effects of delignification on the solvent adsorption of acetylated wood were investigated. Acetylated wood meals rapidly adsorbed organic solvents that were hardly adsorbed by unmodified wood. For nonpolar and low-polarity organic solvents, a clear positive correlation was observed between the amount of adsorption and the lignin content. This indicated that acetylated lignin was responsible for the excellent affinities of acetylated wood for hydrophobic organic solvents. On the other hand, for lower alcohols and water, the amount of adsorption reduced with an increase in the lignin content. It was suggested that the adsorption of such polar solvents was dominated by insufficiently acetylated hydrophilic polysaccharides.

Key words Acetylation · Organic solvents · Adsorption · Delignification

Introduction

It is suggested that in various organic solvents, acetylated wood swells remarkably, while unmodified wood swells slightly.¹ This indicates that the affinity of wood for hydrophobic organic solvents improves significantly due to acetylation. Such improved hydrophobicity increases the range of solvents that can be used for an easier introduction of

additives, such as plasticizers, into the wood cell wall. In addition, the hydrophobicity of acetylated wood may be advantageous to the development of a stronger combination of wood and plastics.² However, it should be noted that the local components of wood are not uniformly modified by acetylation. Among the major wood constituents, lignin can be acetylated rapidly and almost completely, whereas the other polysaccharides are incompletely modified even under severe treatment conditions.^{3–6} This implies that the hydrophobic nature of acetylated lignin is responsible for the excellent accessibility of acetylated wood to organic solvents, although the experimental evidence reported thus far is insufficient. Therefore, we investigated the effects of delignification on the solvent adsorption of acetylated wood in order to clarify the role of lignin in the improved affinity of acetylated wood.

Materials and methods

Delignification and acetylation of wood

Wood meal (150–355 μm) of Sitka spruce (*Picea sitchensis*) was delignified by the Wise method.⁷ In this process, sodium chlorite and glacial acetic acid were added two or four times in order to achieve different degrees of delignification. The lignin contents of the delignified wood meals were determined by the sulfuric acid method⁷ using the following equation:

$$L(\%) = 100 \times \frac{W_L}{W_0}, \quad (1)$$

where W_0 and W_L are the dry weights of the original wood meal and the residue, respectively.

The control and delignified wood meals were transferred into glass filters and weighed after oven drying at 105°C for 24 h. The dry wood meals (1 g) were soaked in a mixture of acetic anhydride (40 ml) and pyridine (10 ml) and subsequently heated at 100°C for 4 h in a flask equipped with a reflux condenser. The acetylated wood meals were leached

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Table 1. Molecular weight (Mw), molar volume (Mv), and proton-accepting power (PAP) of tested solvents

| Liquid | Mw | Mv (cm ³ /mol) | PAP (cm ⁻¹) |
|-----------------------|-------|---------------------------|-------------------------|
| Benzene (BE) | 78.1 | 89.4 | 0 |
| Toluene (TL) | 92.1 | 106.4 | 45 |
| <i>p</i> -Xylene (XL) | 106.2 | 124.0 | 45 |
| Ethyl acetate (EA) | 88.1 | 98.5 | 84 |
| Acetone (AC) | 58.1 | 74.0 | 97 |
| 1,4-Dioxane (DX) | 88.1 | 85.7 | 97 |
| Methanol (MT) | 32.0 | 40.7 | 187 |
| Ethanol (ET) | 4.1 | 58.5 | 187 |
| 1-Propanol (PR) | 60.1 | 75.0 | 187 |
| 1-Butanol (BU) | 74.1 | 91.8 | 187 |
| Water (WT) | 18.0 | 18.0 | 390 |

in ethanol and water to remove the remaining treating reagents and by-product. After complete leaching, the acetylated wood meals were oven-dried at 105°C for 24 h and weighed.

Adsorption of organic compounds

The unmodified and acetylated wood meals were transferred into glass bottles and dried at 105°C for 12 h. After cooling and weighing at room temperature over P₂O₅, the samples were put in glass desiccators containing organic solvents. The air in the desiccators was immediately replaced with dehydrated air in order to prevent the moisture sorption of the wood samples. The desiccators were then placed in an environmental chamber at 20° ± 1°C. The samples were weighed intermittently over 6 days by using a closed box in which the air was completely dried with P₂O₅. These processes were repeated for 11 solvents listed in Table 1. It was confirmed that the moisture sorption of the wood sample during weighing was negligible in comparison with the adsorption of the solvents.

Results and discussion

Effect of delignification on the degree of acetylation

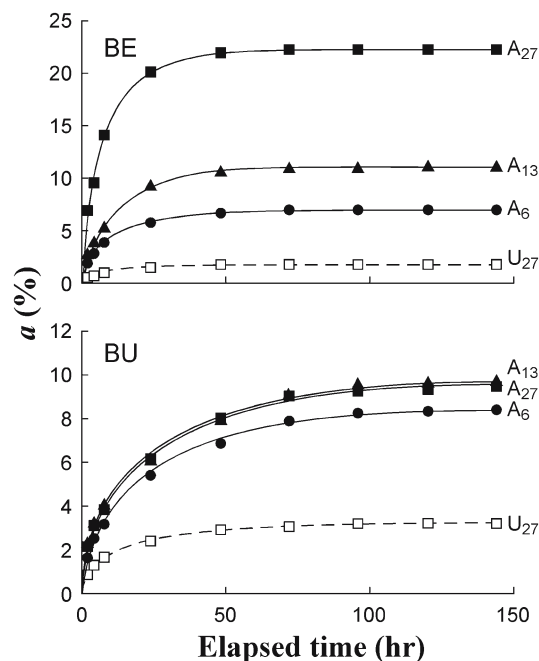
The lignin contents (denoted by *L*) of the unacetylated wood meals and weight percent gains (WPGs) due to acetylation are listed in Table 2. The WPG decreased with *L*. This is in agreement with the results of previous investigations,³⁻⁶ thereby suggesting that the reactivity of lignin is greater than that of the other polysaccharide components.

Adsorption of organic solvents

Figure 1 shows the amount of adsorption (*a*) of benzene (BE) and 1-butanol (BU) by the wood meals. In the BE vapor, acetylated wood attained its adsorption equilibrium within 100 h. In addition, the *a* values of acetylated wood were significantly greater than those of unacetylated wood. This trend was observed in the other low molecular weight

Table 2. Lignin content (*L*) of original wood meals, weight percent gain (WPG) due to acetylation, and relative weight (RW) of wood samples

| Sample | <i>L</i> (%) | WPG (%) | RW |
|-----------------|--------------|---------|------|
| Unmodified | | | |
| U ₂₇ | 27.0 | – | 1.00 |
| U ₁₃ | 12.8 | – | 0.84 |
| U ₆ | 5.5 | – | 0.77 |
| Acetylated | | | |
| A ₂₇ | 27.0 | 29.5 | 1.30 |
| A ₁₃ | 12.8 | 12.7 | 0.94 |
| A ₆ | 5.5 | 7.2 | 0.83 |

**Fig. 1.** Amount of adsorption (*a*) plotted against the elapsed time for benzene (BE, top) and 1-butanol (BU, bottom). A, acetylated; U, unmodified. Subscripts indicate lignin contents

solvents with low polarity. On the other hand, the adsorption of BU was not equilibrated in 6 days. Similar slow adsorption was observed in the case of *p*-xylene (XL), which has a relatively large molecular weight. It is important to monitor the *a* values until complete adsorption equilibrium is attained. However, the *a* values of some solvents were abnormally large when the adsorption period was prolonged; this was probably due to the condensation of the solvent onto the samples. Therefore, we used the *a* values obtained after 120 h.

Figure 2 shows the effects of *L* on *a*. For nonpolar aromatic adsorbates (Fig. 2a), the *a* value of acetylated wood decreased with a decrease in *L* and an increase in the molecular weight of the solvents. A similar trend was observed in the other low-polarity solvents (Fig. 2b). On the other hand, the low molecular weight alcohols [methanol (MT) and ethanol (ET)] produced greater *a* values of acetylated wood at lower values of *L* (Fig. 2c, d), and the *a* values of

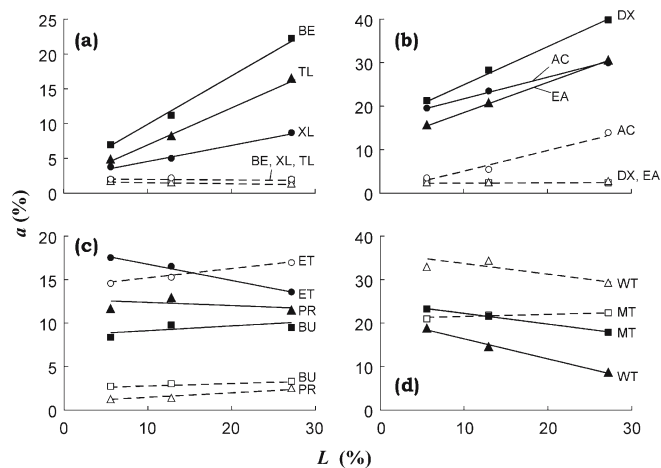


Fig. 2a–d. Effects of lignin content (L) on the amount of adsorption (a) for **a** nonpolar aromatic solvents, **b** low-polarity nonaromatic solvents, **c** moderate-polarity short-chain alcohols, and **d** high-polarity solvents. *Open symbols*, unacetylated; *filled symbols*, acetylated. Solvent abbreviations are listed in Table 1

acetylated wood were comparable with those of unmodified wood.

The clear positive relationships between a and L (Fig. 2a, b) appeared to indicate the contribution of lignin to the accessibility of acetylated wood. However, it should be noted that the a value is not a direct indication of the adsorption properties of amorphous substances in the wood cell wall. It is generally accepted that the amorphous wood constituents are responsible for the solvent adsorption of wood, while crystallized cellulose and a part of highly ordered cellulose are inaccessible to the solvents. Therefore, the a value can be influenced by the removal of the amorphous substances due to delignification and their swelling due to acetylation, even when the accessibility of the amorphous part remains unchanged. To exclude this side effect, we defined the revised amount of adsorption (a') according to the following equation:

$$a' = a \frac{RW}{RW - x}, \quad (2)$$

where x is the weight fraction of the *inactive* part that mainly consists of cellulose, and RW is the relative weight of the wood sample based on its untreated weight. In this definition, the a' value represents the a value of the amorphous wood constituents. By considering the cellulose content of spruce wood,⁸ the possible range of x was assumed to be 0.3–0.4. The RW was calculated from the experimental values of L and WPG using the following equation:

$$RW = \left(\frac{73}{100 - L} \right) \left(\frac{100 + WPG}{100} \right). \quad (3)$$

This calculation is based on an assumption that nonlignin wood components remain unaffected by delignification. Actually, however, a part of polysaccharides is possibly lost in the present case. Therefore, it should be noted that the RW value derived from Eq. 3 may be slightly greater than the real RW value. The RW values of the samples are listed in

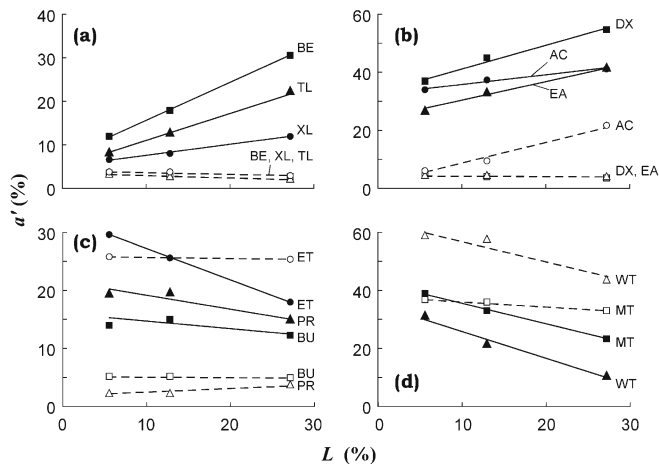


Fig. 3a–d. Revised amount of adsorption (a') plotted against L for **a** nonpolar aromatic solvents, **b** low-polarity nonaromatic solvents, **c** moderate-polarity short-chain alcohols, and **d** high-polarity solvents

Table 2, and Fig. 3 shows a plot of the calculated values of a' ($x = 0.35$) against L . For the low-polarity organic solvents (Fig. 3a, b), the a' values of acetylated wood increased linearly with L . Such a trend remained unchanged when x was varied within its possible range. This proved that acetylated lignin played an important role in the adsorption of low-polarity solvents. On the contrary, for the low molecular weight alcohols (MT and ET) and water (WT), the a' value of acetylated wood increased with a decrease in L (Fig. 3c, d). It was assumed that such polar solvents were not adsorbed by fully acetylated lignin but by insufficiently acetylated hydrophilic polysaccharides.

The clear difference between Fig. 3a and Fig. 3d implies that the local components in the acetylated wood cell wall were not uniformly swollen in the organic solvents. Although the wood swelling in benzene and methanol are almost the same, benzene is selectively adsorbed by lignin, whereas methanol may be mainly introduced into the polysaccharides. This suggests that the solvent should be appropriately selected to introduce additives, such as plasticizers, into the acetylated wood cell wall.

Lignin contribution and characteristics of solvents

The a' value of the zero-lignin (a'_0) sample was calculated from the linear regression between a' and L (Fig. 3), while the a' value of the nondelignified sample was expressed by a'_{27} . The ratio a'_{27}/a'_0 reflects the contribution of lignin to the accessibility of acetylated wood. Meanwhile the relative proton-accepting power (PAP/Mv, where Mv is the molar volume) was used to evaluate the ability of the solvent for wood swelling. It is suggested that unmodified wood swells significantly in liquids with smaller Mv values and greater PAP.⁹ The PAP values of solvents tested¹⁰ are listed in Table 1. Figure 4 shows a'_{27}/a'_0 as a function of PAP/Mv. The clear negative correlation indicates that acetylated lignin

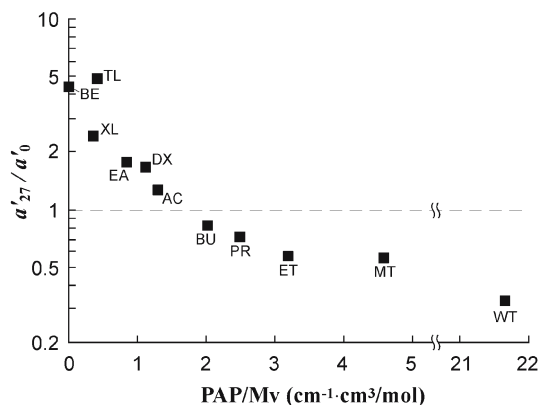


Fig. 4. a'_{27}/a'_0 as a function of relative proton-accepting power (PAP/Mv) of solvents

plays a dominant role in the adsorption of organic solvents with greater Mv values and smaller hydrogen-bonding ability.

Conclusions

Acetylated wood meals rapidly adsorbed low-polarity organic solvents that were hardly adsorbed by unmodified wood. The clear positive correlation between the amount of adsorption and the lignin content indicated that acetylated lignin was responsible for the excellent affinities of

acetylated wood for low-polarity organic solvents. On the other hand, the small contribution of lignin to the adsorption of alcohols suggested that the adsorption of polar solvents was dominated by polysaccharides that remained hydrophilic in acetylated wood.

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