Swelling of acetylated wood in organic solvents

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Various types of wood plastics composites (WPCs) have been proposed as alternatives to wood and plastics. Recent requirements for the utilization of wooden wastes and recycled plastics have enhanced the applications of WPCs. When a WPC contains a large amount of wood fibers, an undesirable dimensional instability occurs under humidity variations because of the swelling and shrinkage of hygroscopic wood fibers. Acetylation, wherein a part of the hydroxyl groups in wood polymers is substituted with bulky hydrophobic acetyl groups, is an effective method to solve this problem. The acetylated wood possesses excellent dimensional stability and anti-weathering and anti-biodegradation performances [1]. In addition, the improved thermal plasticity of acetylated wood [2] may enable easier composite formation with less plasticizer. Although hydrophobization of the fiber surface degrades the performance of certain hydrophilic adhesives [3], it has the advantage of stronger cohesion of fibers and hydrophobic resins [3, 4].

Various organic liquids, however, are useful diluents of high polymers such as recycled resins. If a certain organic liquid has an excellent compatibility with acetylated wood, it might enable effective permeation of resins onto the acetylated fiber surfaces. However, the focus on the affinity of acetylated wood and organic liquids has been limited, while the unmodified wood–liquid interactions have been extensively studied [5, 6]. In this paper, we describe the swelling of acetylated wood in non- and low-polar organic liquids in order to suggest the excellent affinity of organic liquids for acetylated wood. The swelling of wood is a good indicator of wood–liquid compatibility since it directly corresponds to the penetration of liquid into the amorphous wood polymers.

The sapwood of ezomatsu (*Picea yezoensis*) was sliced into blocks of 5 × 20 × 20 mm (longitudinal × radial × tangential) and leached in methanol and water to remove the natural extractives. The extractives-free samples were dried *in vacuo* over P_2O_5 at room temperature for determining their weight and volume in the unmodified state. The average density of 150 unmodified samples was 390 ± 10 kg/m^3. For the acetylation process, a part of the dry wood specimens were soaked in acetic anhydride overnight at room temperature and then heated at 120 °C for 8 hr in a flask equipped with an oil bath. The treated specimens were rinsed in running water to sufficiently remove the remaining chemicals. The leached specimens were then completely dried. This treatment resulted in 21.1 percent weight gain and 6.9% (S.D. = 0.2%) swelling in volume.

The completely dried wood specimens were soaked in dehydrated organic liquids, listed in Table I, under reduced pressure and stored in glass bottles with polytetrafluoroethylene sealing. The dimensions of the sample were measured after 60 days of soaking, which enables dimensional equilibrium of acetylated wood. All the dimensions were measured at 20 °C using a micrometer with an accuracy of ± 0.001 mm. Five specimens were used for each treatment.

The volumetric swellings of the wood specimens are listed in Table I; some of these values are plotted against the proton attracting power of the liquid [7], as shown in Fig. 1. The swelling behavior of unmodified wood followed the general behavior that was suggested by some researchers [5, 6]. They suggested that greater swelling was achieved in liquids having greater proton attracting power, i.e., hydrogen bonding power, while the slow permeation of dioxane results in an exceptionally small swelling [8]. Accordingly, the unmodified wood in both aromatic and aliphatic non-polar liquids was not swollen, because such liquids have weak hydrogen bonding and are unable to penetrate the hydrophilic wood polymers in which strong intermolecular hydrogen bonds are formed. In contrast, the acetylated wood in most organic liquids was remarkably swollen irrespective of their proton attracting power (Fig. 1). This marked swelling is attributed to the fewer or weaker intermolecular hydrogen bonds among the acetylated wood polymers, particularly in completely acetylated lignin polymers [9], which enable greater and faster penetration of organic liquids. In contrast with the excellent affinity of non-polar aromatic liquids, aliphatic liquids either did not exhibit any swelling or exhibited very slight swelling of the acetylated wood. It was speculated that the polar nature of the acetyl groups interfered with the access of the molecules of aliphatic liquids, whereas the partial polarity of aromatic compounds enabled their permeation into the acetylated wood.

Fig. 2 illustrates the swelling of acetylated wood in various cyclohexane (CH) solutions with elevating concentrations. Although there were no wide variations in the maximum swelling levels, alcohols, ethers, esters, and ketones exhibited considerable swelling of acetylated wood even at low concentrations while aromatic

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TABLE I Volumetric swelling of unmodified and acetylated wood specimens in various liquids

Liquids	Abbrevation	MW	$\Delta\nu$ (cm^{-1})	Volumetric swelling(%)	
				Unmodified	Acetylated
Carbon tetrachloride	CT	153.8	−21	0.1 (0.1)	0.8 (0.0)
n-Decane	DE	142.3		−0.1 (0.1)	0.0 (0.1)
n-Heptane	HP	100.2	0	0.0 (0.1)	0.1 (0.1)
n-Hexane	HX	86.2	1	0.0 (0.1)	0.9 (0.0)
Cyclohexane	CH	84.2		−0.1 (0.0)	−0.1 (0.0)
p-Xylene	XY	106.2		1.1 (0.1)	7.9 (0.1)
Toluene	TL	92.1	2	1.3 (0.1)	9.8 (0.2)
Benzene	BE	78.1	0	0.4 (0.1)	10.9 (0.3)
1, 4-Dioxane	DX	88.1	77	*0.7 (0.1)*	12.9 (0.7)
Ethyl acetate	EA	88.1	39	6.5 (0.1)	12.0 (0.2)
Methyl acetate	MA	74.1	36	8.0 (0.1)	12.6 (0.2)
Acetone	AC	58.1	64	9.1 (0.1)	11.8 (0.2)
1-Propanol	PR	60.1		*10.9 (0.2)*	8.9 (0.2)
Ethanol	ET	46.1		11.8 (0.2)	9.6 (0.2)
Methanol	MT	32.0		13.7 (0.2)	10.6 (0.1)
Water		18.0		17.3 (0.1)	6.1 (0.2)

MW, molecular weight; $\Delta\nu$, proton attracting power of liquid [7]. The values in parentheses indicate the standard deviations, and the *italics* indicate that the wood specimen did not attain dimensional equilibrium even after 60 days of soaking in liquids.

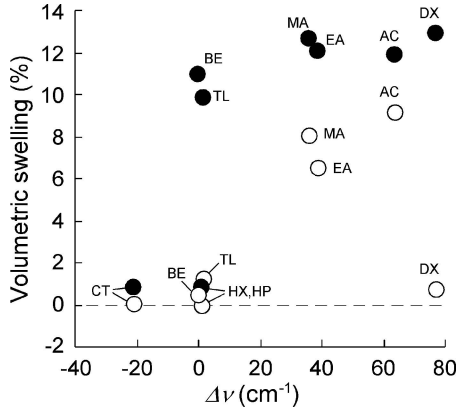

Figure 1 Volumetric swelling of unmodified (○) and acetylated (●) wood specimens as a function of proton attracting power ($\Delta\nu$) of liquids [7]. For abbreviations, see Table I.

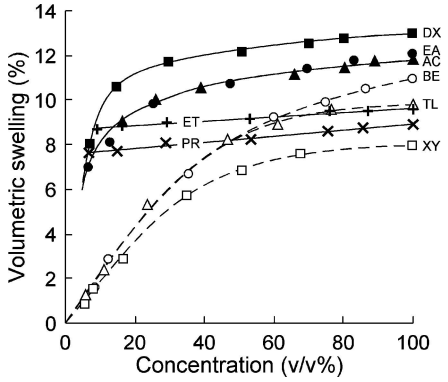

Figure 2 Volumetric swelling of acetylated wood in cyclohexane solutions with elevating concentrations of organic liquids. For abbreviations, see Table I.

liquids caused gradual swelling with an increase in concentration. It is likely that polar liquids such as alcohols easily escaped from their CH solutions to access the acetylated wood, while the aromatic liquids required more energy for separating from the strong cohesive interaction with CH molecules. This implies that the polar molecules or polar portions of polymers might be

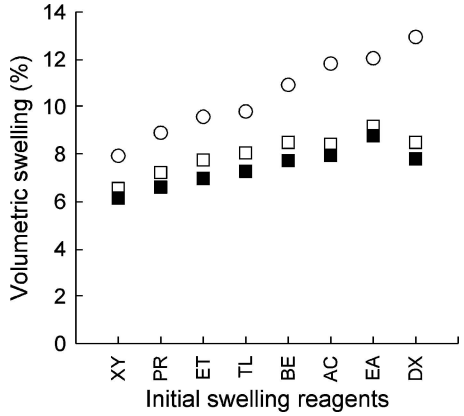

Figure 3 Changes in the swollen volume of acetylated wood due to the solvent exchange of organic liquids with cyclohexane. ○ Indicates swelling in organic liquids; □ indicates swelling after solvent exchange with cyclohexane; ■ indicates boiling in cyclohexane at 50 °C for 4 hr. For abbreviations, see Table I.

selectively introduced into the acetylated wood when aliphatic liquids are used as diluents.

Fig. 3 illustrates the changes in the swollen volume of acetylated wood during the exchange of organic liquids with CH. Despite its low affinity for acetylated wood, the CH was sufficiently introduced into the acetylated wood through solvent exchange. In addition, the CH-swollen acetylated wood did not shrink on heating at 50 °C, whereas the unmodified wood frequently exhibited marked shrinkage in such cases [10]. These facts suggest that various hydrophobic compounds can be introduced into the acetylated wood polymers by appropriately selecting the solvent, even when the adducts have no affinity for acetylated wood.

In conclusion, various organic liquids were found to have an excellent affinity for acetylated wood irrespective of their hydrogen bonding power. Further investigations are being conducted on the swelling rates of acetylated wood in organic solvents and cohesive interaction of acetylated wood and recycled high polymers.

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