Fundamental Research on Waterlogged Archeological Wood Conservation Using Lignophenol

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To improve the strength of waterlogged wood with highly degraded, a waterlogged wood was treated with *t*-butyl alcohol solution of 10% and 20% lignophenol (mass percentage), and physical properties were examined by dimensional measurements before and after the preservation and compression tests. In the tests, maximum moisture content (MMC) of waterlogged wood was used as the degradation degree because higher MMC means larger degradation of the cell wall. Used species of waterlogged wood was doronoki (*Populus maximowiczii* A. Henry) with an MMC of 1178%. Hardness of the waterlogged woods treated with lignophenol were greater than those treated with PEG4000 (polyethylene glycol). Especially, an increase in lignophenol concentration from 10% to 20% showed 1.7 times larger value in hardness. In longitudinal and radial direction, lignophenol and PEG4000 treatments showed good dimensional stabilities (less than 2%) for conservation. However, in the tangential direction, shrinkages less than 5% were found. It is necessary to examine another method for drying and/or to increase chemical concentration.
Key words: waterlogged wood, conservation, archaeology, lignophenol, and polyethylene glycol

1. INTRODUCTION

Various wooden relics, such as building components, industrial tools, farming implements, arms, and ceremonial tools, have been excavated from wet terrestrial ruins in Japan. These wooden artifacts are known as waterlogged woods, and due to their high academic value as a means of studying human history and culture, it is important that they be effectively preserved for future generations.

In waterlogged wood, certain chemical and the physical changes have taken place. Ordinary wood consists chiefly of polysaccharides and lignin. When wood is buried in wet ground, polysaccharides are degraded in preference to lignin, and hence the relative lignin content of waterlogged woods is higher than that of fresh wood.[1] Voids are formed in cell walls due to degradation of the materials, and these are filled by water when the wood is waterlogged. Therefore, the maximum moisture content (MMC) of waterlogged wood is increased and the basic specific gravity and mechanical strength are decreased as compared to fresh wood.[2] In addition, the degree of degradation may vary in different waterlogged woods. Generally, the MMC of waterlogged wood is considered equivalent to the degree of degradation, because a higher MMC means greater degradation of the cell wall.

Drying waterlogged wood can cause the wood to shrink to a significant degree. In order to exhibit waterlogged wood in museums, a preservation technique that increases strength and dryness without causing shrinkage is necessary. PEG4000 (Polyethylene glycol the average molecular weight is 3350.) is commonly used as a treatment of this type.[3] PEG4000 enters cell lumens as well as other permanent voids in waterlogged wood, while water from the wood is removed by air-dry method. Freeze-dry method by substituting water for *t*-butyl alcohol (TBA) can prevent shrinkage of waterlogged wood more effectively.

We have developed a new method for conservation of waterlogged wood by use of lignophenol.[4] Lignophenol is a lignin derivative of wood and is readily soluble in solvents such as acetone and alcohol and has been shown to improve the strength of lignocellulosic materials.[5, 6] The design of our treatment was that the lignophenol, which has a high affinity for waterlogged wood, would strengthen cell walls and increase the specific strength of the waterlogged wood.[7]

In our previous achievements[8], hardness of waterlogged woods treated with TBA solution of 5% lignophenol (mass percentage) were greater than that of the samples treated with PEG4000 regardless of the MMC level. Larger amount of adsorption of lignophenol to the cell wall contributed to the hardness. As mentioned above, the decrease in mechanical properties of waterlogged wood is brought by the increase in MMC. To develop a conservation treatment using lignophenol, an improvement of mechanical properties of highly degraded waterlogged wood is necessary.

In this study, waterlogged wood with MMC of 1178% was treated with TBA solution of 10% or 20% lignophenol, and the physical properties of the samples were examined by dimensional measurements before and after the preservation and compression tests, and compared the samples treated with PEG4000.

2. MATERIALS AND METHODS

2. 1 Sample

A waterlogged wood of doronoki (*Populus maximowiczii* A. Henry) with an MMC 1178% was used as a sample.

2. 2 Lignophenol

Lignophenol was obtained by TBA extraction of lingo-*p*-cresol prepared from sugi wood (*Cryptomeria japonica* D. Don).[9]

2. 3 Adsorption test

The sample was ground into wood meals (60 - 80 mesh) and extracted with TBA for 96 hours using a Soxhlet apparatus. Lignophenol and PEG4000 were used as adsorbates in TBA solution. Adsorption isotherms were obtained while maintaining the sample at 55°C for a week. Saturation adsorption amounts were calculated based on Langmuir plots from the adsorption isotherms.

2. 4 Preservation method

Wood plates (longitudinal, radial and tangential direction ware 20, 20 and 5 mm respectively.) were cut from areas of the sample containing no knots or cracks. Table I shows treatment conditions of the wood plates. After saturation in TBA, the plates were soaked in 5% lignophenol or PEG4000 in TBA solution, and concentrations of these solutes were gradually raised up from 5% to the final concentrations at 70°C (solubility of the lignophenol in TBA at 70°C was 18g per 100g). They were followed by freeze-dry, then maintained at 20°C and 65% RH for three days. Dimensions of the wood plates before saturation in TBA and after freeze-dry were measured respectively.

Table I Treatment conditions of wood plates.

Adsorbate	Chemical	Final concentration of chemical (%)
Control	Unused	Unused
10%LP	Lignophenol	10
20%LP	Lignophenol	20
10%PEG	PEG4000	10
20%PEG	PEG4000	20

2. 5 Compression test

After preservations, the wood plates were tested using a compression jig (diameter was 7 mm) with a crosshead speed of 0.5 mm/1 min. The load at a distance of 2 mm from the displacement of the crosshead vs. the load curve was defined as hardness (Fig.1). Values of hardness of radial face of the wood plates were used for evaluation of strength properties.

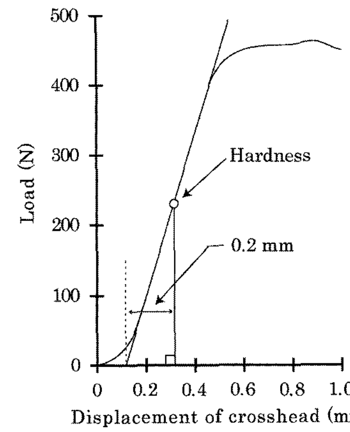

Fig. 1 Relationship between load and crosshead displacement.

3. RESULTS AND DISCUSSION

3. 1 Adsorption of lignophenol in waterlogged wood

Fig.2 shows adsorption isotherms of lignophenol and PEG4000 from TBA at 55°C. Both of them, amounts of adsorption increased with the increase of equilibrium concentration, and became constant above 1mg/g in the equilibrium concentration. The shape of the adsorption isotherms was categorized in the Langmuir type.

Fig.3 shows c/u vs. c based on the data of Fig.2. From the Langmuir formula, following straight line (1) is given, and saturation adsorption amount (u_s) was calculated from the slope.

$$\frac{c}{u} = \frac{1}{k \times u_s} + \frac{c}{u_s} \quad (1)$$

, where c is equilibrium concentration (%), u is amount of adsorption (mg/g), k is adsorption constant, u_s is saturation adsorption amount.

Table II shows saturation adsorption amounts of lignophenol and PEG4000. The saturation adsorption amount of lignophenol was 1.4 times greater than that of PEG4000. The reason for this is thought to be that the solubility of lignophenol in TBA is lower than that of PEG4000.[7),8)]

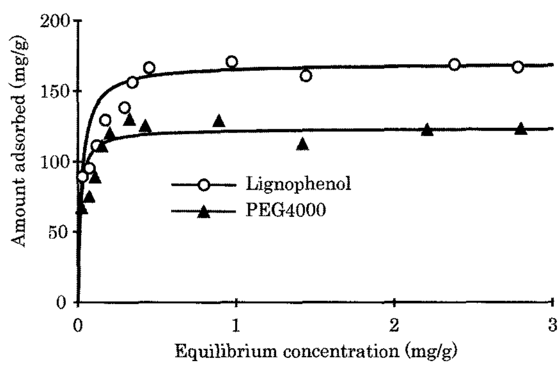

Fig. 2 Adsorption isotherms of lignophenol and PEG4000 on waterlogged wood from TBA at 55°C.

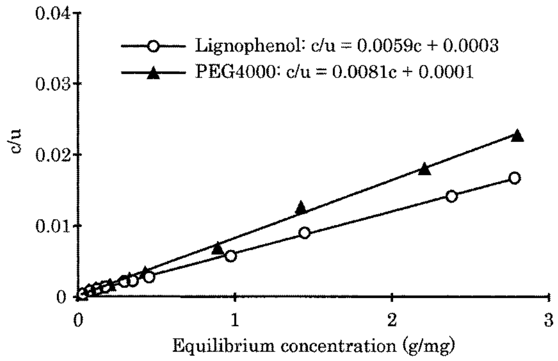

Fig. 3 Langmuir plots for adsorption of lignophenol and PEG4000 from TBA and deionized water respectively at 55°C.

Table II Saturation adsorption amounts of lignophenol and PEG4000.

Adsorbate	Solvent	Amount of adsorption (mg/g)
Lignophenol	TBA	169
PEG4000	TBA	123

3. 2 Dimensional changes of lignophenol-treated wood plates

Fig.4 shows dimensional changes of longitudinal direction in wood plates before and after preservation. Compared with the value of non-chemically-treated plate (Control, 2.9%), the shrinkages of wood plates treated with lignophenol or PEG4000 were significantly reduced (less than 1.2%). Although the shrinkages in lignophenol-treated samples are large comparing with the values in PEG4000-treated ones, the differences are few. It is thought that the improvement of dimensional change of the longitudinal direction can be attributed to the adsorption of lignophenol or PEG4000.

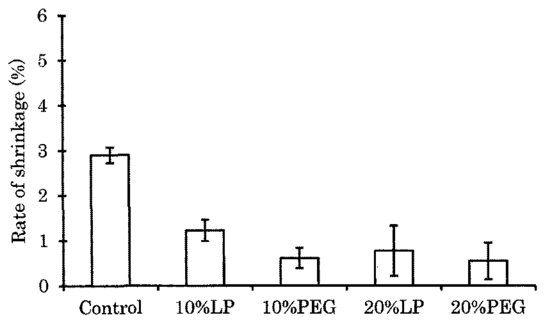

Fig. 4 Dimensional changes of longitudinal direction in the wood plates before and after preservation.

Fig.5 shows dimensional changes of radial direction. No relationships were found in the shrinkages between control and chemically treated samples, because the values of all samples were less than 1%.

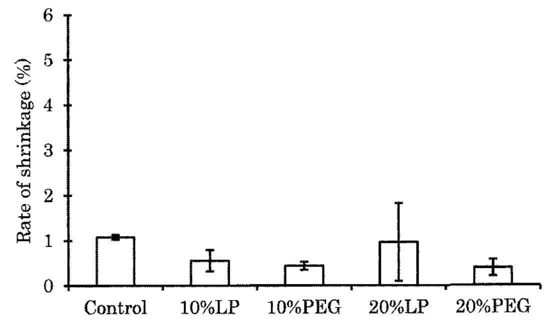

Fig. 5 Dimensional changes of radial direction in the wood plates before and after preservation.

Fig.6 shows dimensional changes of tangential direction. As shown in Fig.6, the shrinkages lignophenol-treated and PEG4000-treted samples were significantly reduced from 14.1% to less than 5%. However the value, 5%, is not suitable for conservation of waterlogged wood. To improve the values, we are planning to examine another methods for drying and/or to increase the lignophenol concentration.

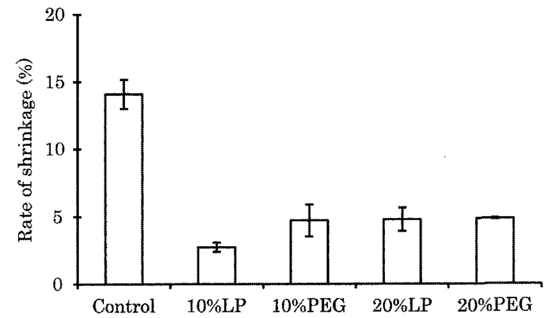

Fig. 6 Dimensional changes of tangential direction in the wood plates before and after preservation.

3. 3 Strength properties of lignophenol-treated wood plates

Fig.7 shows hardness for radial faces of control, lignophenol- and PEG4000-treated wood plates. Hardness of wood plates treated with lignophenol and PEG4000 were larger than those underwent no chemically treatment (Control). The adsorption of lignophenol or PEG4000 resulted in the improvement of strength of waterlogged wood.

The increases in the concentration of lignophenol and PEG4000 significantly increased the hardness. In the case of lignophenol-treated plates, the hardness were increased from 4.9N to 8.3N as the concentration increased, while the value was increased from 4.0N to 4.8N in the case of PEG4000-treated plates. The increase rate of lignophenol treatment is 2.5 times larger than that of PEG4000. One of the reasons for the difference is thought to be the saturation adsorption amount. Now, molecule structures of lignophenol and relationships between the lignophenol and the cell wall are considering.

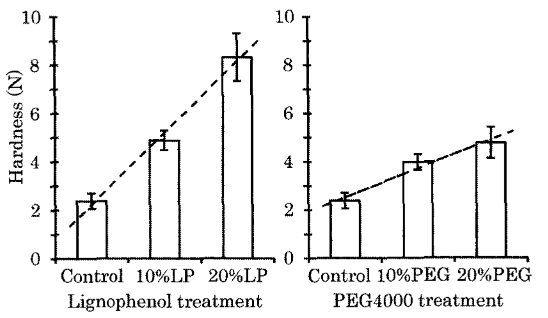

Fig. 7 Hardness values on radial face of wood plates after treatment with lignophenol or PEG4000.

4. CONCLUSION

To improve the strength of waterlogged wood at high degradation level, we studied the treatments with TBA solution of 10% or 20% lignophenol, and compared with the treatments using PEG4000.

The treatment with lignophenol effectively enhanced the hardness of waterlogged wood, and showed good dimensional stabilities in longitudinal and radial direction. However, the dimensional change in tangential direction was unsuited for conservation treatment. We are planning to improve the problem.

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